

71-1494

MAHONEY, Joseph Patrick, 1942-
PARAMAGNETIC SUSCEPTIBILITY OF IRON, CHROMIUM
AND NICKEL DOPED II-VI COMPOUNDS.

The University of Oklahoma, Ph.D., 1970
Physics, solid state

University Microfilms, A XEROX Company, Ann Arbor, Michigan

PARAMAGNETIC SUSCEPTIBILITY OF IRON, CHROMIUM
AND NICKEL DOPED II-VI COMPOUNDS

A DISSERTATION
SUBMITTED TO THE GRADUATE FACULTY
in partial fulfillment of the requirements for the
degree of
DOCTOR OF PHILOSOPHY

BY
JOSEPH PATRICK MAHONEY
Norman, Oklahoma
1970

PARAMAGNETIC SUSCEPTIBILITY OF IRON, CHROMIUM
AND NICKEL DOPED II-VI COMPOUNDS

APPROVED BY

cc Lin

S. E. Bell Jr.

R. J. Bell

Richard J. Meehan

K. M. St. John

DISSERTATION COMMITTEE

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Professor Chun C. Lin for suggesting the research problems considered in this work and for his many enlightening discussions on the experimental and theoretical aspects of the problems.

It is also a pleasure to acknowledge the work of Professor W. H. Brumage and Professor C. F. Dorman for the theoretical work which explains the experimental results described herein.

Thanks are due to Professor Jurgen Schneider for furnishing two iron doped crystals for the magnetic measurements.

It is also a pleasure to express appreciation to my wife, Donna, for her constant encouragement and aid.

TABLE OF CONTENTS

	Page
LIST OF TABLES	vi
LIST OF ILLUSTRATIONS	viii

Chapter

I.	Introduction	1
II.	Magnetic Susceptibility Apparatus	4
	Faraday Balance - Room Temperature	
	Range and Detection of Faraday Balance	
	Sample Tube Detail	
	Temperature Control for 300°K to 5.5°K	
	Temperature Control for 4.2°K to 1.8°K	
III.	Doping Diamagnetic Crystals with Paramagnetic	
	Ions of Iron, Chromium and Nickel	30
	Introduction	
	Doping Procedures	
	Special Considerations	
	Summary	
IV.	Fe ²⁺ in Tetrahedral Sites - Theory	45
	Introduction	
	Crystal Structure	
	Hamiltonian Used in Calculations	
	Magnetic Susceptibility	
	Application of Group Theory for Qualitative	
	Features	

TABLE OF CONTENTS (Continued)

Chapter	Page
IV. (Continued)	
Paramagnetic Susceptibility Calculations for Fe^{2+} in a Tetrahedral Crystal Field	
Paramagnetic Susceptibility Calculations for Fe^{2+} in a Tetrahedral Crystal Field with a Trigonal Distortion	
V. Fe^{2+} in Tetrahedral Sites - Experiment	74
Introduction	
Fe^{2+} in Tetrahedral Crystal Field	
Fe^{2+} in Tetrahedral Field with Trigonal Distortion	
VI. Cr^{2+} in Tetrahedral Sites.	98
Introduction	
Jahn-Teller Effect	
Magnetic Susceptibility Measurements	
VII. Ni^{2+} in Tetrahedral Sites	112
Introduction	
Magnetic Susceptibility Measurements	
CONCLUSIONS	119
LIST OF REFERENCES	121

LIST OF TABLES

Table	Page
1. Variation of Deflection d with Reduction of Pole Gap	13
2. Spring Constant C Determined Using Platinum Standard	13
3. Range of Spring Constant C	13
4. Fe^{2+} Doped in II-VI Compounds	42
5. Cr^{2+} Doped in II-VI Compounds	42
6. Ni^{2+} Doped in II-VI Compounds	43
7. Calculated Magnetic Susceptibility of Fe^{2+} in Cubic Crystal Field	64
8. Calculated Magnetic Susceptibility of Fe^{2+} in Cubic Crystal Field with Trigonal Distortion	73
9. Measured Magnetic Susceptibility of $\text{Fe}^{2+}:\text{ZnS}$	77
10. Measured Magnetic Susceptibility of $\text{Fe}^{2+}:\text{ZnSe}$	79
11. Measured Magnetic Susceptibility of $\text{Fe}^{2+}:\text{CdSe}$	82
12. Measured Magnetic Susceptibility of $\text{Fe}^{2+}:\text{ZnTe}$	84
13. Measured Magnetic Susceptibility of $\text{Fe}^{2+}:\text{CdTe}$	86
14. Measured Magnetic Susceptibility of $\text{Fe}^{2+}:\text{CdS}$	90
15. Measured Magnetic Susceptibility of $\text{Fe}^{2+}:\text{CdS(S)}$	91
16. Measured Magnetic Susceptibility of $\text{Fe}^{2+}:\text{ZnO}(\chi)$	94
17. Measured Magnetic Susceptibility of $\text{Fe}^{2+}:\text{ZnO}(\chi)$	95

LIST OF TABLES (Continued)

Table	Page
18. Concentrations of Fe^{2+} in Host Crystals. . . .	96
19. Summary of Experimental Results for Fe^{2+} . . .	97
20. Measured Magnetic Susceptibility of $\text{Cr}^{2+}:\text{ZnS}$ and $\text{Cr}^{2+}:\text{CdS}$	107
21. Measured Magnetic Susceptibility of $\text{Cr}^{2+}:\text{ZnSe}$ and $\text{Cr}^{2+}:\text{CdSe}$	108
22. Measured Magnetic Susceptibility of $\text{Cr}^{2+}:\text{ZnTe}$ and $\text{Cr}^{2+}:\text{CdTe}$	109
23. Concentrations of Cr^{2+} in Host Crystals . . .	110
24. Measured Magnetic Susceptibility of $\text{Ni}^{2+}:\text{ZnSe}$, $\text{Ni}^{2+}:\text{CdSe}$ and $\text{Ni}^{2+}:\text{ZnTe}$	115
25. Concentrations of Ni^{2+} in Host Crystals . . .	118

LIST OF ILLUSTRATIONS

Figure	Page
1. Orientation of Cartesian Coordinates with Magnet	6
2. Variation of χ/dz along z-axis	6
3. Faraday Balance with 300°K to 5.5°K Dewars in Place	9
4. Detail of Sample Tube	16
5. $\text{Cr}^{3+}:\text{Al}_2\text{O}_3 - \chi$ vs. $1/T$	18
6. Temperature Control for 80°K to 5.5°K	20
7. Differential Power Amplifier Schematic	21
8. 4.2°K to 1.8°K Dewar Assembly	25
9. Low Temperature Control Mechanism	26
10. $R(\text{ohm})$ vs. $T(^{\circ}\text{K})$ for Carbon Resistor Sensor	28
11. Vacuum Evaporation Apparatus	33
12. Crystal Oven	37
13. Variation in Magnetic Susceptibility with Concentration	39
14. Impurity Ion in Zincblende Structure	48
15. Tetrahedron with Trigonal Distortion Along Body Diagonal $\overline{AB}$	50
16. Magnetic Susceptibility from Two Energy Levels	54
17. Energy Levels of Fe^{2+} in Cubic Crystal Field	58

LIST OF ILLUSTRATIONS (Continued)

	Page
Figure	
18. Levels Affecting $\chi_{ }$ and $\chi_{\perp}$	62
19. Calculated χ_M vs. T (Fe^{2+})	66
20. Calculated χ_M vs. $1/T$ (Fe^{2+})	67
21. Calculated $\chi_M T$ vs. T (Fe^{2+})	70
22. Measured Magnetic Susceptibility Curve for $\text{Fe}^{2+}:\text{ZnS}$	78
23. Measured Magnetic Susceptibility Curve for $\text{Fe}^{2+}:\text{ZnSe}$	80
24. Measured Magnetic Susceptibility Curve for $\text{Fe}^{2+}:\text{CdSe}$	83
25. Measured Magnetic Susceptibility Curve for $\text{Fe}^{2+}:\text{ZnTe}$	85
26. Measured Magnetic Susceptibility Curve for $\text{Fe}^{2+}:\text{CdTe}$	87
27. Measured Magnetic Susceptibility Curve for $\text{Fe}^{2+}:\text{CdS}$	89
28. Measured Magnetic Susceptibility Curve for $\text{Fe}^{2+}:\text{ZnO}$	92
29. Measured Magnetic Susceptibility Curve for $\text{Fe}^{2+}:\text{ZnO}$	93
30. Energy Levels of Cr^{2+} in Crystal Field	99
31. Energy Levels of Cr^{2+} in Crystal Field with Jahn-Teller Effect	102
32. Measured Magnetic Susceptibility Curve for $\text{Cr}^{2+}:\text{ZnS}$	105
33. Measured Magnetic Susceptibility Curve for $\text{Cr}^{2+}:\text{CdS}$	106
34. Energy Levels of Ni^{2+} in Cubic Crystal Field	113
35. Calculated χ_M vs. $1/T$ (Ni^{2+})	116

CHAPTER I

INTRODUCTION

It is the intention of this study to further the investigations of iron group transition metals doped into II-VI compounds by examining the magnetic properties of the paramagnetic impurity ion while under the influence of the diamagnetic host crystal. The investigation will be limited to the impurity ion and its interaction with the host crystal; and therefore, concentrations of impurity ions must be low enough to avoid interactions between the impurities themselves.

Observation of the magnetic properties will enable us to determine the electronic energy level separations with respect to the ground state¹ and compare experimentally determined values to those predicted by theory after assuming some theoretical model. Actually, in the cases discussed here, the energy level separations are expressed theoretically in terms of parameters which must be determined experimentally.

There are different experimental techniques available to investigate the electronic energy levels, and all have advantages and disadvantages as well as different ranges

of effective application. Optical spectroscopy has been utilized to study electronic energy level separations from the near infrared to the vacuum ultraviolet² (2000 cm^{-1} to $50,000\text{ cm}^{-1}$ or $5.0\text{ }\mu$ to $0.1\text{ }\mu$), although more work is being done recently in the far infrared.³

Magnetic susceptibility can be used to determine electronic energy level separations in the range of 3 or 4 cm^{-1} to 1200 cm^{-1} ⁴ and is limited primarily by the range of temperatures over which the sample under investigation can be varied. This technique is especially useful when studying paramagnetic ions with nonmagnetic ground states, as we shall see later.

Electron spin resonance is best used to study ground state electronic energy levels and direct transitions between these levels when split by the Zeeman effect.⁵ The energy level separations studied depend on the microwave frequency used and are generally in the range of 0.03 cm^{-1} and 3 cm^{-1} .

The technique used in this study is that of magnetic susceptibility, and this choice is very appropriate for Fe^{2+} and Ni^{2+} in crystal sites of tetrahedral symmetry because of the nature of the electronic energy levels involved. Optical spectroscopy is made difficult in Fe^{2+} because of Jahn-Teller distortions in the higher electronic energy levels, and because the energy separations of the lower levels are in the far infrared, making experimental measurements and sample preparation difficult. On the other hand,

electron spin resonance is rather difficult because the ground state of the Fe^{2+} and Ni^{2+} ions are nonmagnetic. Therefore, once the problems of low temperature measurements of magnetic susceptibilities are solved, the use of magnetic susceptibility can supply information difficult or impossible to obtain by other methods.

Magnetic susceptibility could also be expected to be an effective means of studying Cr^{2+} in tetrahedral sites. From crystal field theory alone one would expect Cr^{2+} to have a nonmagnetic ground state as in the cases of Fe^{2+} and Ni^{2+} . However, it is found that the Jahn-Teller effect plays an important role in determining the symmetry at the impurity ion site. Magnetic susceptibility can still be used, but the results are not as revealing and unique as they are in Fe^{2+} and Ni^{2+} .

The extension of the magnetic susceptibility measurements to temperatures below 4.2°K is described, and measurements have been made at temperatures as low as 1.8°K . Results of the magnetic susceptibility measurements for Fe^{2+} in host crystals of ZnO , CdS , ZnS , CdSe , ZnSe , CdTe , and ZnTe ; for Cr^{2+} in ZnS , CdS , ZnSe , CdSe , ZnTe and CdTe ; and for Ni^{2+} in CdSe , ZnSe , and ZnTe will be reported, as well as the problems involved and the procedures used in doping the impurity ions of Fe^{2+} , Cr^{2+} and Ni^{2+} in their respective host crystals.

CHAPTER II

EXPERIMENTAL APPARATUS

Faraday Balance - Room Temperature

The apparatus used in these experiments is known as a Faraday balance.^{4,6,7} This particular technique of measuring magnetic susceptibilities is very well suited for our investigations of the iron-group transition ions in the II-VI compounds in that the only real requirement on the sample is that its size be less than 1 cm on a side, and that the paramagnetic susceptibility be large enough to detect. This freedom from a particular sample size or shape allows us to study crystals as we receive them. This can be a very important point if we want to use more than just one experimental technique to gather information about the nature of the sample. Therefore, magnetic susceptibility can easily be used to study the same crystals which are, for example, cut or grown for study by electron spin resonance, optical spectroscopy, photoconductivity, and Hall effect, or luminescence experiments.

The Faraday balance is a rather old technique of measuring magnetic susceptibilities⁸ and was used extensively by Pierre Curie⁹ in his classical studies. In this technique

one simply needs a source of an inhomogeneous magnetic field and a means of detecting the resulting force on the sample under investigation. Let us first look at how this force arises.

First, we need a source of an inhomogeneous magnetic field. In our case we have used a large permanent magnet. Let us arrange the rectangular coordinates such that the x-axis is along the center line running through the poles of the magnet as drawn in Fig.1. If we determine the magnetic field (H) at points along the z-axis and then multiply H by the gradient of the field at each of these points, we would find the values of $H \frac{dH}{dz}$ associated with the points along the z-axis as plotted in Fig. 2. We note for future reference that there are two points of maximum $H \frac{dH}{dz}$. So now that we have our inhomogeneous magnetic field, let us look at the magnitude of the force acting on our sample, say at point b.

Next, if we place a small sample (small enough that the magnetic field is not significantly distorted) at point b, there is a resulting change in the potential energy as described in Eq. 1.

$$P. E. = \frac{1}{2} m \chi H^2 \quad (2-1)$$

where m = mass in grams,

χ = magnetic susceptibility in dgs-emu/gram,

H = magnitude of the magnetic field.

If we take the gradient of the potential energy along the

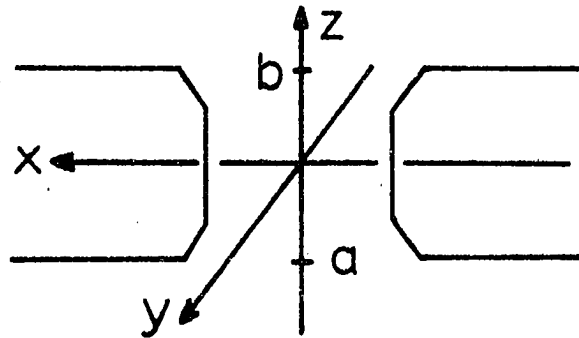


Figure 1. Orientation of Cartesian Coordinates with Magnet.

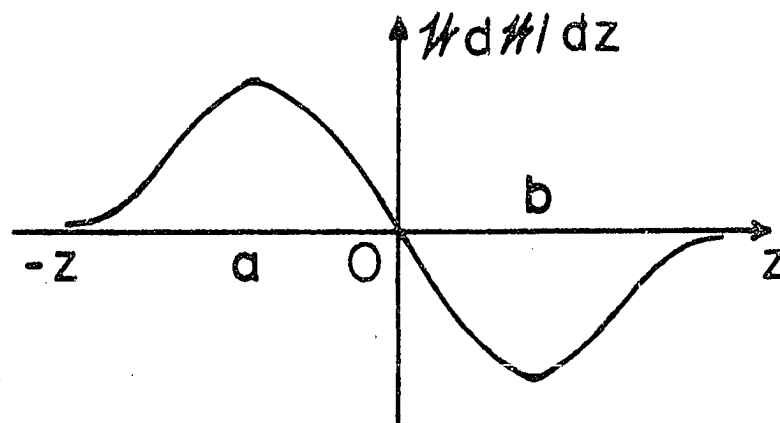


Figure 2. Variation of $\frac{dH}{dz}$ along z-axis.

z-axis, we find the force to be

$$F = m \chi (H_x dH_x/dz + H_y dH_y/dz + H_z dH_z/dz). \quad (2-2)$$

In most cases the last two terms can be neglected, and we are left with

$$F_z = m \chi H_x dH_x/dz \quad (2-3)$$

which is the force to be measured. We note here that the magnetic susceptibility in the formula refers to the paramagnetic susceptibility of the impurity ion which is under study. We shall soon see that, in our experiments, changes of magnetic susceptibility as a function of temperature from an initial value are the real parameters of interest and not the absolute susceptibility. Therefore, we can neglect the diamagnetic contributions to Eq. (3) arising from the host crystal and its quartz holder since they are independent of the temperature and do not contribute to the change in the measured force.

It is of interest to give here an example of the magnitude of the force changes measured. In some cases we wish to measure changes in the paramagnetic susceptibility as low as 1×10^{-7} emu/gram in samples weighing approximately 50 mg. Then with a permanent magnet of 3000 gauss (H) and a dH/dz of 200 gauss/cm., these numbers can be inserted in Eq. (3) to find

$$\begin{aligned} F_z &= 5 \times 10^{-2} \times 10^{-7} \times 3 \times 10^3 \times 2 \times 10^2 \\ &= 0.3 \times 10^{-3} \text{ dyne} \end{aligned} \quad (2-4)$$

or a force change of 0.3 millidynes. One reason that such

small forces must be detected is that only crystals with low concentrations of impurity ions are available either commercially or by doping pure crystals in our laboratory.

Once the force is generated by positioning a small sample in an inhomogeneous magnetic field, some means of force detection must be found. The detection method chosen is actually quite simple. First, the sample is attached to a long quartz fiber which in turn is suspended by a quartz spring. The end of the spring is loaded with extra weight, if needed, so that the quartz spring is always extended one meter in length (Fig. 3). Now the permanent magnet is mounted such that it can be moved along the vertical direction (z-axis) at a controlled and variable speed. With the quartz spring and the sample aligned in the vertical z-axis which runs between the poles of the magnet, the magnets can be raised or lowered with respect to the sample. By starting with the magnet below (above) the sample and then moving it slowly upward (downward), the sample is first pushed one way and then the other from the equilibrium position. So now if we view a point fixed with respect to the sample with a measuring microscope (cathetometer), we see the point move from the equilibrium point to a minimum position, up to a maximum position, and then back to the equilibrium position again. The distance from the minimum position to the maximum one, as seen in the cathetometer, we will call d . There can now be a deflection d associated with a given sample,

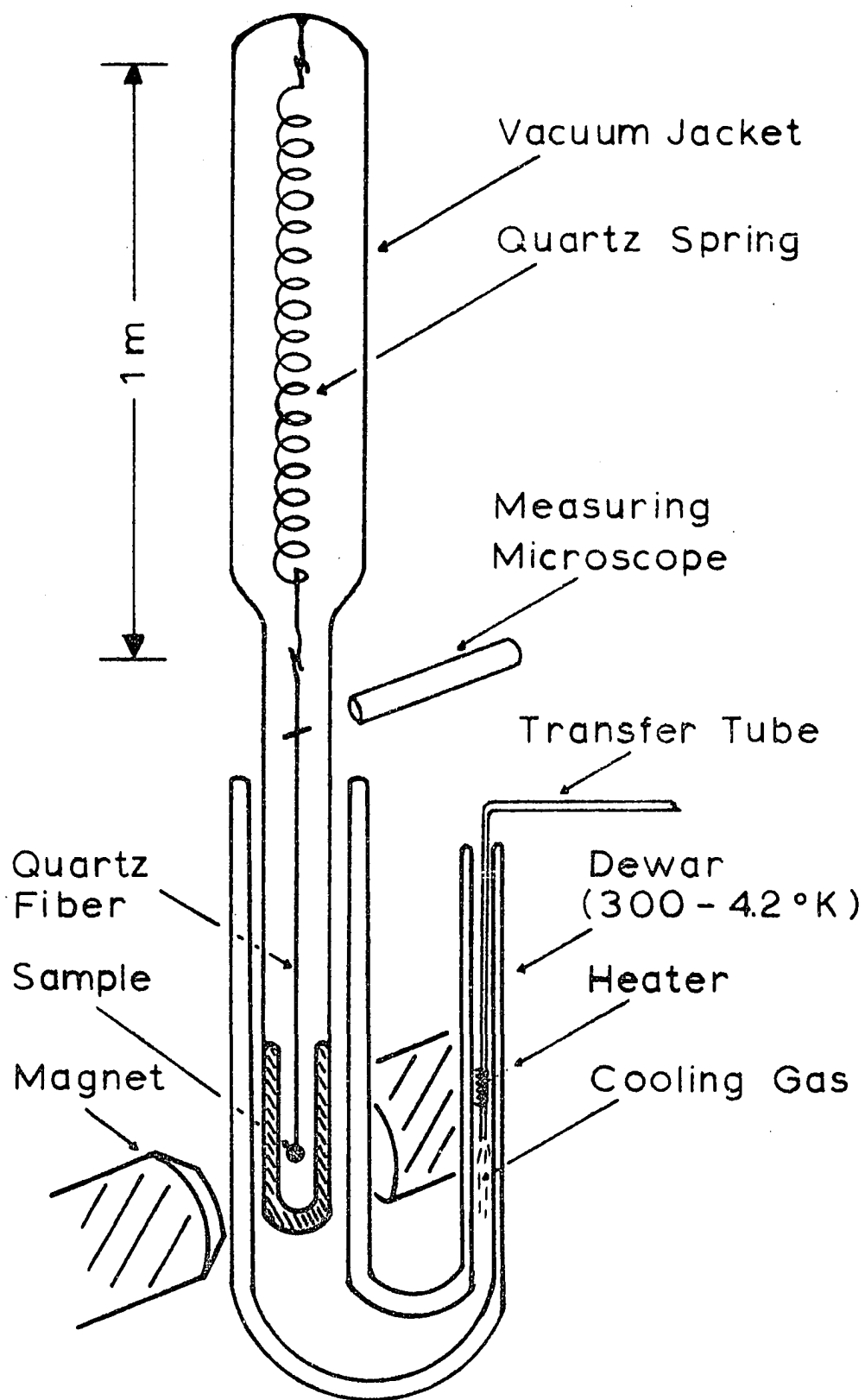


Figure 3. Faraday Balance with 300°K to 5.5°K dewars in place.

spring, cathetometer, and magnetic configuration at a given temperature.

The force on a given sample in the inhomogeneous magnetic field was given by Eq. (3). The quartz spring resists a movement from the equilibrium position by a force

$$F = kx \quad (2-5)$$

where k is the usual spring constant, and x is the distance from the equilibrium point. For our application, we can calibrate the deflection as read in the cathetometer in terms of a magnetic susceptibility value within a given spring-magnet-cathetometer configuration. By combining equations (3) and (5) we find that

$$F = kx = kd/2 = m \chi H d H / dz \quad (2-6)$$

$$\text{or} \quad = (d/m) [k/2 H (dH/dz)] = C (d/m) \quad (2-7)$$

$$\text{where} \quad C = k/2 H (dH/dz) \quad (2-8)$$

and x = spring displacement from equilibrium point,

d = deflection (between min. and max. points),

χ = magnetic susceptibility (ogs-emu/gram),

m = mass of sample in grams,

H = magnetic field strength,

C = constant to relate measured magnetic susceptibility to platinum standard.

Once the system is calibrated by measuring the magnetic susceptibility of platinum to determine the constant C , the absolute magnetic susceptibility associated with any sample which gives a deflection as seen in the measuring

microscope can be determined.

Let us now review the entire procedure followed for a measurement of magnetic susceptibility at some particular temperature. The apparatus is set up as in Fig. 3, and the magnet is lowered to a position below the sample. A fixed point is viewed in the cathetometer, and then the magnet is slowly raised. The fixed point will move down as seen in the eyepiece until the sample reaches point b of Fig. 1. At this time the reference line of the cathetometer is set marking the location. The magnet is then moved up slowly until the sample reaches point a in Fig. 1. Now the other reference line of the cathetometer is set on this point of maximum deflection, and the distance between the maximum and minimum deflection as seen and measured with the cathetometer is read on a scale varying from 0.00 to 23.00. Either a high or a low power objective lens is available for the cathetometer. With the high power objective, 0.10 scale divisions is found to measure a distance of 3.8 microns. The error in reading the deflection under the best conditions is approximately ± 0.05 . A deflection of this size corresponds to a small force of approximately 0.4 millidyne or a weight change of 0.4 microgram on the most sensitive spring. For constant room temperature magnetic susceptibility measurements the above procedure is quite easy to use.

Range and Detectivity of Faraday Balance

The range of the paramagnetic susceptibility values which can be determined by this balance is quite large. If a sample is suspended by the quartz fiber, and its deflection as measured at room temperature is too large or small to be optimally viewed in the cathetometer, three simple adjustments can be made singly or jointly.

First, the air gap of the permanent magnet can be varied. If we start with a three inch air gap and assume a unit deflection, then the deflection increases with the reduction in air gap, as shown in Table 1. Note that a reduction of the air gap from three inches to one inches causes a change in the size of the deflection by a factor of approximately 13.

Another way to vary the size of the deflection as seen in the cathetometer is to change the objective lens. The deflection can be increased by 1.737 by going from low to high power or reduced by 0.567 by going from the high power to the low power objective lens. The third way is to vary the size of the quartz spring used. The spring constant C for each spring used in these experiments is given in Table 2. In this table the notation LLS-H-1 refers to the very light spring, the high power objective lens, and a 1" air gap. Likewise LS, MS, and HS refer to light spring, medium spring, and heavy spring, respectively. The parameter $K(\text{mm/mg})$ is the nominal spring sensitivity which is quoted

TABLE 1

VARIATION OF DEFLECTION
WITH CHANGE IN AIR GAP

Gap	d
1"	1.00
2"	3.20
3"	12.80

TABLE 2

SPRING CONSTANT C AS DETERMINED USING Pt. STANDARD

Spring	K(mm/mg)	C(emu/s.d.)	Max. load (mg)
LLS-H-1	10.0	4.0×10^{-10}	100
LS-H-1	4.0	10.8×10^{-10}	250
MS-H-1	2.0	17.5×10^{-10}	500
HS-H-1	0.6	62.0×10^{-10}	1800

TABLE 3

RANGE OF SPRING CONSTANT C

Configuration	C
LLS-H-1	4×10^{-10} emu/s.d.
HS-L-3	1400×10^{-10} emu/s.d.

by the manufacturer (Worden Quartz Products, Houston, Texas), and note that it is the reciprocal of the spring constant k in Eq. (6). C is the constant of Eq. (8), and the maximum load is just the weight which will achieve the maximum extension of 1000 mm. A comparison of the value of C for the most and least sensitive configurations is given in Table 3.

At this point it is important to make some statements concerning the sensitivity or detectivity of the Faraday balance. Sensitivities are often given in terms of the minimum detectable magnetic susceptibility in units of cgs-emu/gram. For research work of crystals of which the size may be a limiting factor of the ultimate sensitivity, this practice is acceptable if one also states the size of the sample under investigation. A better approach when dealing with small and varied samples is to give the detectability in terms of mass times the magnetic susceptibility ($m\chi$) in units of cgs-emu.

The Faraday balance used in this investigation could be pushed to detect a change of approximately 5×10^{-11} cgs-emu, but a more realistic value is 1×10^{-10} cgs-emu. Although quite simple in principle, the Faraday balance is quite sensitive even when compared to a sample magnetometer (Princeton Applied Research Corporation, Princeton, New Jersey) or a commercial microbalance using an electromagnet producing strong magnetic fields. Both of the latter options are also much more expensive than the balance just described.

Sample Tube Detail

Thus far we have assumed that the magnetic susceptibility measurements were at room temperature. Since we are using magnetic susceptibility to study the electronic energy levels of paramagnetic ions in II-VI crystals, we need the experimental magnetic susceptibility as a function of temperature. Therefore, we need to control the temperature of a crystal on the end of a sensitive spring, as well as, know the actual temperature to better than 0.1°K , especially at low temperatures. Let us first consider the sample tube.

A detail drawing of the sample tube is given in Fig. 4. The vacuum jacket consists of a 22 mm. pyrex o-ring joint which is joined by a graded glass seal to 16 mm. quartz with a test tube end. Since the coolant will be outside this vacuum jacket, an exchange gas must be placed inside the vacuum jacket. Since we want to measure the magnetic susceptibility to 4°K and lower, the gas chosen is helium, and it is admitted into the system after the air is evacuated.

The exchange gas will allow the crystal temperature to reach an equilibrium with the quartz vacuum jacket and the copper surrounding the sample area. This copper mass is added in order to reduce small temperature fluctuations, and it sits at the bottom of the quartz tube on a teflon spacer. It is the temperature of this copper mass which is actually monitored since a thermocouple cannot be

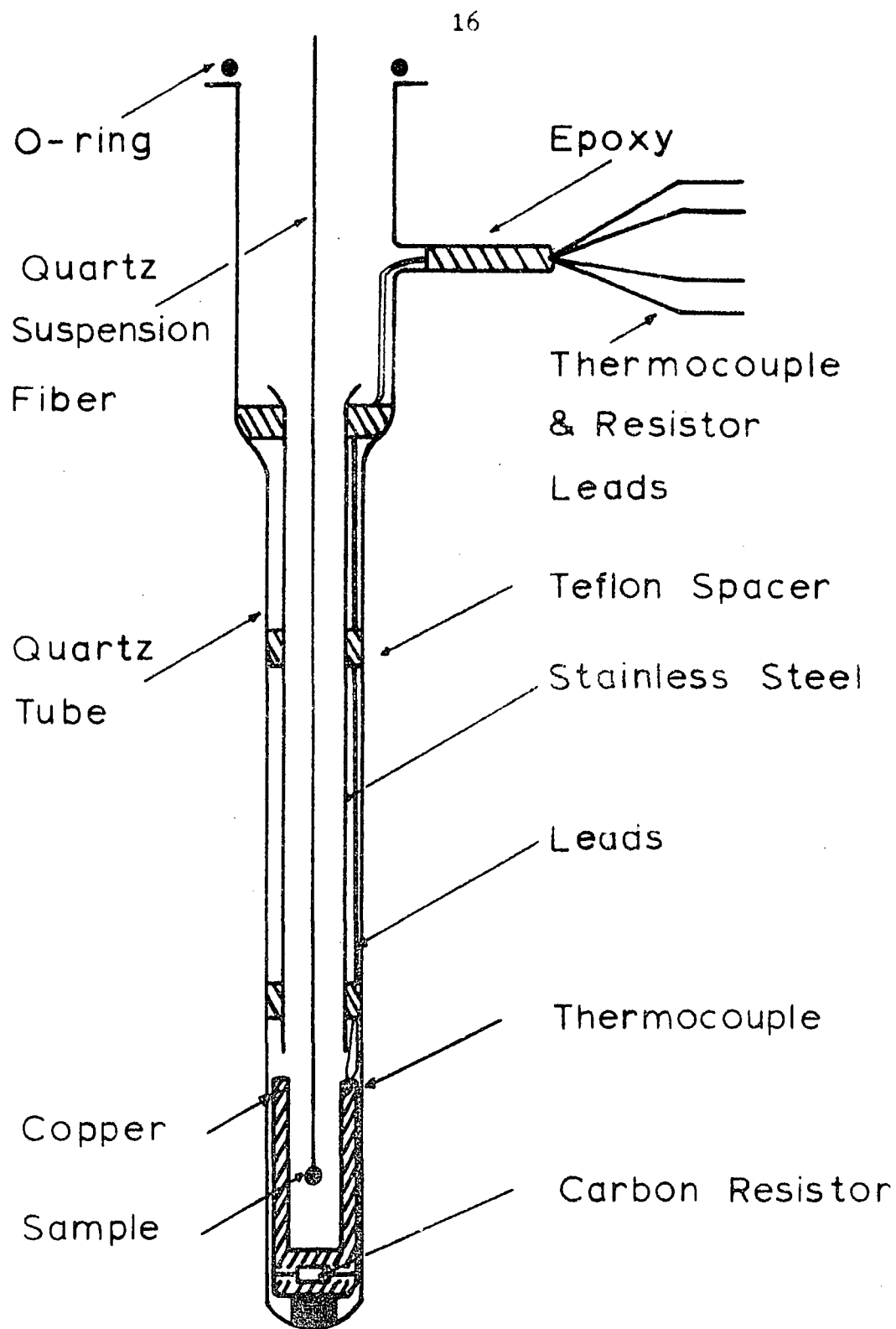


Figure 4. Detail of sample tube.

directly attached to the sample without disturbing the magnetic susceptibility measurements. The assumption is made that the crystal temperature is in equilibrium with the copper mass. This assumption has been checked,^{4,10} and, in my particular apparatus, was checked using $\text{Cr}^{3+}:\text{Al}_2\text{O}_3$ whose magnetic susceptibility is a straight line when plotted against $1/T(^{\circ}\text{K})$. These results are shown in Fig. 5.

As mentioned above, a thermocouple is used to monitor the temperature of the sample. At lower temperatures (less than 10°K) a carbon resistor may be used to monitor the temperature, and it is mounted in the base of the copper mass. The leads from the resistor and the thermocouple go up the side of the tube to the area of room temperature and run out a side tube of pyrex. It has been found for our purposes that the leads may be run through an epoxy plug which is formed in and around the end of the small pyrex tube. The leads are kept clear of the central area by a thin-walled (0.005"), non-magnetic stainless steel tube which is held in place by teflon spacers. At the top of the sample tube is an o-ring joint which makes it easy to remove the tube and change samples.

Temperature Control for 300°K to 5.5°K

The temperature around the sample area is controlled by a coolant of either cold nitrogen gas (300°K to 80°K), liquid nitrogen (77.3°K), cold helium gas (80°K to 5.5°K), or liquid helium (4.2°K). For these ranges the U-shaped

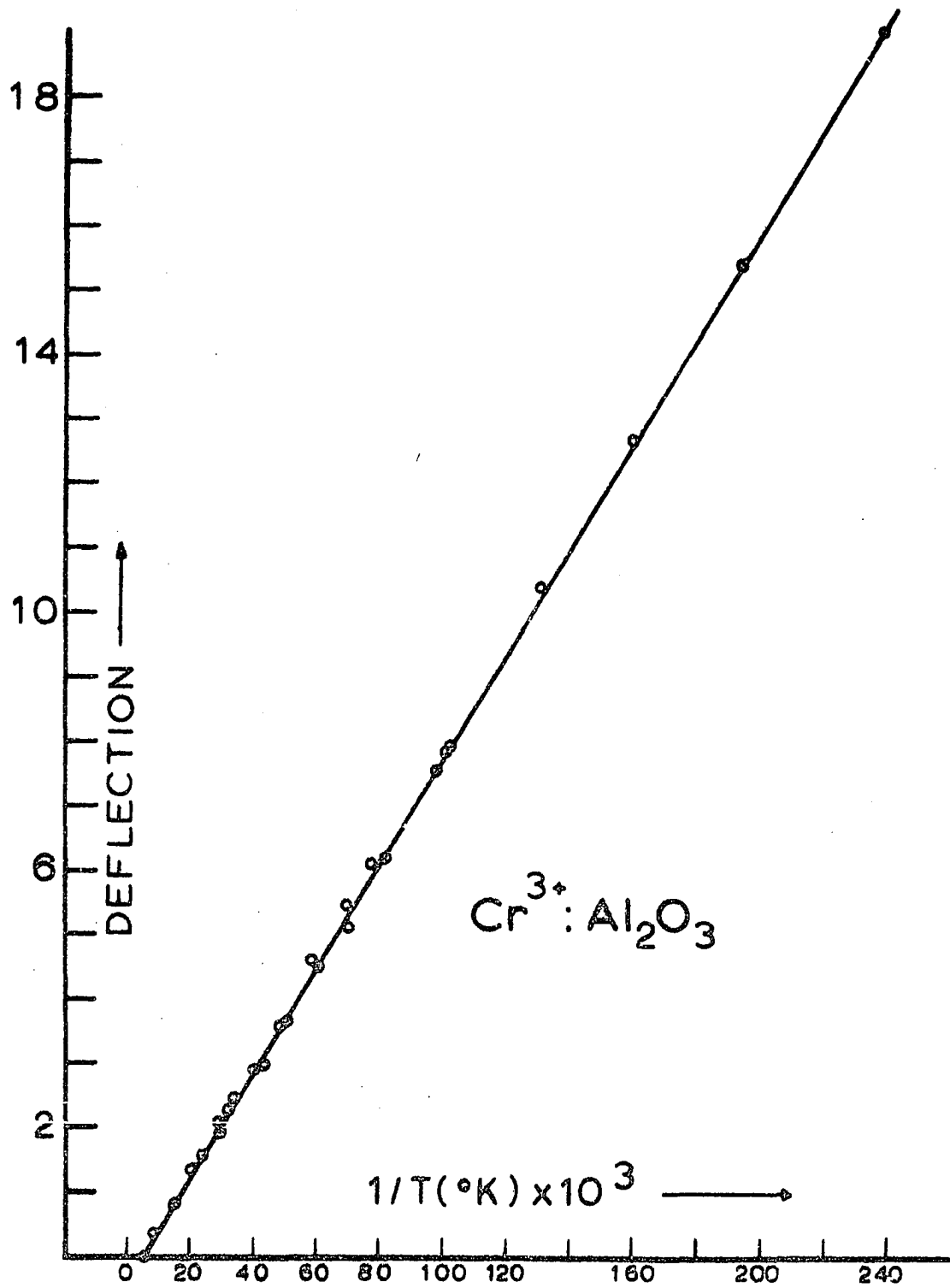


Figure 5. $\text{Cr}^{3+}:\text{Al}_2\text{O}_3 - \chi$ vs. $1/T$

dewars shown in Fig. 3 are used. The cold gas or liquid is introduced into one arm of the dewar, and the gas or liquid flows up the other arm and cools the sample area. In the 300°K to 80°K range, the method of measurement is identical to the method described by Brumage.³ The technique in the 80°K to 4.2°K range is a little different.

The temperature control system for the 80°K to 4.2°K range is shown schematically in Fig. 6. Here we have used a thermocouple as the temperature detecting device with the calibration curves of Powell, Bunch, and Corruccini.¹¹ We shall discuss the use of the carbon resistor in the later section. The thermocouple is soldered to the copper mass surrounding the sample. The other end is maintained at liquid nitrogen temperatures and serves as a reference junction. The output voltage is read using a Leeds and Northrup K-5 potentiometer, and its associated D-C null detector. The null detector has a voltage output representing an error signal. This error voltage is fed into the differential power amplifier shown in Fig. 7. The differential power amplifier powers a small heater on the exit end of the helium transfer tube. Once a steady current to the heater is set manually by adjusting a variac to the desired voltage, and a nearly steady temperature is reached, the differential power amplifier is switched to automatic, and the current to the heater is raised or lowered in response to the error voltage from the D-C null detector. This device

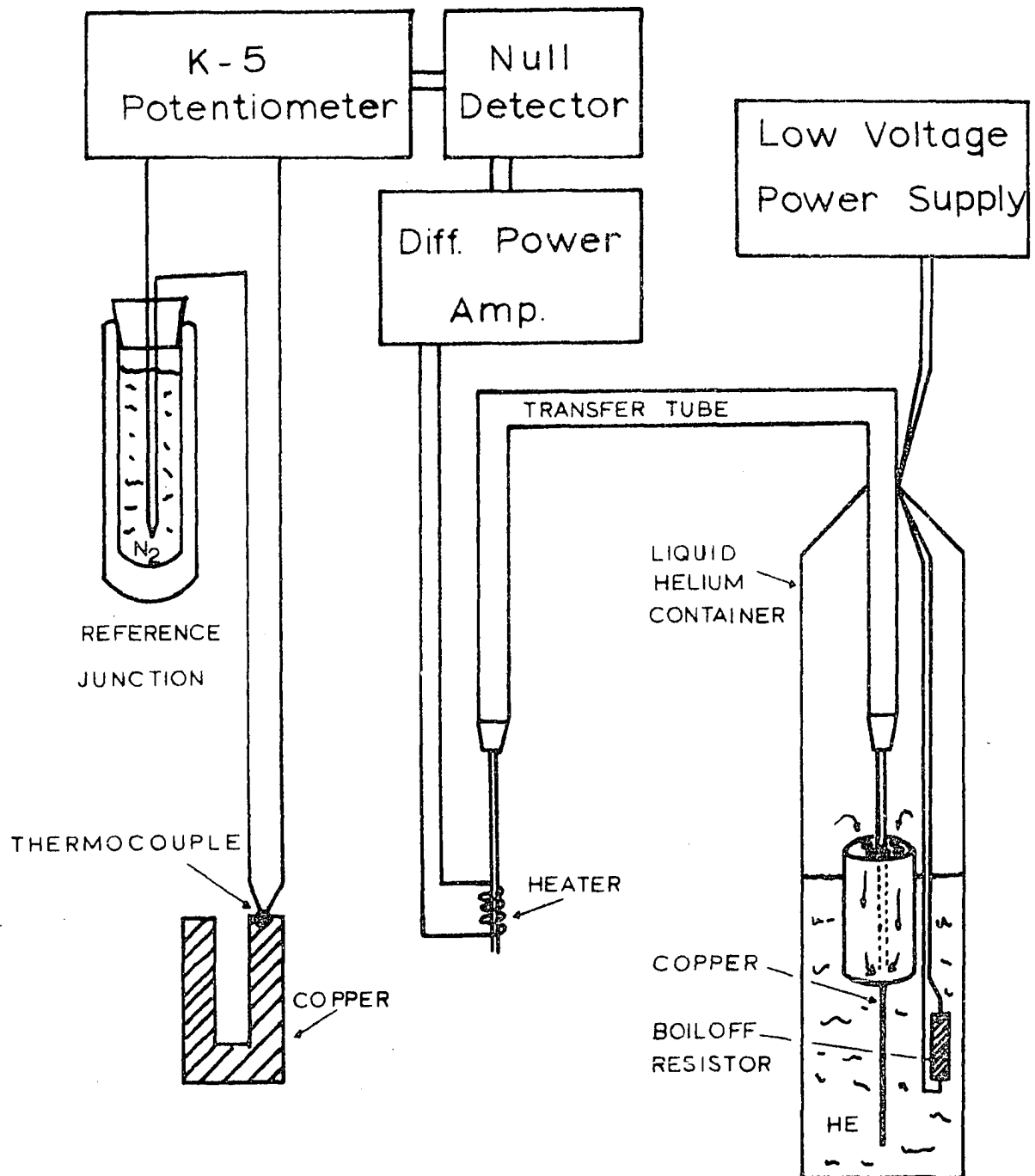


Figure 6. Temperature control for 80°K to 5.5°K .

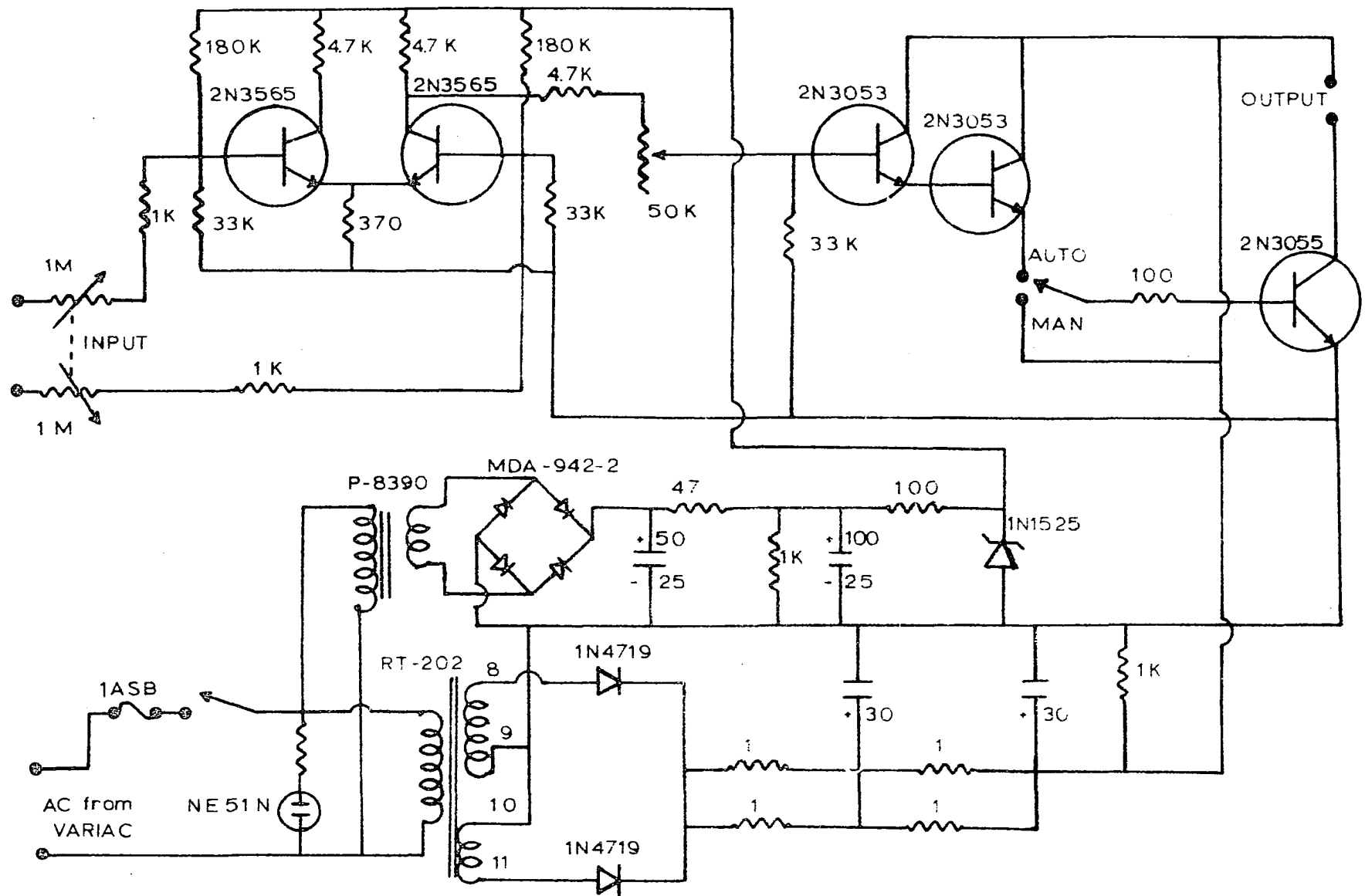


Figure 7. Differential power amplifier schematic.

is quite useful when it is desired to hold a steady temperature for long periods of time.

Cold helium gas is supplied by a helium dewar containing liquid helium which can be slowly evaporated by supplying current to a 100 ohm wire-wound resistor placed in the liquid helium from a regulated low voltage source. This power varies from 0.25 watts to 5 watts. The gas is kept at 4.2°K by a long copper rod which is always immersed in the liquid helium and keeps the lower end of the transfer tube in the helium dewar at 4.2°K (Fig. 6). This system works quite well down to 10°K and has been used to as low as 5.5°K ; although it consumes more helium in the 10°K to 5.5°K range, because we are only using a single dewar system. Even down to 5.5°K the system can be considered useful in that it is easy to use, allows good control of sample temperature, and can be quickly adjusted to different temperatures. Liquid helium is always introduced at the end of a run in the 80°K to 5.5°K range to measure the magnetic susceptibility at that point and to get the thermocouple reading when it is immersed in liquid helium. The thermocouple reading at liquid helium temperature is used to calibrate the thermocouple. The sensitivity of the copper-constantan thermocouple begins to decrease below 20°K , and points below 10°K must always be compared to the helium temperature. The technique used to measure magnetic susceptibilities at temperatures lower than 4.2°K will be

discussed in the next section.

One problem which causes considerable trouble at less than 20°K is a jumping around of the sample which is suspended on a quartz spring. This is probably due, in part, to heat leaks, which cause currents in the exchange gas, and which, in turn, move the sample around. These forces are often larger than the magnetic susceptibility being measured. Another possible cause is the Taconis effect¹² which occurs when a small tube is cold at the open end and warm at the closed end. This effect is often used to measure the liquid level in liquid helium dewars. A thin piece of rubber is placed over the warm end, and then the change in the pressure oscillations is monitored as the open end moves in and out of the liquid helium. It is found that this effect can be minimized by varying the exchange gas pressure, and in some cases the pressure must be varied for different temperature ranges below 10°K .

Temperature Control for 4.2°K to 1.8°K

The technique of pumping on a liquid helium bath to lower the temperature of the system is well known, and the vapor pressure of He^4 (1958 scale)¹³ is given for temperature from 1°K to 5.2°K . The problem is to adapt this technique for use with the Faraday balance.

The first step is to design a double dewar system which will fit in the pole gap of the magnet and hold enough helium for an experiment of 4 to 5 hours' duration. The

dewars are shown in Fig. 8. Styrofoam spacers are used in the liquid nitrogen jacket to support the inner helium dewar. The outer dewar is supported by a vertical aluminum bar and clamps. Since we want to reduce the vapor pressure above the liquid helium bath, a cap was built which allows the liquid helium to be transferred into the dewar while in place. After the transfer the helium fill and vent holes may be plugged and the cap fitted to the sample tube so that it is air tight. The cap is shown in Fig. 8. Note that the cap is fitted to the sample tube by a swagelok with teflon ferrels soldered to a metal bellows which is between the swagelok and the vacuum cap to allow some flexibility and movement of the cap itself as the dewar is filled and then the pressure is reduced by the vacuum pump. The brass cap has an o-ring groove identical to that of the glass o-ring joint of the helium dewar. This is the airtight seal between the dewar and the cap. Extreme care must be taken in alignment so that the sample tube is not moved from side to side and thereby making contact with the crystal.

Let us now look at the method used to control the vapor pressure of the liquid helium. This system is shown in Fig. 9 and consists of a group of valves in parallel between the vacuum pump and the liquid helium. Valve A is a milturn needle valve, and B and C are successively larger valves. These valves are adjusted as desired to control the pumping speed and therefore the vapor pressure of the liquid helium.

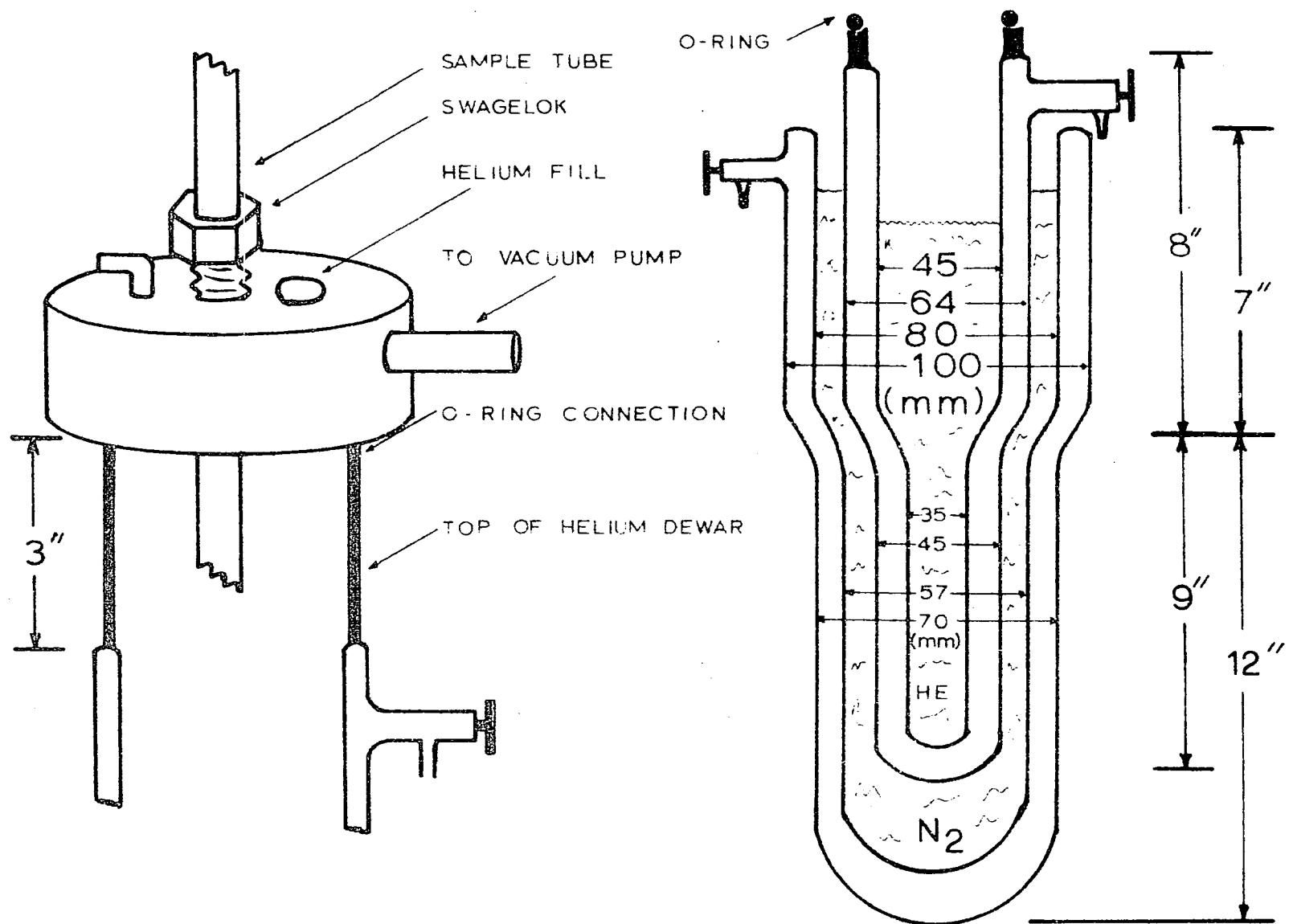


Figure 8. 4.2°K to 1.8°K dewar assembly.

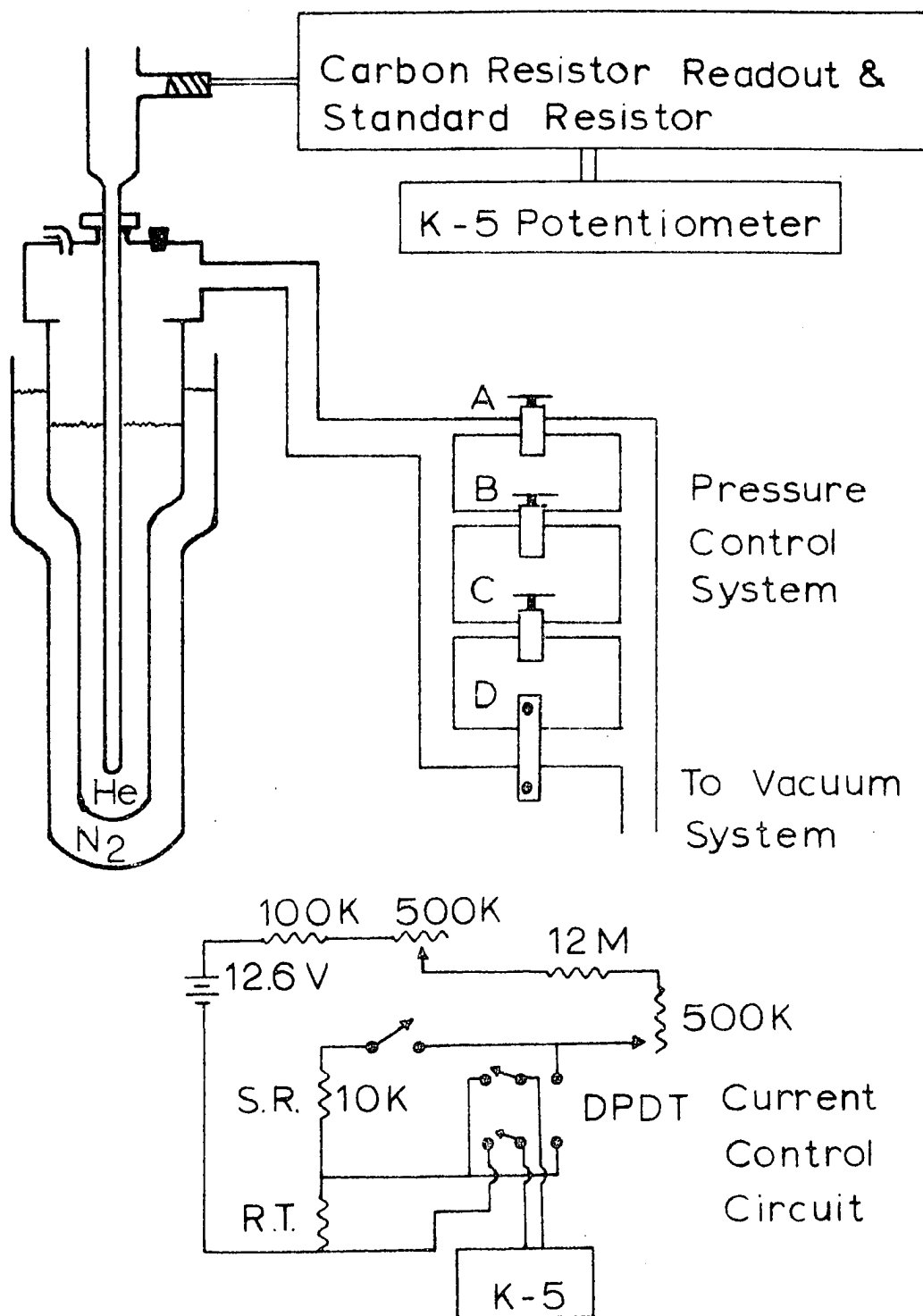


Figure 9. Low temperature control mechanism.

Part D is merely a piece of vacuum hose which has a clamp to close it off. This is only open for temperatures below 2°K when a high pumping speed is needed. This system was adequate for the measurements in the temperature range of 4.2°K to 1.8°K .

Temperature monitoring is accomplished by using a carbon resistor calibrated by F. L. Scarpace at the University of Wisconsin physics department. This is a $1/8$ watt carbon resistor which was cycled between 300°K and 4.2°K several times before calibrating. This procedure seems to reduce the change in calibration due to temperature cycling as it is used. The temperature was controlled for calibration by basically the same method as described above. After approximately a dozen calibration points were taken, the data was fed into a standard program which found the best fit for the formula $\ln R = A + B/T + C \ln T$. The curve R vs. T for the resistor used in these experiments is plotted in Fig. 10. This particular curve was not used to find the temperature associated with a measured resistance, but rather a table was used which gave the resistance for each millidegree between 1.7°K and 5°K . The resistor could, of course, be used up to higher temperatures, and although calibration data points were taken up to 27°K , the curve fit was not good to more than 0.1°K above 10°K .

A block diagram of the temperature detection circuit is given in Fig. 9. The temperature sensing carbon resistor

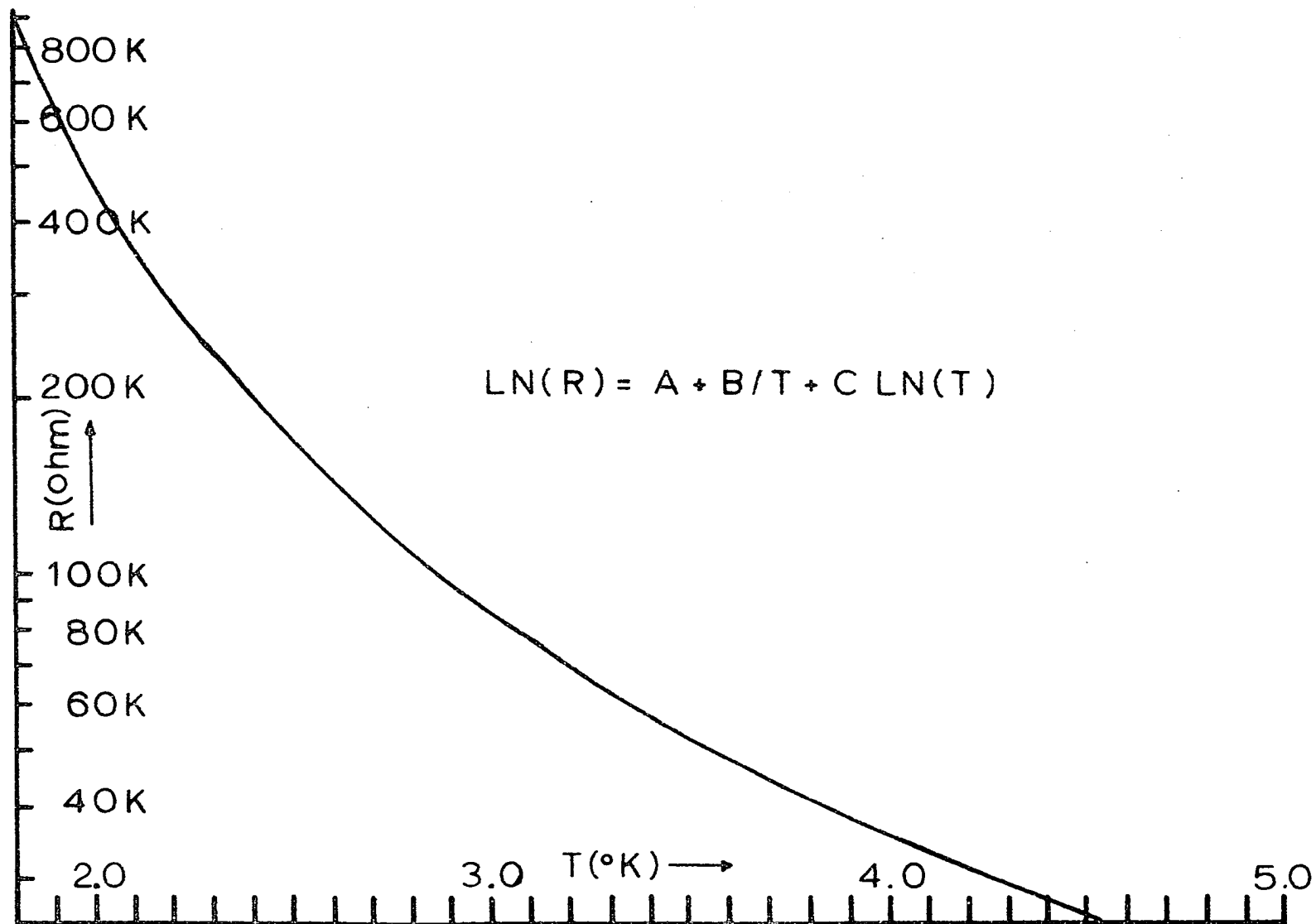


Figure 10. $R(\text{ohm})$ vs. $T(^{\circ}\text{K})$ for carbon resistor sensor.

in Fig. 9 is connected to a current control circuit which allows us to read either the potential across a 10K standard resistor or the potential across the temperature sensing resistor. Current in the circuit was maintained at 1 microamp by monitoring the standard resistor potential. Heating due to the temperature measuring resistor is negligible since even at 1.8°K where $R = 900K$ ohms, the power dispersed by the resistor is only around 1 microwatt. The schematic for the current control circuit is also given in Fig. 9.

CHAPTER III

DOPING DIAMAGNETIC CRYSTALS WITH PARAMAGNETIC IONS OF IRON, CHROMIUM, AND NICKEL

Introduction

Early in the course of this research we became interested in studying a series of II-VI compounds doped with particular transition metal ions. Since we could not always obtain the crystals we wanted, experimentation with crystal doping began. Some copper and nickel doping had been done in our laboratory, and it was decided to try doping iron, chromium and nickel into various II-VI compounds in order to study the magnetic susceptibility of the paramagnetic ions and thereby gain some information about the positions of the lower lying electronic energy levels.

The general problem of doping transition metal ions in II-VI compounds is in many cases not very well documented or even understood.^{14,15} However, as interest in the effects of impurity ions in II-VI and III-V compounds has grown in the last ten years, more investigation in these areas has been completed. Of special interest as a reference text is the rather lengthy book by Kroger¹⁵ and the more introductory volume to defect chemistry by Van Gool.¹⁵ These books

deal with the physical chemistry aspects of the problem.

Since the physical chemistry of binary compounds is not the primary concern here, we shall be content to report the procedures which we used to dope different II-VI compounds with Fe, Cr and Ni. Previous investigators have doped transition metals in II-VI compounds in order to study optical absorption,^{17,18,19} electron spin resonance,²⁰ and luminescence.²¹ Generally our first attempt followed previously described procedures, and then certain procedures were modified on a trial and error basis until the desired transition metal concentration and distribution was achieved.

Before we go into the detail of the doping procedures, let us first consider what we want in the end product. We want to study an impurity ion which goes into the zinc-blende structure of, say, ZnS by measuring the paramagnetic susceptibility of the paramagnetic ion in the diamagnetic crystal as a function of temperature.

This places some requirements on concentration and distribution of the impurity ion in the crystal. We want at least 10^{17} to 10^{18} ions/c.c. in order to see the magnetic effects due to the impurity ion; a uniform distribution so that each impurity ion is influenced only by the electrostatic field of the host crystal; and the impurity ion to replace a Zn^{2+} ion at its lattice site in the crystal. These requirements are rather demanding because the measured magnetic susceptibility arises from the entire volume of the

crystal, which in turn sets distribution standards for the whole crystal. This is a different situation than one encounters in doping a crystal for cathodoluminescence, for instance, where the electron beam excited luminescence centers to a depth of only 4 to 5 microns. In this case one need only worry about the surface concentration of impurity ions.

Procedure for Doping

If we want to study the magnetic properties of a particular impurity ion in the electrostatic environment of the host crystal, then we must require that the host be free of any other magnetic impurities. To check for this the magnetic susceptibility of the host crystal is measured as a function of temperature. The pure crystal should be diamagnetic and therefore independent of temperature. This was not the case for some of the crystals until we discovered that the crystals could be contaminated when cut or cleaved and had to be etched in an acid to remove the paramagnetic surface impurities.

Once the host crystal is known to be magnetically pure (for our use), then it is ready to be plated with the dopant. This is accomplished by a vacuum evaporation apparatus shown in Fig. 11. The charts and descriptions in the books by L. Holland²² and J. D. Strong²³ aid in the choice of filaments and techniques to use with a given metal. In these texts one finds techniques and refractory support materials for

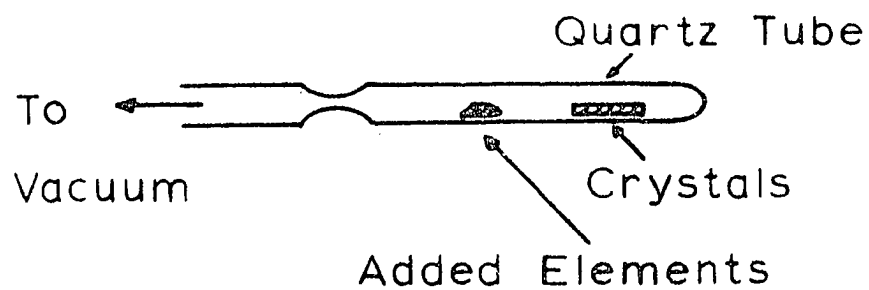
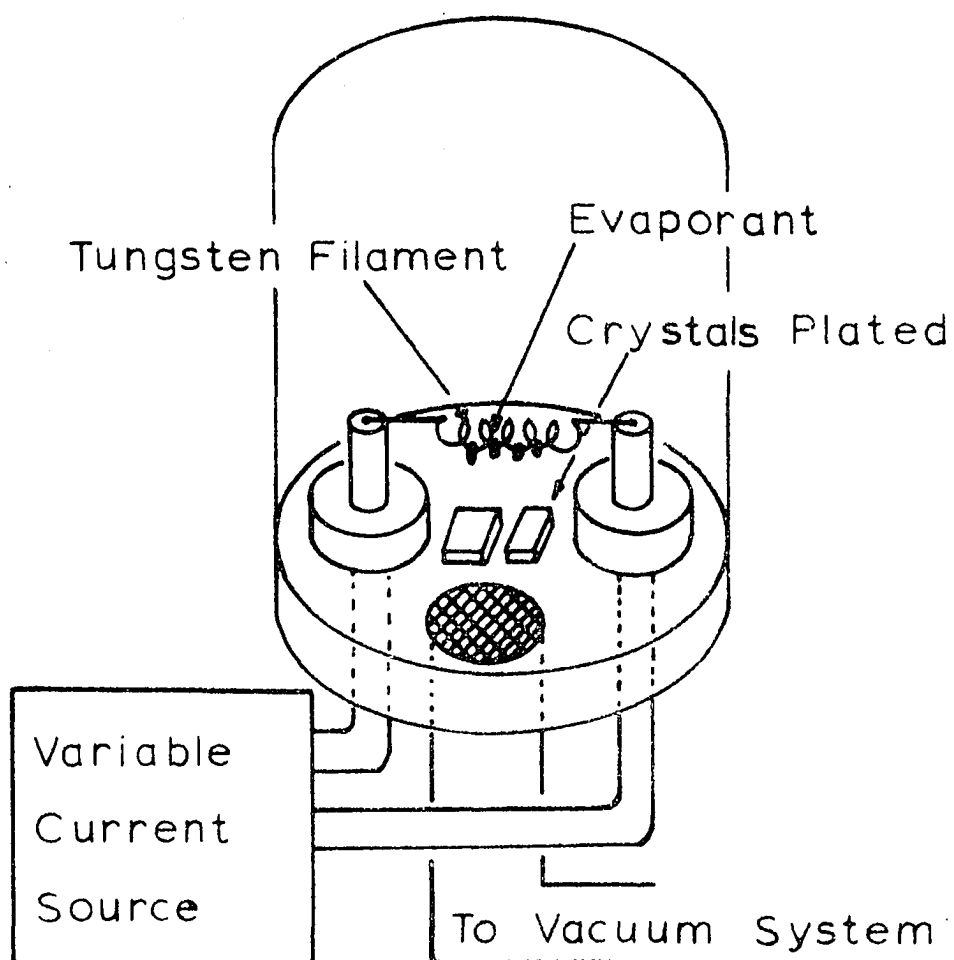


Figure 11. Vacuum Evaporation Apparatus.

for evaporating metals; as well as useful vapor pressure data. For the evaporation of iron, chromium and nickel a tungsten filament is recommended. However, the iron alloys with tungsten, and care must be taken so that the evaporant does not exceed 35% of the weight of the tungsten filament. The evaporant is heated by passing a current through the filament. Current control is obtained by adjusting the potential with a variac on a step-down transformer which, in turn, supplies the high currents at low voltages to the tungsten filament. The exact values of current required due to the temperature requirements of the heating filament depends upon the particular evaporant. For example, iron and nickel both melt around 1500°C , and their evaporation temperature is about the same value. (Evaporation temperature²² is defined as the temperature at which the vapor pressure of the evaporant reaches 10 microns Hg.) However, chromium melts at around 1900°C , but its evaporation temperature is 1200°C . During evaporation the iron and nickel boil while the chromium sublimes to plate the crystals. The molten metal is kept in the heating coil by surface tension.

The crystals which are to be plated with the desired metal are placed on a glass slide and positioned beneath the heating filament. The current in the filament is increased slowly until the filament is red, and then the increase is even slower until the iron or nickel melts.

The chromium pellet is heated until it becomes red. Evaporation of the metal usually begins at this point, and the rate of evaporation can be controlled by increasing or decreasing the current to the filament. The thickness of the metal film on the crystal can be monitored to some degree by looking through the glass slide. In our case the evaporation was continued until the glass slide was opaque. This insures that the metallic film is at least a minimum thickness of approximately $1000 \text{ \AA}$ or 0.1 micron .²³ Both sides of the crystal are plated with a uniform thickness of metal.

After plating, the crystal is placed in a quartz tube which is closed at one end and has been "necked-down" by heating around the tube and then pulling it slowly apart, as shown in Fig. 11. The constriction aids in sealing the quartz tube after evacuation. As the crystal is put into the quartz tube, any additional elements are added. The quartz tube is now evacuated to less than 5×10^{-6} torr and then sealed off by carefully heating the constriction with a torch. The metal plated crystal is now ready for the oven.

The crystal is heated at temperatures from 800°C to 1200°C for a period of approximately 100 hours. The temperature depends upon the host crystal, and we seem to get more consistent results by heating for several days. The oven and block diagram of its temperature controller are

shown in Fig. 12. The heating element is a cylinder $1 \frac{1}{8}$ " ID x $1 \frac{3}{4}$ " OD x 15" long, 7" of which is the actual heating element. The cylinder is cut so that the current flow does not give rise to a magnetic field along its axis. The heating element is placed in a ceramic tube, and this is wrapped by felted micro-quartz which in turn is covered with asbestos paper to protect the felted micro-quartz. When the oven is maintaining a temperature of 1000°C , the power input is less than 500 watts. Temperature is maintained at a given setting by an API Model 603K SCR Driver, Compact I Controller associated with an API Model 603 pyrometer, type R with 1% accuracy calibration and a Platinum/Platinum 13% Rhodium thermocouple.

Once the crystal has been heated the prescribed length of time, we quench it rapidly in a large beaker of water to "freeze in" the solubility and distribution properties of the impurity ion characteristic of the higher temperature. A rapid quench is necessary because in some cases (Ni diffuses quite rapidly) the impurity ion will try to diffuse out of the crystal again and cause precipitation or clustering of the impurity ions.¹⁴ In the cases of Fe, Cr and Ni this clustering is completely unacceptable because it leads to ferromagnetic behavior. Ferromagnetic behavior becomes noticeable at some lower temperature and masks the properties of the individual impurity ion under investigation.

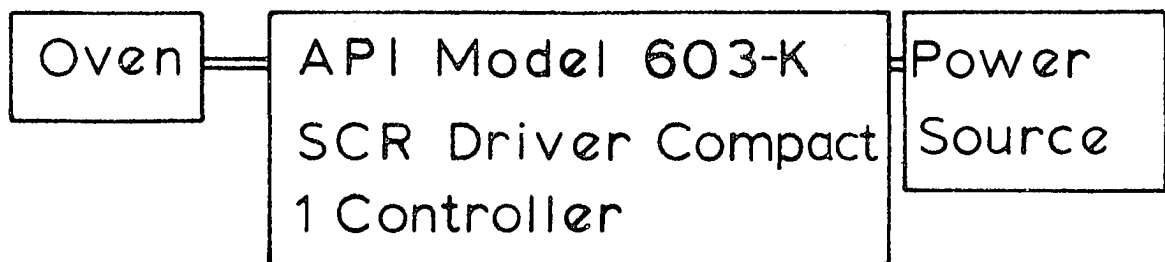
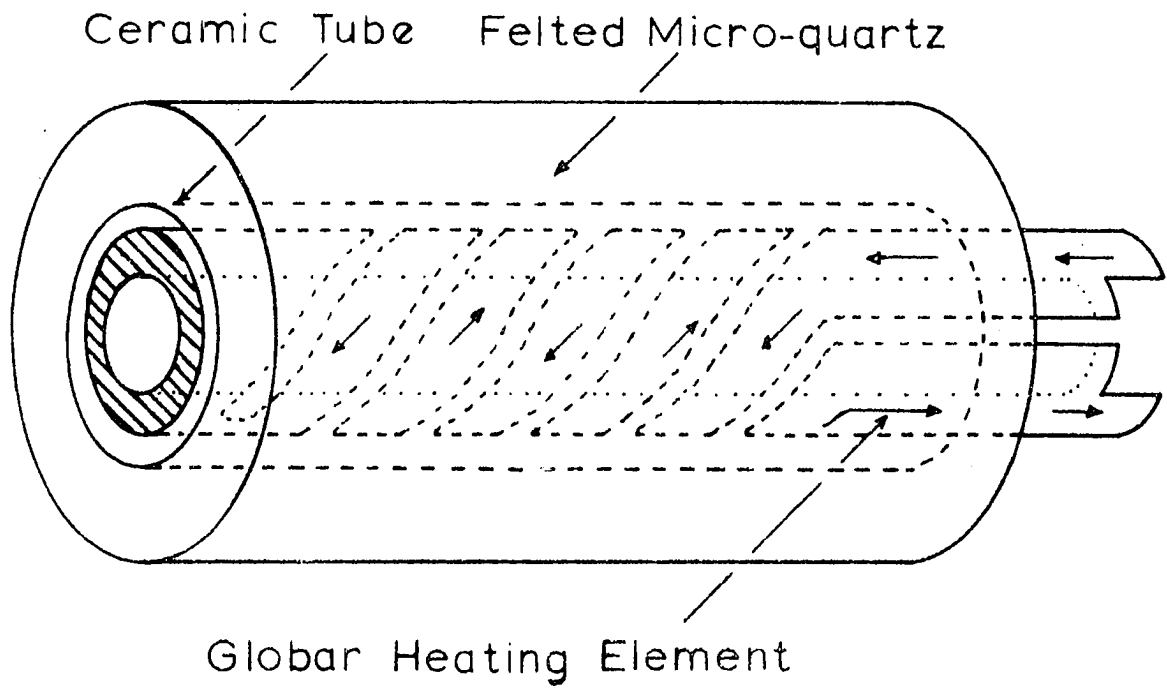


Figure 12. Crystal Oven.

After the crystals have been quenched, they must be etched again in an appropriate acid such as HCl or HNO_3 to remove the residual metal on the surface.

It is observed that one must also remove those surface layers in which the impurity ion is so concentrated that the onset of the exchange phenomena between the impurity ions is seen as the temperature is decreased. This phenomena is very easy to observe when the impurity ions have non-magnetic ground states as in Fe^{2+} and Ni^{2+} . In chapter IV it will be shown that if a paramagnetic ion has a nonmagnetic ground state, its magnetic susceptibility will become constant at sufficiently low temperatures. For an example, let us choose Ni^{2+} because the magnetic susceptibility becomes constant at higher temperatures for it than for Fe^{2+} .

In chapter VII we will find that if Ni^{2+} is located at a tetrahedral site, the expected magnetic susceptibility curve will look like curve D in Fig. 13. If the crystals are not properly etched, the magnetic susceptibility can look like curve A, and we see the magnetic susceptibility increase rapidly with a decrease in temperature. Further etching results in curve B, and careful etching is continued after each magnetic susceptibility measurement until curve D is obtained.

Now we have assumed that Ni^{2+} is the ion which gives rise to the paramagnetic susceptibility. Since the host crystal was checked and found to be diamagnetic and inde-

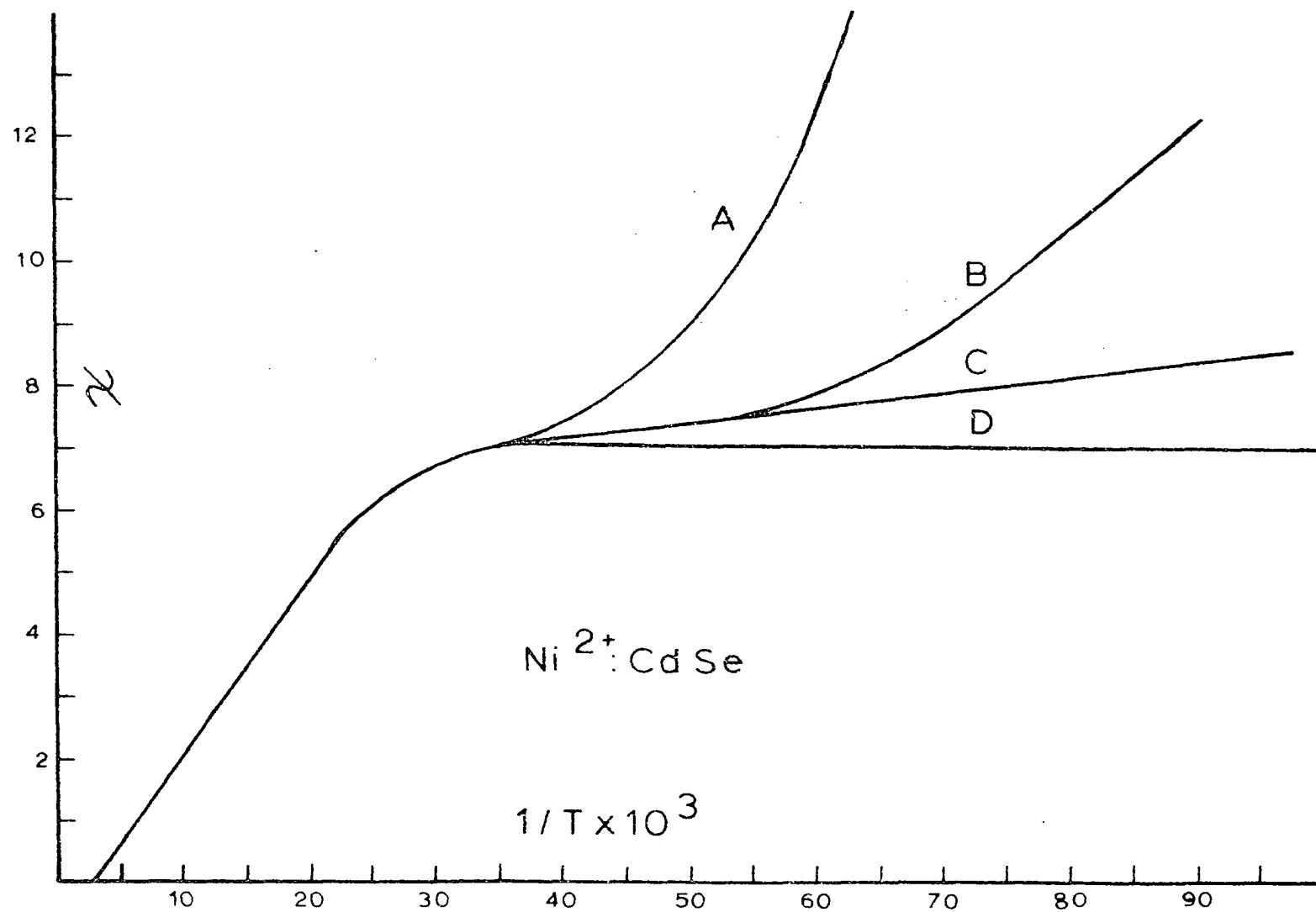


Figure 13. Variation in magnetic susceptibility with concentration.

pendent of temperature; and if care is taken to introduce no other impurities in the doping procedure, any paramagnetic susceptibility should be due to the nickel. However, the Ni could be either monovalent or trivalent and contribute to the paramagnetic susceptibility. If these contributions were added to that of Ni^{2+} , a curve such as C could result in which the magnetic susceptibility increases slowly with a decrease in temperature. If Ni^+ or Ni^{3+} were known to be present, their contribution could be, in principle, subtracted out in the same manner as the contribution of Gd^{3+} was subtracted from the measured magnetic susceptibilities of $\text{Eu}^{3+}:\text{YGaG}$.²⁴ However, if we can obtain crystals which give measured magnetic susceptibility curves like curve D in Fig. 13, then we can strongly argue that the measured magnetic susceptibility is due to Ni^{2+} . Similar arguments hold for Fe^{2+} , although we shall see that in the case of Cr^{2+} , Jahn-Teller effects reduce the usefulness of the above arguments. In this study, both Fe^{2+} and Ni^{2+} doped crystals had a constant magnetic susceptibility at appropriate low temperatures and then remained constant as the temperature was decreased to as low as 1.8°K in the case of $\text{Fe}^{2+}:\text{ZnO}$.

Procedure Variations with Different Host Crystals

Although in principle the process for doping crystals is very straightforward, in practice there is not yet enough known to completely predict the most effective conditions

and/or manner of incorporating impurity ions in a diamagnetic host crystal. Variables such as temperature and length of time for the impurity ion to diffuse into the crystal; and the choice of either adding elements to control vapor pressure or heating the crystal in a vacuum are not well known. In fact, many reported cases of crystal doping are conflicting. The possibility of the crystal subliming from in between the metal plating when heated in a vacuum at too high a temperature has been unintentionally verified through experiment. A summary of the conditions under which crystals with the desired properties were obtained is given in Tables 4, 5, and 6. In the cases where solid elements were added (all of around 99.999% purity), an amount approximately equal to the mass of the host crystal was added. In the case of ZnO the quartz capsule was evacuated, and the pure oxygen was added at an approximate pressure of 1 atmosphere. This additional element has a significant effect upon the impurity concentration in the host crystal^{3,14,15,16}, but this effect was not investigated after an acceptable crystal doping was achieved. The choice of the element to be added was aided by the vapor pressure tables in the book by A. N. Nesmeyanov²⁵.

Summary

The particular method of vacuum evaporation of a metal on a host crystal, and then the heating of the crystals in an evacuated quartz capsule, to dope paramagnetic impurity

TABLE 4

Fe²⁺ DOPED IN II-VI COMPOUNDS

Host	Mass (mg)	Temp. (°C)	Time (hrs.)	Atm.	Conc. $\times 10^{-18}$ (#Fe/o.o.)
ZnO	65.5	1200	200	O	2.5
CdS	21.1	950	120	S	11.8
ZnS	51.4	950	132	S	23.7
CdSe	74.3	950	100	Se	2.5
ZnSe	69.7	950	100	Se	2.5
CdTe	40.7	925	142	Cd	6.8
ZnTe	69.8	925	142	Zn	7.6

TABLE 5

Cr²⁺ DOPED IN II-VI COMPOUNDS

Host	Mass (mg)	Temp. (°C)	Time (hrs.)	Atm.	Conc. $\times 10^{-18}$ (#Cr/o.o.)
ZnS	60.8	900	264	S	0.8
CdS	324.3	900	131	S	1.9
ZnSe	100.0	900	96	Se	1.2
CdSe	189.4	900	96	Se	0.3
ZnTe	113.8	900	96	Zn	0.3
CdTe	98.7	900	96	Cd	1.2

TABLE 6

 Ni^{2+} DOPED IN II-VI COMPOUNDS

Host	Mass (mg)	Temp. (°C)	Time (hrs.)	Atm.	Conc. $\times 10^{-18}$ (#Ni/c.c.)
ZnS	53.5	900	94	S	27.0
ZnSe	56.4	900	94	Se	15.4
CdSe	52.4	900	94	Se	5.0
ZnTe	68.8	900	94	Zn	18.0

ions in a diamagnetic host crystal was chosen for its simplicity and its ability to produce the desired crystals (other methods are discussed in ref. 2, p. 32). With this method Fe^{2+} has been doped into the seven host crystals of ZnO , CdS , ZnS , CdSe , ZnSe , CdTe , and ZnTe ; Cr^{2+} into the six host crystals of CdS , ZnS , CdSe , ZnSe , CdTe , and ZnTe ; and finally Ni^{2+} into CdSe , ZnSe , ZnTe , CdS , and ZnS . These doped crystals were satisfactory for the measurement of magnetic susceptibilities to temperatures as low as 1.8°K . The concentrations can be determined from magnetic susceptibility measurements and are reported in later chapters on each impurity ion. Fe^{2+} and Ni^{2+} will be found to be primarily in the divalent state due to the constant magnetic susceptibility at low temperatures; however, we shall see that this argument is inappropriate for Cr^{2+} . All that can be said about the distribution of the impurity ions in the host crystals is that the ions are influenced only by the crystalline environment of the host, since we observe no exchange interaction in the reported magnetic susceptibility data.

CHAPTER IV

Fe^{2+} IN TETRAHEDRAL SITES—THEORY

Introduction

Our intention in this investigation is to further studies of iron group transition metals in II-VI compounds. Here, we are interested in Fe^{2+} in the cubic tetrahedral crystal fields of ZnS, CdSe, ZnSe, CdTe, and ZnTe. Then the cases of CdS and ZnO will be considered which have, respectively, a small trigonal distortion and a rather large trigonal distortion.

Let us first look at an isolated iron atom in the divalent state. The electronic configuration of iron is $(1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6 (3d)^6 (4s)^2$ or $(\text{Ar}) (3d)^6 (4s)^2$ where (Ar) represents the filled inner core which is identical to the argon atom. In the divalent state the iron atom loses the two outer 4s electrons, leaving the argon core and the incomplete 3d shell. Since we are concerned only with the magnetic properties of the atom which arise when the shells are not completely filled, we can neglect the inner core of filled shells. Therefore, we will consider only the six 3d electrons and their magnetic properties.

The electrostatic repulsion of the six electrons of

the 3d shell will lift the degeneracy of the electronic energies and form energy levels labeled by the terms S, P, D, F, G, etc.²⁶ In the case of iron we need only concern ourselves with the ground state of 5D since the next term is far enough away from the ground state that it does not effect the magnetic susceptibility (approximately $20,000 \text{ cm}^{-1}$ in free ion for next highest term of 3H).

Now, for our studies, we want the impurity ion to replace a positive ion of the host crystal for about every thousand positive ions, although the solubility of the impurity ion in the host crystal is often much less than this. We do not want the impurity ion in an interstitial site or any other non-substitutional site since this would complicate our problem. When the impurity ion is so placed in the host crystal, there will be an effect upon its electronic energy levels arising from interactions with the host crystal.

Since we are studying an isolated impurity ion (all other impurities are far enough away from this site that they have no effect), we can lump together the crystalline effects due to the individual host ions into a crystal field potential.^{27,28,29} The crystal field is developed in terms of a power series of tesseral harmonics in explicit terms of the charge and the positions of ions giving rise to the field. In our studies we are assuming that there are no significant distortions to the host lattice by the substitution of the impurity ion. Two important properties of

this crystal field are those of the symmetry and the strength of the electrostatic field. The symmetry of the host is, of course, determined by the lattice structure, but the strength of interaction, as seen by the effects on the impurity ion, is better determined experimentally for each particular case.

Crystal Structure

The crystals investigated in this study have either the zincblende or wurtzite crystal structure.³⁰ The zincblende structure³¹ may be considered as two interpenetrating cubic face centered structures translated with respect to each other by $1/4$ of the body diagonal or c-axis (Fig. 14). The wurtzite structure³¹ may be considered as two interpenetrating hexagonal close-packed structures displayed with respect to each other by $3c/8$ along the c axis. These two structures are identical out to the third nearest neighbor. In both structures the nearest neighbors form identical tetrahedral units as shown in Fig. 14. Nine of the twelve next nearest neighbors also have identical locations, and the other three are rotated by an angle of 60° in the zincblende structure with respect to the wurtzite structure. Therefore, significant differences between the two structures arise only in the third nearest neighbors, and this is one of the reasons some compounds exist in both structures. ZnS, CdSe, ZnSe, CdTe, and ZnTe all have the cubic tetrahedral symmetry either in zincblende or wurtzite structures. The tetrahedral symmetry of the negative ions surrounding the impurity

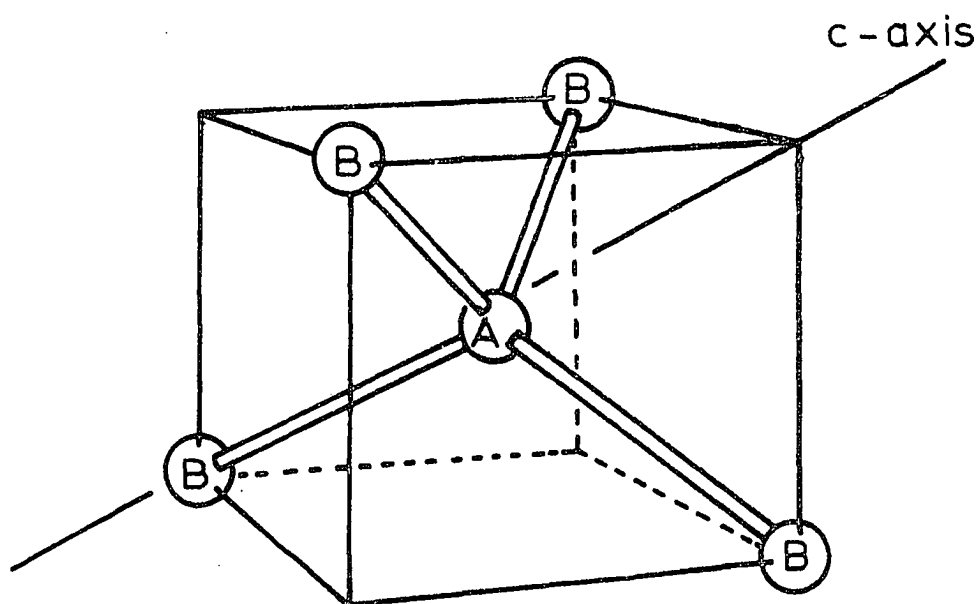
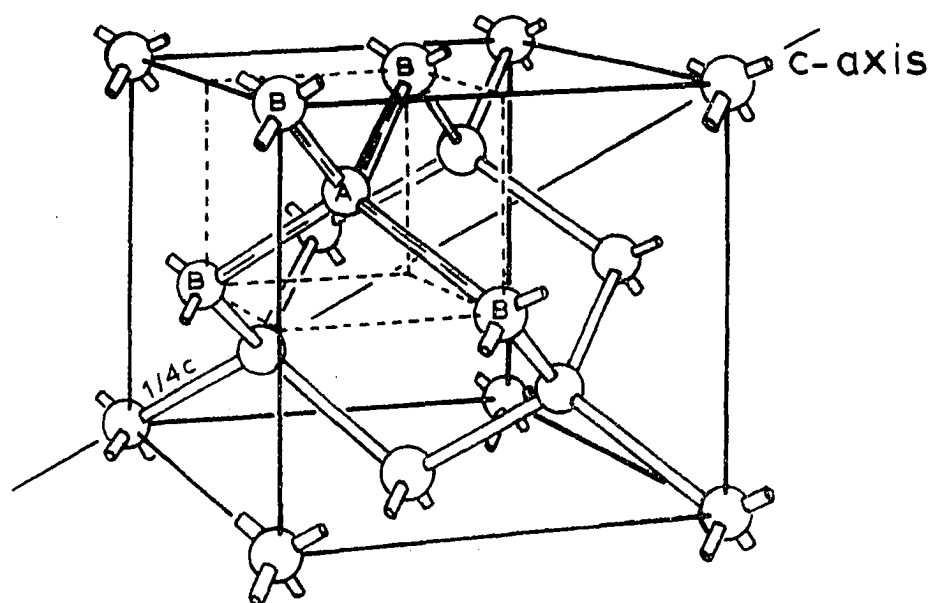


Figure 14. Impurity ion in zincblende structure.

ions is shown in Fig. 14. The cases of CdS and ZnO are basically the same with the addition of a trigonal distortion which amounts to a stretching of the crystal along the body diagonal or c-axis of the crystal. This is illustrated in Fig. 15 where the bond length of one of the negative ions is longer than the other three (a).

Hamiltonian

Once we have our crystal potential, we can use the approach known as crystal field theory, which was suggested by Bethe,²⁹ to calculate the splitting of the terms of the impurity ion. The crystal field is not the only interaction which will split the energy levels, and we must consider, therefore, the effects due to the spin-orbit interaction, slight distortions from the cubic tetrahedral field, and the effects of the applied magnetic field.

At this point, let us look at the Hamiltonian used in calculations of this type and list the terms in order of decreasing effect on the electronic energy levels. In our particular case, we can use the weak-field approximation in which the crystal field strength is less than the electrostatic repulsion of the electrons of the free ion. This electrostatic interaction is included in the unperturbed Hamiltonian (H_0) of the free ion. The complete Hamiltonian can be written as

$$H = H_0 + V_c + H_{s-o} + V_t + H_m, \quad (4-1)$$

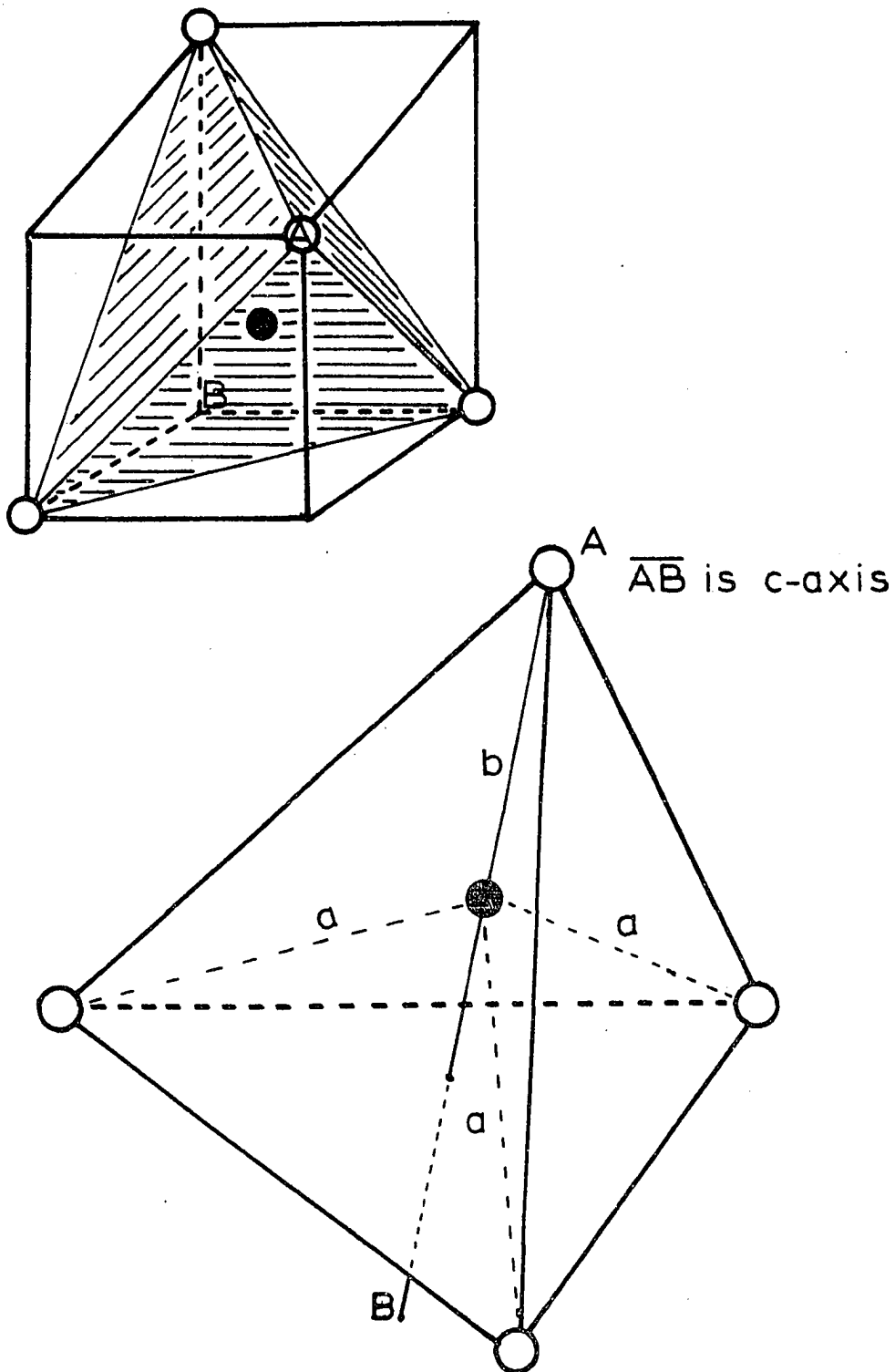


Figure 15. Tetrahedron with trigonal distortion along body diagonal $\overline{AB}$.

where
$$H_0 = \sum_{i=1}^n \left[(p_i^2 / 2m) - (Ze^2 / r_i) \right] + \sum_{i < j}^n (e^2 / r_{ij})$$

(4-2)

and corresponds to the Hamiltonian of the free ion;

$$V_c = \sum_{i=1}^n A_4^0 r_i^4 \{ Y_4^0(\theta_i, \phi_i) + \sqrt{\frac{10}{7}} [Y_4^3(\theta_i, \phi_i) - Y_4^{-3}(\theta_i, \phi_i)] \}$$

(4-3)

represents the crystal field term where the z-axis is along the trigonal axis (c-axis of the crystal);

$$H_{S-O} = \lambda \vec{L} \cdot \vec{S}$$

(4-4)

represents the spin-orbit interaction for the case of Russell-Saunders coupling with the radial integration included in λ ; (λ is defined as the spin-orbit coupling parameter and is determined from the experimental measurements);

$$V_t = \sum_{i=1}^n B_2^0 r_i^2 Y_2^0(\theta_i, \phi_i) + B_4^0 r_i^4 Y_4^0(\theta_i, \phi_i)$$

(4-5)

represents the trigonal distortion of the tetrahedron along the body diagonal with the z-axis along the crystalline c-axis; and

$$H_m = -\vec{\mu} \cdot \vec{H} = \mu_0 (\vec{L} + g_S \vec{S}) \cdot \vec{H}$$

(4-6)

represents the term arising from the presence of the magnetic field. We can then with the above Hamiltonian, calculate the electronic energy level splittings in terms of some parameters which are to be determined experimentally. Although these parameters could be calculated from first principle, even with many approximations the calcula-

tions are still laborious, and the results generally do not fit the experiment well. This is due to a variety of reasons, among which are that the crystal field theory calculations have assumed point charges in the host lattice, and covalency effects of the crystal are difficult to assess except by experiment.

Magnetic Susceptibility

Once the energy level splittings are known, the magnetic susceptibilities can be calculated by the standard methods of Van Vleck.³² Van Vleck finds that the paramagnetic susceptibility is given quantum mechanically by

$$\chi_m = \frac{L \sum_n \omega_n \{ [W^{(1)}(n,n)]^2 / kT - 2W^{(2)}(n,n) \} \exp(W^0(n,n)/kT)}{\sum_n \omega_n \exp(-W^0(n,n)/kT)} \quad (4-7)$$

where ω_n = degeneracy of the state,

L = molecules / mole,

and the coefficients (W 's) used above are defined by expansion of the perturbed energy as a power series in the magnetic field $\vec{H}$.

$$E(\text{perturbed}) = W_{njm}^{(0)} + W_{njm}^{(1)} H + W_{njm}^{(2)} H^2 \quad (4-8)$$

where $W_{njm}^{(0)}$ = solution of unperturbed problem, (4-9)

and $W_{njm}^{(1)} = (njm | \beta(L+2S) H | n'j'm')$ (4-10)

which is independent of field strength H and is the first order correction to the small perturbation $\beta(L+2S)$,

$$\text{and } W_{njm}^{(2)} = \sum_{n'j'm'} \frac{|(njm | \beta(L+2S) H | n'j'm')|^2}{h\nu(njm) - h\nu(n'j'm')} \quad (4-11)$$

which is the second order correction term. A point worth noting here is made by comparing the approach of the experimental work of Curie in 1895, and the subsequent theoretical justification of Langevin in 1905 with that of the more recent quantum mechanics. Curie's work was oriented towards the determination of the magnetic moment associated with a particular sample. In quantum mechanics the magnetic moment is not associated with the entire volume but is associated with each electronic energy level. This makes the calculation of magnetic susceptibilities more cumbersome; however, with the application of the quantum mechanical approach, many apparent deviations from Curie's law could be explained. This property also makes magnetic susceptibility very useful for the study of lower lying energy levels of paramagnetic ions in diamagnetic host crystals. Since the effect of the host is constant with the temperature change due to its diamagnetism, the temperature dependent paramagnetism of the impurity ion can be studied. In fact, it is these very deviations from the Curie behavior that makes the detection of the positions of electronic energy levels possible.

Let us look at the simple case of just two electronic energy levels and examine the change in magnetic susceptibility as the temperature is varied. In Fig. 16 we see electronic energy levels 1 and 2 which are separated by an energy Δ . Initially the thermal energy of the system (kT)

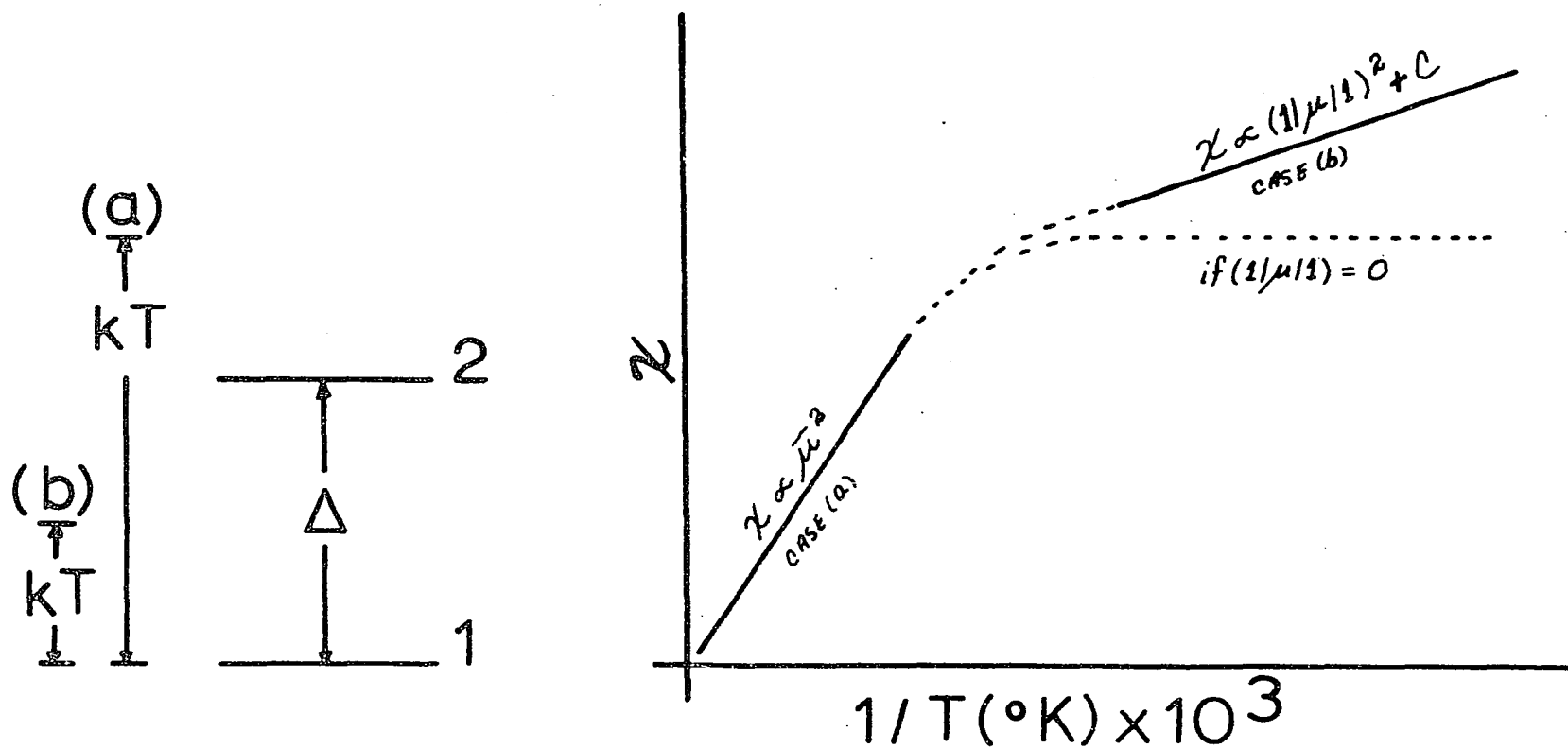


Figure 16. Magnetic susceptibility from two energy levels.

is much greater than the energy Δ . (Assume energy of level 1 is zero.) In this case, the effect of the two levels on the magnetic susceptibility is to contribute a constant magnetic moment $\bar{\mu}$. Then in the region where kT is much greater than Δ , the magnetic susceptibility χ is proportioned to $\bar{\mu}^2/kT$; and therefore, it exhibits Curie-like behavior. Next, if we look at the region where the energy separation Δ is much greater than the thermal energy kT , we will again see a Curie-like dependence of the magnetic susceptibility on the temperature. The magnetic susceptibility is now

$$\chi \propto \frac{|(1|\mu|1)|^2}{kT} + \frac{2|(1|\mu|2)|^2}{\Delta} \quad (4-12)$$

where $(1|\mu|1)$ is the diagonal matrix element of the magnetic moment operator, and $2|(1|\mu|2)|^2/\Delta$ is the temperature independent contribution to the ground state magnetic moment which arises since there is a matrix element connecting levels 1 and 2, and level 2 is close enough to level 1 to make a significant contribution.

Because the temperature dependent magnetic susceptibility is different in the two regions ($kT \gg \Delta$ and $kT \ll \Delta$), the slope of the curve is different for the two regions when the magnetic susceptibility is plotted vs. the reciprocal of the temperature. This is shown in Fig. 16. This property can be very useful in determination of the position of electronic energy levels lying near the ground state. If it happens that the diagonal matrix element of the magnetic

moment operator is zero for the ground state, then the magnetic moment depends only on the factor $2|(1|\mu|2)|^2/\Delta$ which is temperature independent.

Therefore, in those cases where there is an electronic energy level or levels which lie close to the ground state, and their separation from the ground state is greater than the energy associated with the lowest temperature which can be reached by the experimental apparatus, then the measured magnetic susceptibility can be used to determine the position of these levels. The application of this technique will be illustrated later for the cases of Fe^{2+} , Cr^{2+} and Ni^{2+} . In this work with our present magnetic susceptibility apparatus, we can determine the magnetic susceptibility to such an extent that the error in determining the Δ value is $\pm 0.5\text{cm}^{-1}$, and the sensitivity compares quite favorably with the as yet sparse data^{3,33} available from work done in the far infrared range (10 to 120 cm^{-1} or 1000 to $83\text{ }\mu$) for transition metal ions in II-VI compounds.

Application of Group Theory

Group theory can be used to advantage in the prediction of the maximum splittings of the electronic energy levels as the free ion is placed in the host crystal, resulting in a loss of symmetry as the effects of the host crystal field, spin-orbit, trigonal crystal field, and the applied magnetic field are considered. As we have mentioned, the six 3d electrons of Fe^{2+} free ion split into a series of

terms, the lowest of which is 5D as predicted from Hund's rules.³⁴ Since the other terms are much higher in energy, we need only concern ourselves with the 5D term.

When the Fe^{2+} is placed substitutionally for the positive ion in the host lattice (Fig. 14), it is influenced by the crystal field strength and symmetry of the host. In our study, the crystals have a cubic tetrahedral symmetry with, at most, a small trigonal distortion along the body diagonal (Fig. 15). Now, as the 5D term is subjected to the crystal field of tetrahedral symmetry, it splits into two levels

$$^5D \longrightarrow ^5E + ^5T_2 \quad (4-13)$$

as shown in Fig. 17. The energy level separation here is commonly denoted by $10Dq$ or Δ (not the same Δ as in Fig. 16). This spacing is usually determined from optical spectroscopy alone, but in this case, magnetic susceptibility data or far infrared data is needed as well. In the cases discussed here, $10Dq$ ranges from 2000 cm^{-1} to 3000 cm^{-1} .

Next, we must consider the spin-orbit interaction and its effect on the 5E and 5T_2 levels. Group theory tells us that we can expect the levels to decompose under spin-orbit interaction³⁷ as

$$D_S \times \Gamma_j = \sum_k p_k \Gamma_k \quad (4-14)$$

where D_S is the appropriate rotation group for spin S , and Γ_j is the representation of the level under consideration. In this case we have

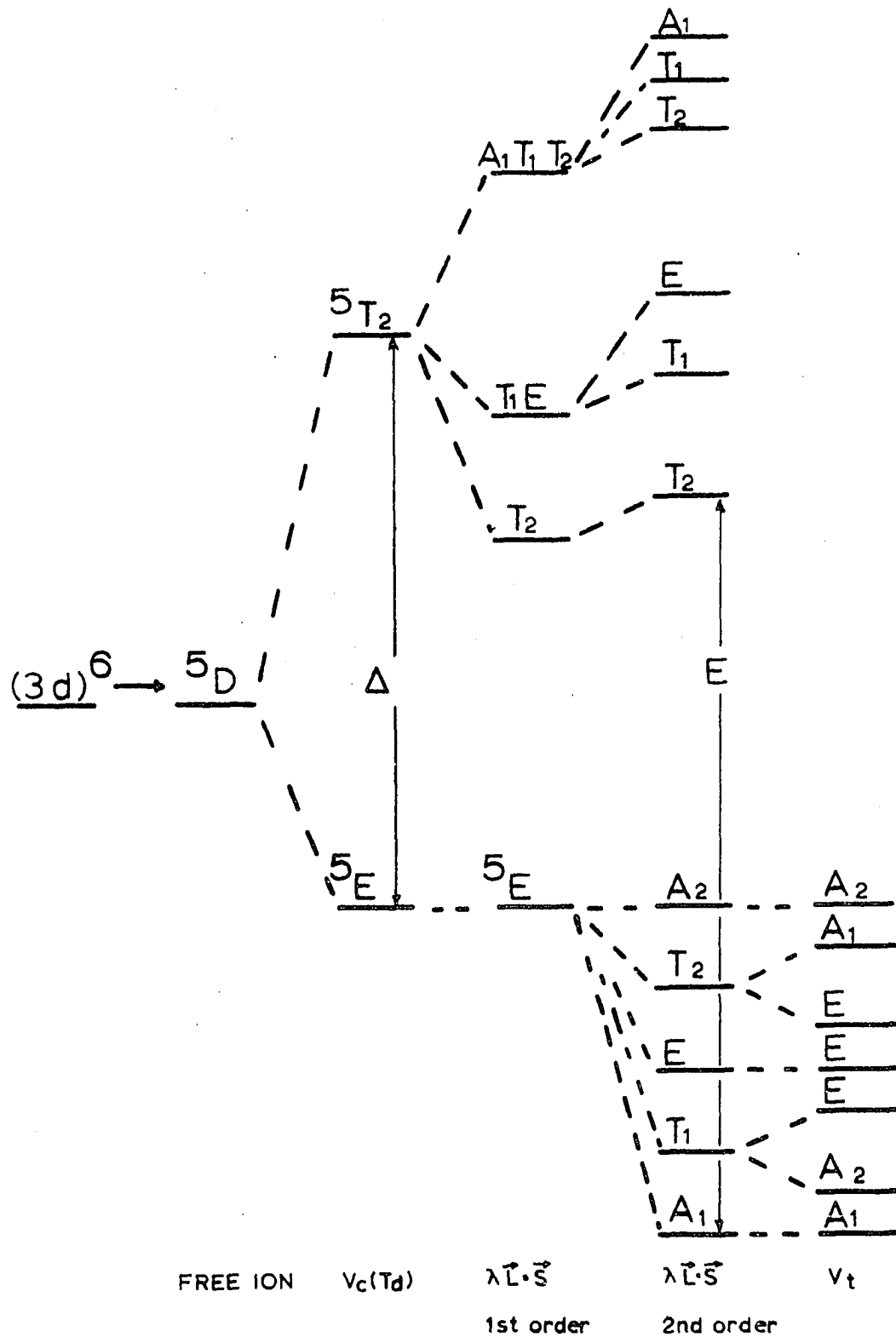


Figure 17. Energy levels of Fe^{2+} in cubic crystal field.

$$D_2 \times E = A_1 + A_2 + E + T_1 + T_2 \quad (4-15)$$

and

$$D_2 \times T_2 = A_1 + E + 2T_1 + 2T_2 \quad (4-16)$$

since spin = 2, and we are interested in T_2 and E levels.

Group theory only predicts the maximum splittings under a reduction of symmetry, and these splittings may or may not occur in the real case considered. One must resort to actual calculation, such as that of Low and Weger,³⁸ to determine the precise ordering of the electronic energy levels.

It turns out that the 5T_2 level is split by the first order spin-orbit interaction, but the 5E level is untouched.

Here we must go to the second order spin-orbit coupling to obtain any splitting of the 5E level. Then from the actual calculations^{17,38,39} we can list the energy levels in their proper order, as shown in Fig. 17.

Next, we consider the effects of a trigonal distortion to the cubic field. Here one can use a correlation table⁴⁰ or perform a multiplication similar to the one above. This splitting is also shown in Fig. 17.

Group theory can also be used to reduce the number of matrix elements to be calculated for the magnetic susceptibility by indicating the matrix elements that must be zero by symmetry considerations alone under the magnetic moment operator $\vec{\mu}$.⁴¹ This is done by considering the transformation properties of the magnetic moment operator which acts as an axial vector.

In a tetrahedral field the magnetic moment operator $\vec{\mu}$ can be represented in group theoretical notation by T_1 . By taking the product of appropriate rotation groups representing $\vec{\mu}$ and the electronic energy levels in question (described by Bethe,²⁷ Low,³⁵ and Tinkham⁴¹), we find that $\vec{\mu}$ is isotropic, all the electronic energy levels are connected, and the magnetic susceptibility (χ) is also isotropic.

When a trigonal distortion is considered, the symmetry changes from T_d to C_3 , and the crystal is no longer isotropic. A z-axis is defined along the body diagonal (Fig. 15) or the crystalline c-axis. The bond length b is no longer the same as the other three. The ions numbered 1, 2, and 3 form the x-y plane which is isotropic.

If we apply a magnetic field along the z-axis, the magnetic susceptibility parallel to this z-axis can be measured ($\chi_{||}$). A_2 now represents the magnetic moment operator μ_z , and we find that the ground state is only connected through μ_z to the A_2 levels (Fig. 18). If the magnetic field is applied perpendicular to the z-axis (in the x-y plane), the magnetic susceptibility perpendicular to the z-axis can be measured ($\chi_{\perp}$). The magnetic moment operator $\mu_{x,y}$ is represented by E, and we find that the ground state is only connected to the E levels through the operator $\mu_{x,y}$. Therefore, the distortion which removes the isotropic nature of the crystalline symmetry leads to an anisotropic magnetic

susceptibility. This anisotropic magnetic susceptibility is labeled $\chi_{\parallel}$ or $\chi_{\perp}$ depending upon the axis of measurement.

We see in the case of $\chi_{\parallel}$ that only the ground state A_1 (nonmagnetic) and the upper A_2 levels contribute to the magnetic susceptibility. In the case of $\chi_{\perp}$ the ground state A_1 level and the upper E levels contribute to the magnetic susceptibility. Therefore, since along either axis we have a case which looks similar to the simple two-level magnetic susceptibility described previously, we would expect to be able to determine the energy spacings between the ground state and the higher spacings if we reach low enough temperatures. And by measuring the magnetic susceptibility along the two different axes to determine S_1 and S_2 , as shown in Fig. 18, we can obtain some information concerning the strength of the trigonal crystal field as seen by its effect on the impurity ion.

Summary of Paramagnetic Susceptibility Calculations for Fe^{2+} in Tetrahedral Field

Before the paramagnetic susceptibility can be calculated, the energy level splittings must be calculated. As we have noted, the first calculations were those of Low,³⁵ and these have been extended recently by Slack, et al.³ The calculations of the electronic energy levels and the subsequent paramagnetic susceptibility calculation (for the case of cubic tetrahedral symmetry which is reported here) were done by William H. Brumage of Louisiana Polytechnic

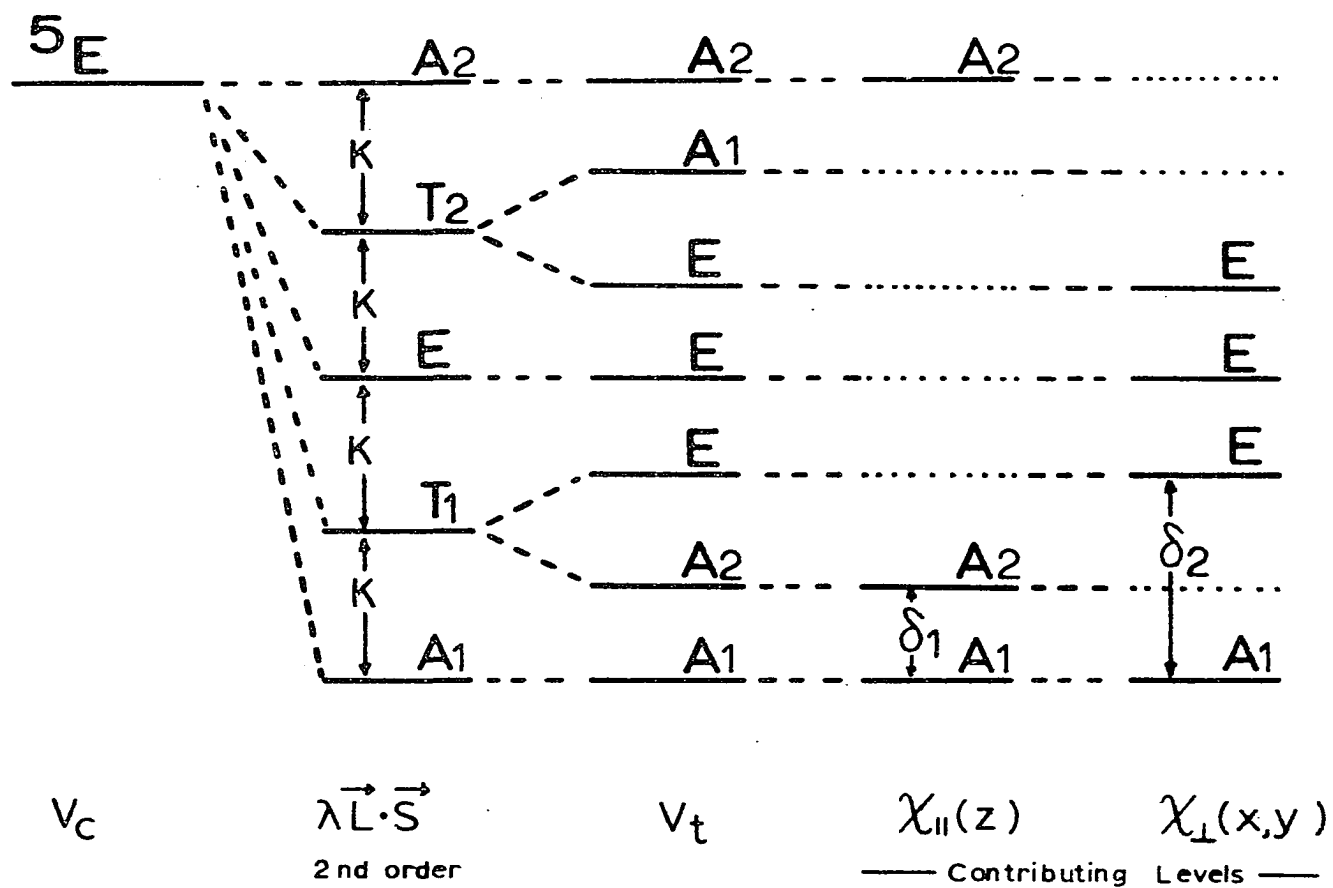


Figure 18. Levels affecting $\chi_{||}$ and $\chi_{\perp}$.

Institute, and they follow the methods reported in previous publications.^{4,39,40} The calculations all show that the second order spin-orbit splitting causes a uniform separation of the 5E level into five components a parameter K apart (Fig. 5) where $K = 6\lambda^2/\Delta$. This parameter K is to be determined from the paramagnetic susceptibility measurements. The results of the Brumage calculations are shown in Table 7. These results are listed for different temperatures in the range of 1 to 300°K and for values of K ranging from 11.8 cm^{-1} to 18.8 cm^{-1} .

Once the paramagnetic susceptibilities have been calculated, we will want to plot a graph showing the results at a glance, and the most direct way is to plot the paramagnetic susceptibility χ vs. the temperature T in °K. This has been done, and the results are shown in Fig. 19. Note that it is only at low temperature that the paramagnetic susceptibility values are very different for a small change in the value of K ; therefore, accurate data must be taken in the low temperature region where the susceptibility measurements are most difficult. At temperatures higher than 20°K the paramagnetic susceptibility is very nearly the same for all values of K in the range of interest.

Another way of representing the paramagnetic susceptibility data is to plot χ vs. $1/T$ where T is again in degrees Kelvin. This particular method is shown in Fig. 20 and is quite useful because here we see the Curie behavior at high

TABLE 7

CALCULATED MAGNETIC SUSCEPTIBILITY FOR
 Fe^{2+} IN CUBIC CRYSTAL FIELD

T (°K)	$1/T$ $\times 10^3$	$\chi_m \times 100$ (cgs-emu/mole)		
		$K=11.8$	$K=13.2$	$K=14.6$
1	1000.0	42.01	37.59	34.01
2	500.0	41.99	37.58	34.01
3	333.3	41.71	37.45	33.95
4	250.0	40.73	36.90	33.64
5	200.0	39.02	35.79	32.92
6	166.6	36.86	34.23	31.81
7	142.8	34.55	32.44	30.45
8	125.0	32.27	30.58	28.95
9	111.1	30.12	28.77	27.43
10	100.0	28.15	27.05	25.95
20	50.0	16.20	15.99	15.77
30	33.3	11.11	11.05	10.98
40	25.0	8.40	8.37	8.45
50	20.0	6.74	6.73	6.72
100	10.0	3.37	3.37	3.37
200	5.0	1.68	1.68	1.68
250	4.0	1.34	1.34	1.34
300	3.3	1.12	1.12	1.12

Table 7 (continued)

T (°K)	$1/T$ $\times 10^3$	$\chi_m \times 100$ (cgs-emu/mole)		
		$K=16.0$	$K=17.4$	$K=18.8$
1	1000.0	31.05	28.57	26.45
2	500.0	31.05	28.57	26.45
3	333.3	31.02	28.55	26.44
4	250.0	30.85	28.46	26.39
5	200.0	30.39	28.16	26.20
6	166.6	29.61	27.62	25.83
7	142.8	28.58	26.85	25.25
8	125.0	27.39	25.91	24.52
9	111.1	26.13	24.88	23.68
10	100.0	24.87	23.81	22.78
20	50.0	15.53	15.28	15.02
30	33.3	10.90	10.82	10.73
40	25.0	8.33	8.29	8.25
50	20.0	6.71	6.69	6.67
100	10.0	3.37	3.37	3.37
200	5.0	1.68	1.68	1.68
250	4.0	1.34	1.34	1.34
300	3.3	1.12	1.12	1.12

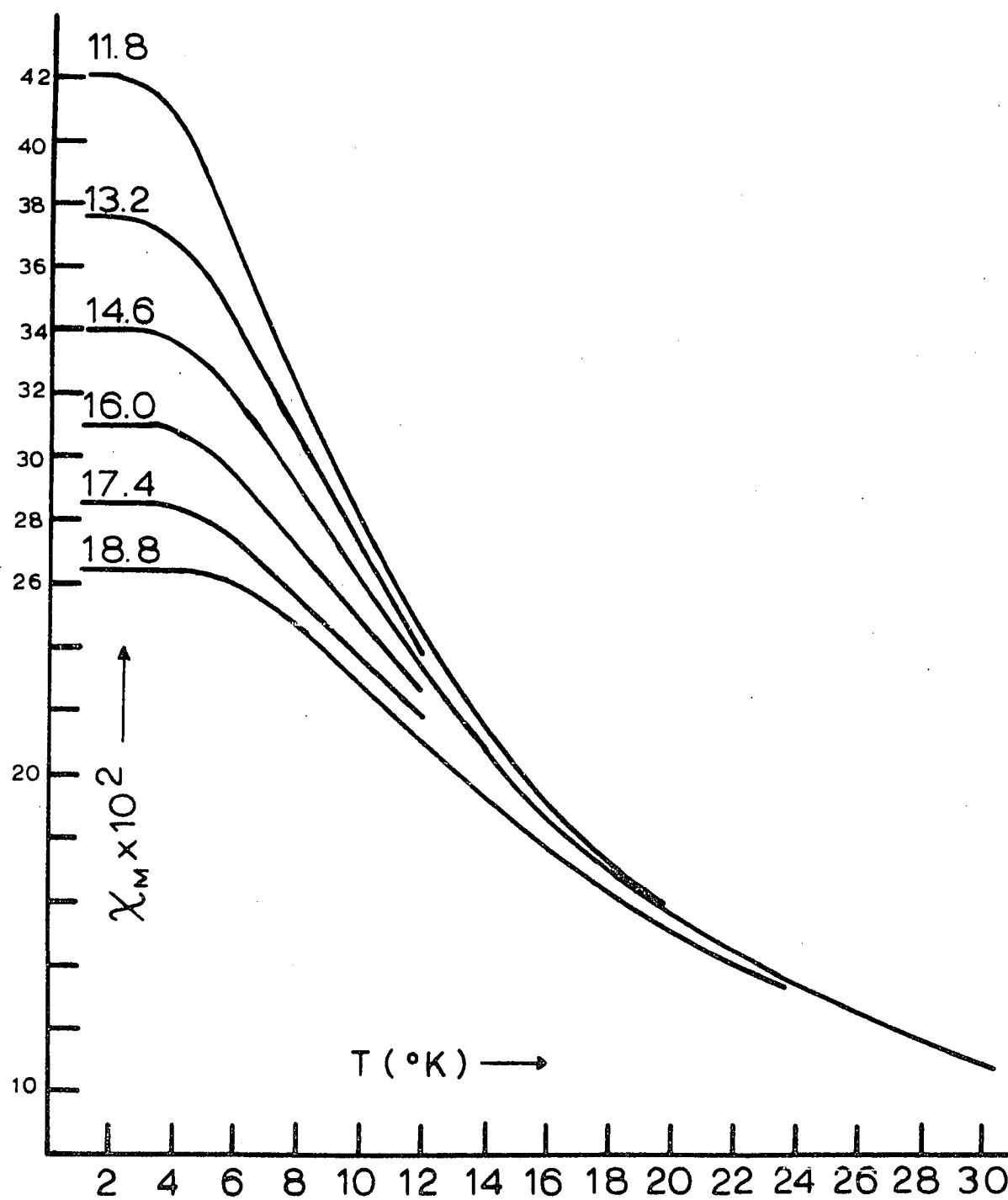


Figure 19. Calculated χ_M vs. T (Fe^{2+}).

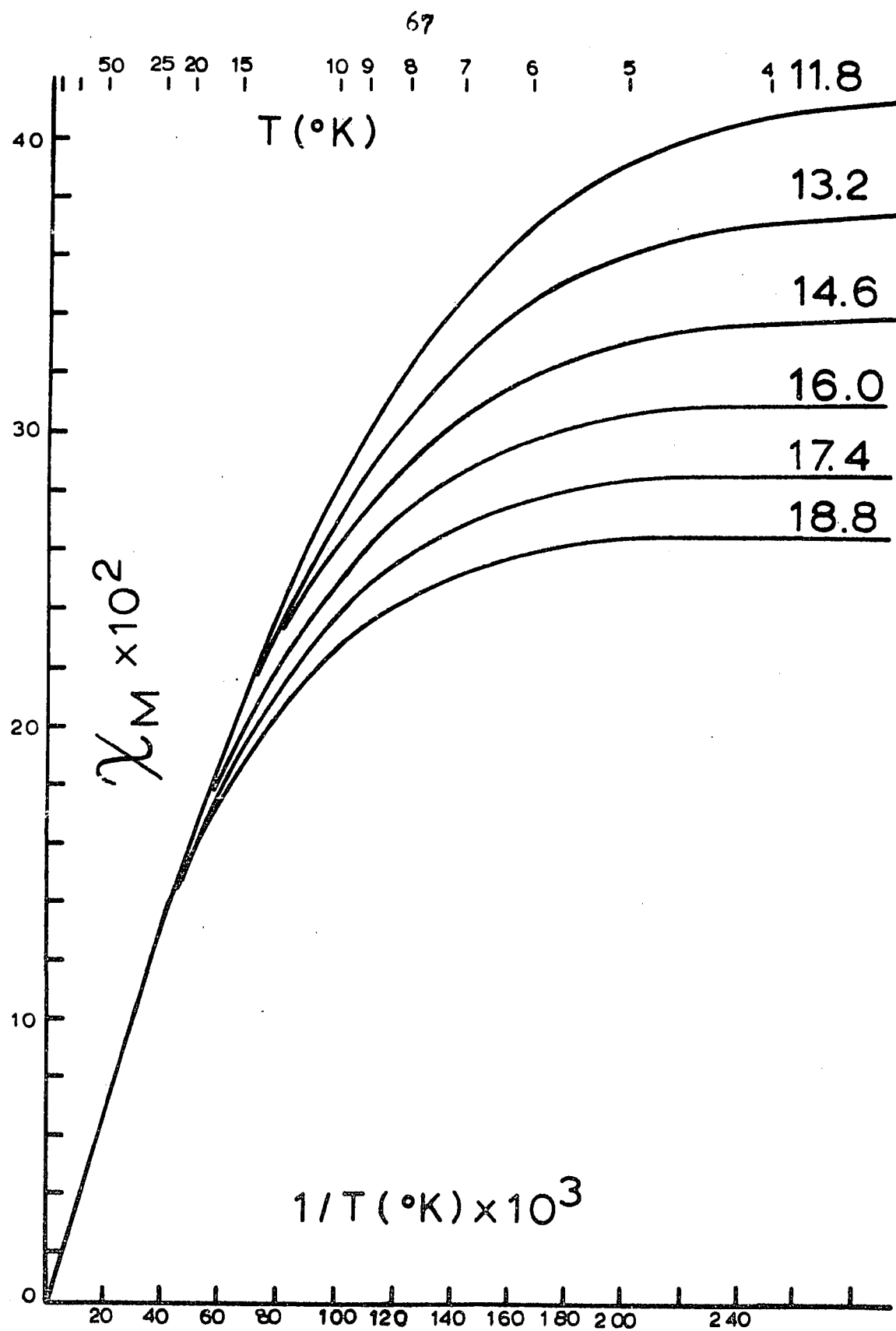


Figure 20. Calculated χ_M vs. $1/T$ (Fe^{2+}).

temperatures (above 20°K) and then the gradual turn to a new slope at lower temperatures. In the case of Fe^{2+} with its six 3d electrons in a tetrahedral crystal field, the ground state is non-degenerate resulting in a zero magnetic moment, and there is only the constant paramagnetism due to perturbations of the upper levels. Therefore, the low temperature component of the magnetic susceptibility becomes constant with lower temperatures as expected, and the curve becomes flat earlier (at higher temperatures) as the value of K is increased. This method is used for the preliminary analysis of the experimental data. Also the approximate concentration of the impurity ions in the host crystal can be obtained from this plot by comparing the Curie portion of the experimental curve to the same portion of the calculated curve. The ratio (R) of $\chi_M^{\text{experimental}} / \chi_M^{\text{calculated}}$ gives the fraction of the expected paramagnetic susceptibility from one mole of Fe^{2+} ions in a tetrahedral crystal field that was actually measured. The conversion of this ratio (R) to the number of Fe^{2+} ions per cubic centimeter, the molar fraction, and the mole fraction is illustrated in the next chapter. Due to the Curie-like linearity of the magnetic susceptibility at high temperatures, the scale in Fig. 20 is such that the low temperature effects are emphasized. The scale can be expanded to check for deviations from the Curie behavior and to better determine the slope which in turn will improve the

determination of the impurity concentration.

There is yet a third useful way to present the temperature dependent paramagnetic susceptibility. As demonstrated in Fig. 21, the values of $\chi \cdot T$ can be plotted against T . In this presentation the curves for all values of K will go through the origin ($T = 0^\circ\text{K}$), and near the origin the curves will be linear. This method will prove most useful for the case of $\text{Fe}^{2+}:\text{ZnO}$ where data was taken to temperatures as low as 1.8°K . At high temperatures (greater than 30° to 40°K) the $\chi \cdot T$ values become constant with increasing T and are the same for all values of the parameter K . This allows us to scale the experimental curve to the theoretical curves at high temperatures. After this is completed, the experimental values can be plotted in the low temperature region and matched to one of the theoretical curves associated with a particular K value. The experimental data is plotted by all three methods and compared to the theoretical curves to check the consistency of the experimental values.

It should be pointed out that the measured magnetic susceptibility is the sum of the paramagnetic susceptibility of the impurity ion, the diamagnetic susceptibility of the host crystal, and the diamagnetic susceptibility of the small quartz holder containing the sample. Remember that it is the magnetic susceptibility curve shape which allows us to determine the position of the electronic energy levels. Noting also that the value of the paramagnetic susceptibility

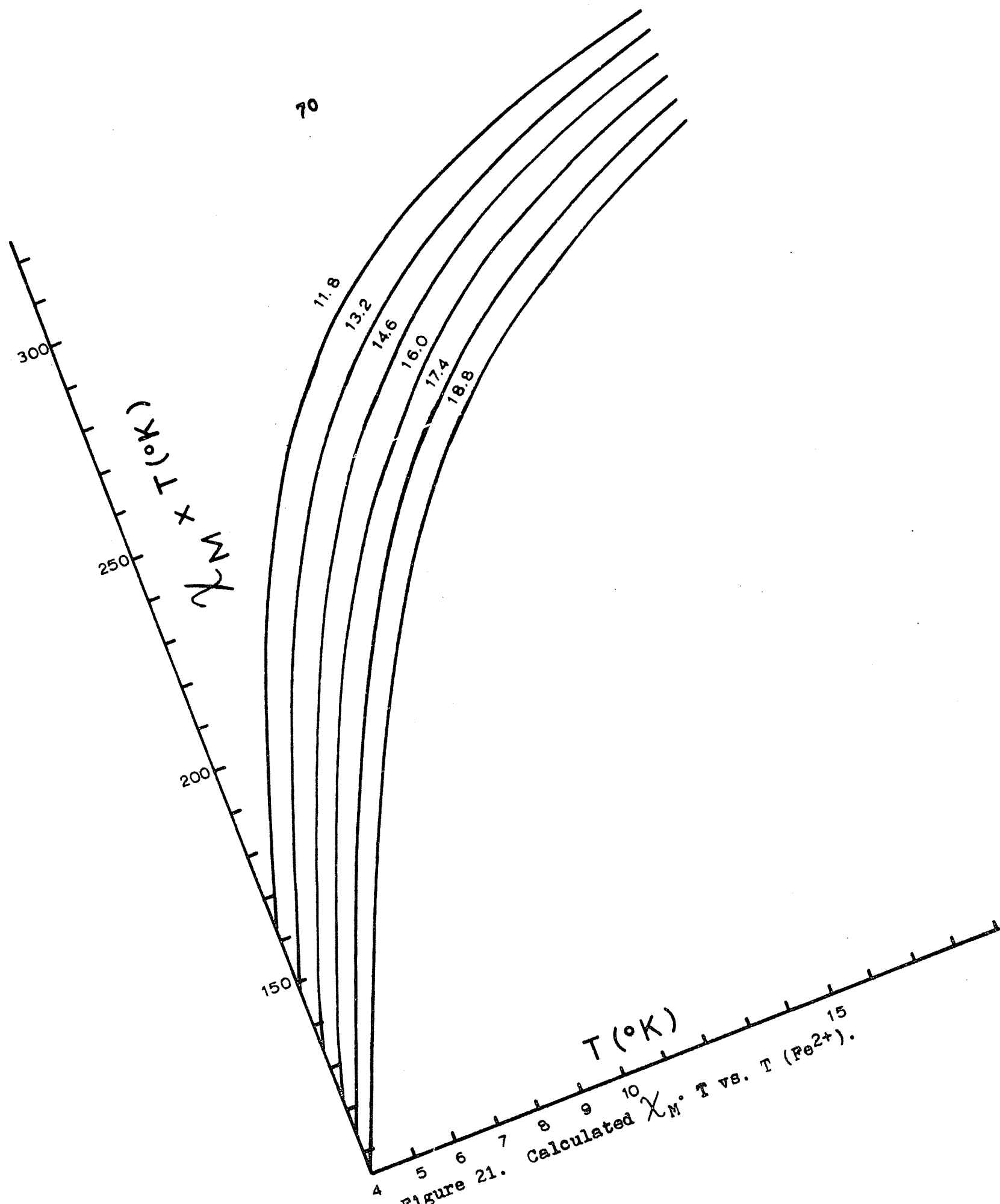


Figure 21. Calculated $\chi_M \cdot T$ vs. T (Fe^{2+}).

is the same for all choices of K at room temperatures, and that we can use the spring calibration to determine the change in paramagnetic susceptibility from the room temperature value, we are not required to determine the absolute diamagnetic contribution to the magnetic susceptibility reading. The diamagnetic contributions are constant with temperature changes; and therefore, they can be ignored. This situation allows us to be concerned with only the changes in paramagnetic susceptibility which is the physical phenomena of interest here.

Summary of Paramagnetic Susceptibility Calculations
for Fe^{2+} in Tetrahedral Field
with a Trigonal Distortion

The paramagnetic susceptibility calculations for Fe^{2+} in a cubic crystal field have been extended by W. H. Brumage and C. F. Dorman to include the effects of a trigonal distortion. The effects of the trigonal distortion are shown in Fig. 17 and Fig. 18. By measuring the magnetic susceptibility as a function of temperature with the z-axis parallel to the magnetic field ($\chi_{\parallel}$) and then with the z-axis perpendicular to the magnetic field ($\chi_{\perp}$), we expect to determine the parameters δ_1 and δ_2 of Fig. 18.

If we can determine the values of δ_1 and δ_2 , we can also expect to determine the value of K . The parameters λ and Δ can also be determined if the value of E is available from optical spectroscopy. The trigonal case is more

complicated than the cubic case, and a larger portion of the work is done by the computer. The best fit for our measured magnetic susceptibility curves is given in Table 8. The measured values will be discussed in the next chapter.

TABLE 8

CALCULATED MAGNETIC SUSCEPTIBILITY OF Fe^{2+} IN
CUBIC CRYSTAL FIELD WITH TRIGONAL DISTORTION

T (°K)	$1/T \times 10^3$	$\chi_{\parallel} \times 100$ (emu/mole)	$\chi_{\perp} \times 100$ (emu/mole)
1	1000.0	94.83	22.37
2	500.0	94.25	22.37
3	333.3	90.89	22.39
4	250.0	84.74	22.36
5	200.0	77.29	22.21
6	166.6	69.72	21.90
7	142.8	62.63	21.47
8	125.0	56.27	20.95
9	111.1	50.69	20.37
10	100.0	45.84	19.76
20	50.0	21.19	14.25
30	33.3	13.12	10.71
40	25.0	9.43	8.45
50	20.0	7.36	6.93
100	10.0	3.53	3.57
200	5.0	1.76	1.80
250	4.0	1.41	1.45
300	3.3	1.18	1.21

CHAPTER V

Fe^{2+} IN TETRAHEDRAL SITES - EXPERIMENT

Introduction

In Chapter IV a theoretical model was assumed which would allow one to handle mathematically the calculation of electronic energy levels of a transition metal ion in the crystalline environment of a host crystal, and then the calculation of the paramagnetic susceptibility arising from the electronic energy levels. Let us now consider how this model is verified by experiment.

In the energy level diagram of Fig. 17, the energy levels are calculated in terms of two major parameters. The first is Δ or $10Dq$ which gives some indication of the strength of the electrostatic field of the host crystal and is usually determined from optical absorption experiments. The second parameter is K which denotes the splitting of 5E into five equally spaced levels. Now, when these parameters are to be measured experimentally, problems immediately arise.

The first problem is that Δ or $10Dq$ is not directly determined from the optical absorption experiments. What can be found are the optically allowed transitions from the

ground state A_1 (5E) to the various levels of the 5T_2 multiplet. The strongest line which is observed is the absorption labeled E in Fig. 17. From the theoretical calculations, it is found that

$$E = \Delta + 3\lambda + 3K/5 + 4K \quad (5-1)$$

$$\text{or } E = \Delta + 3\lambda + 138\lambda^2/5\Delta. \quad (5-2)$$

$$\text{since } K = 6\lambda^2/\Delta. \quad (5-3)$$

Therefore, the experimental value of E alone will not be enough to determine the value of Δ .

On the other hand, the value of K will be determined from magnetic susceptibility data, but the value of the spin-orbit coupling parameter cannot be determined without the value of Δ . This is a good example of a situation where one experiment alone is not enough to confirm the predicted situation. Therefore, we will need data obtained from optical absorption experiments to complement the magnetic susceptibility data. The value of E is available from the publications of Slack, Ham, and Chrenko⁴⁴ and of Baranowski, Allen, and Pearson¹⁸ for CdS, ZnS, ZnSe, CdTe, and ZnTe. The value of CdSe can be estimated by comparing the lattice parameter of CdSe to a graph on page 630 of ref. 19. No value of E has been measured, to our knowledge, for the case of Fe^{2+} :ZnO.

Once the values of E and K have been experimentally determined, values of λ and Δ can be calculated from the following:

$$\lambda = \frac{K}{12} \left(-3 - \sqrt{\frac{24E}{K} - 101.4} \right) \quad (5-4)$$

and then

$$\Delta = 6 \lambda^2 / K. \quad (5-5)$$

Equation (5-4) was found by combining equations (5-2) and (5-3).

As mentioned before, the value of K can also be determined from optical absorption and luminescence in the far infrared.^{3,33,44,45} These results are available for ZnS and CdTe and compare favorably with the value of K as determined from magnetic susceptibility. Far infrared data for the other five iron-doped crystals is not, to our knowledge, available at this writing.

Fe²⁺ in Tetrahedral Crystal Field

Again the magnetic susceptibility is measured as a function of temperature, and then the results are compared to the theoretical curves of Fig. 20. This procedure is followed for the case of Fe²⁺:ZnS and the results are shown in Table 9 and Fig. 22. The parameter K is determined to be $15.0 \pm 0.5 \text{ cm}^{-1}$, and the concentration is found to be $23.7 \times 10^{18} \text{ Fe}^{2+}$ per cubic centimeter by comparing the Curie part of the experimental magnetic susceptibility curve to the theoretical value. The χ_M reported in the tables is the paramagnetic susceptibility per mole of impurity ion.

The measured magnetic susceptibility for Fe²⁺:ZnSe is given in Table 10 and Fig. 23; for Fe²⁺:CdSe in Table 11

TABLE 9

MEASURED MAGNETIC SUSCEPTIBILITY OF $\text{Fe}^{2+}:\text{ZnS}$

m = 51.4 mg (our crystal)			m = 37.5 mg (Schneider)		
C = 24×10^{18} Fe/o.o.			C = 254×10^{18} Fe/o.o.		
T (°K)	$1/T$ $\times 10^3$	$\chi \times 10^8$ (emu/gram)	T (°K)	$1/T$ $\times 10^3$	$\chi \times 10^6$ (emu/gram)
295.0	3.4	3.27	295.0	3.4	0.61
56.0	17.9	16.84	88.3	11.3	2.09
52.6	19.0	18.11	70.5	14.2	2.52
45.0	22.2	21.34	39.1	25.6	4.56
39.6	25.3	24.15	36.5	27.4	4.80
35.6	28.1	26.99	31.6	31.6	4.53
31.6	31.6	29.80	25.6	39.1	6.71
26.7	36.5	33.81	22.5	44.4	7.52
23.7	42.2	37.82	19.4	51.6	8.49
19.5	51.3	46.13	16.5	60.6	9.72
16.3	61.3	53.57	14.2	70.4	10.96
13.6	73.5	59.31	11.5	87.0	12.78
10.6	94.3	72.48	9.5	105.3	14.66
7.8	128.0	82.80	8.4	119.1	15.15
4.2	238.1	93.11	4.2	238.1	17.30

* Two crystals from different sources were used in these measurements. One grown from the melt (Schneider), and the other doped in our laboratory. The temperature dependence of the magnetic susceptibility is identical.

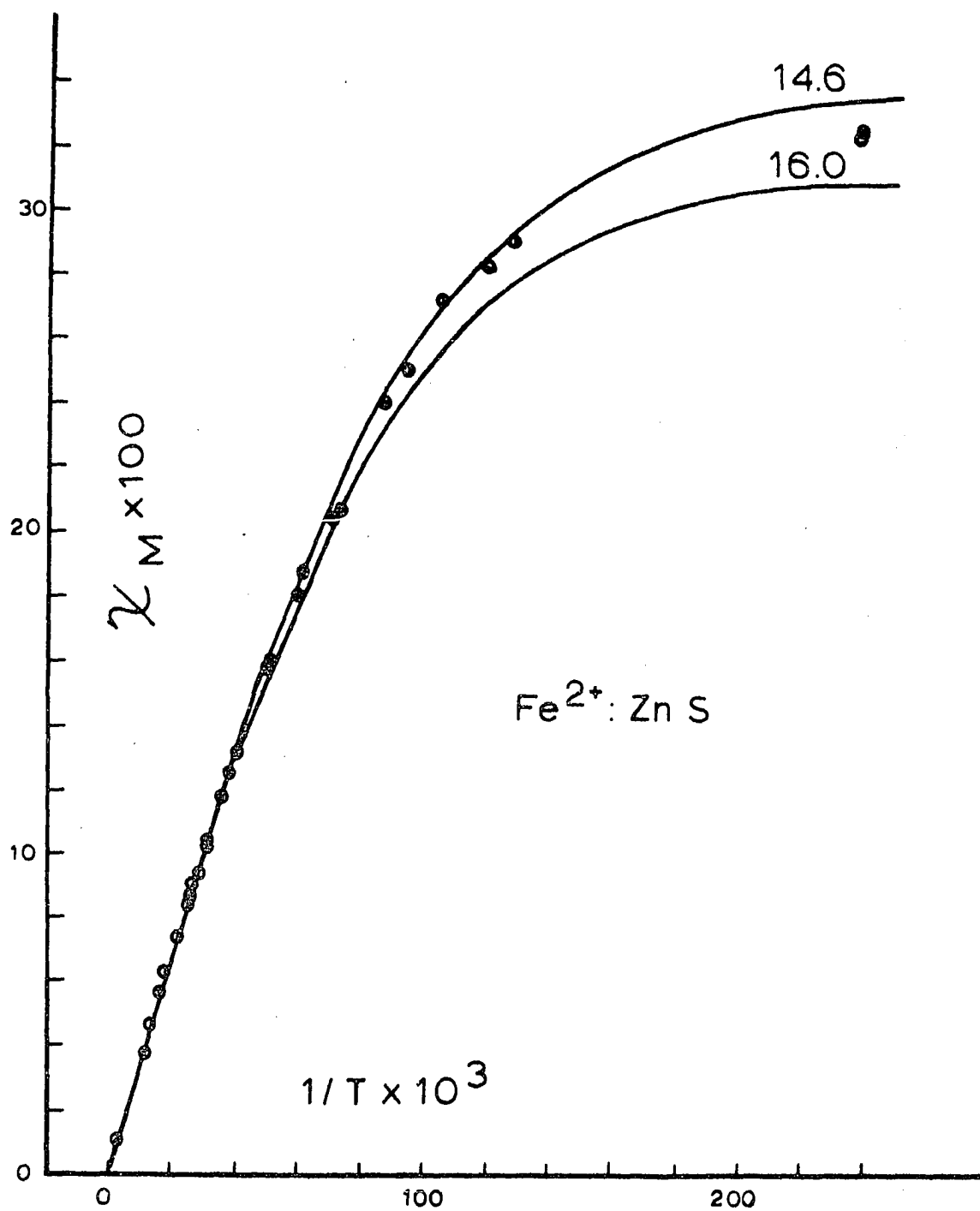


Figure 22. Measured magnetic susceptibility curve for $\text{Fe}^{2+}:\text{ZnS}$.

TABLE 10

MEASURED MAGNETIC SUSCEPTIBILITY OF $\text{Fe}^{2+}:\text{ZnSe}$

$m = 69.7 \text{ mg}$ $C = 2.5 \times 10^{18} \text{ Fe/c.c.}$					
T (°K)	$1/T$ $\times 10^3$	$\chi \times 10^9$ (emu/gram)	T (°K)	$1/T$ $\times 10^3$	$\chi \times 10^9$ (emu/gram)
295.0	3.4	6.12	19.5	51.3	85.9
79.0	12.7	23.90	17.2	58.1	90.8
77.3	12.9	23.85	15.2	65.8	109.0
71.0	14.1	26.32	15.2	65.8	109.0
34.1	29.3	52.64	13.7	73.0	111.2
33.0	30.3	53.66	10.4	96.2	141.8
30.1	33.2	61.77	10.4	96.2	144.0
27.6	36.2	63.38	9.4	106.4	154.2
25.6	39.1	66.61	4.2	238.1	217.5
24.1	41.5	68.22			

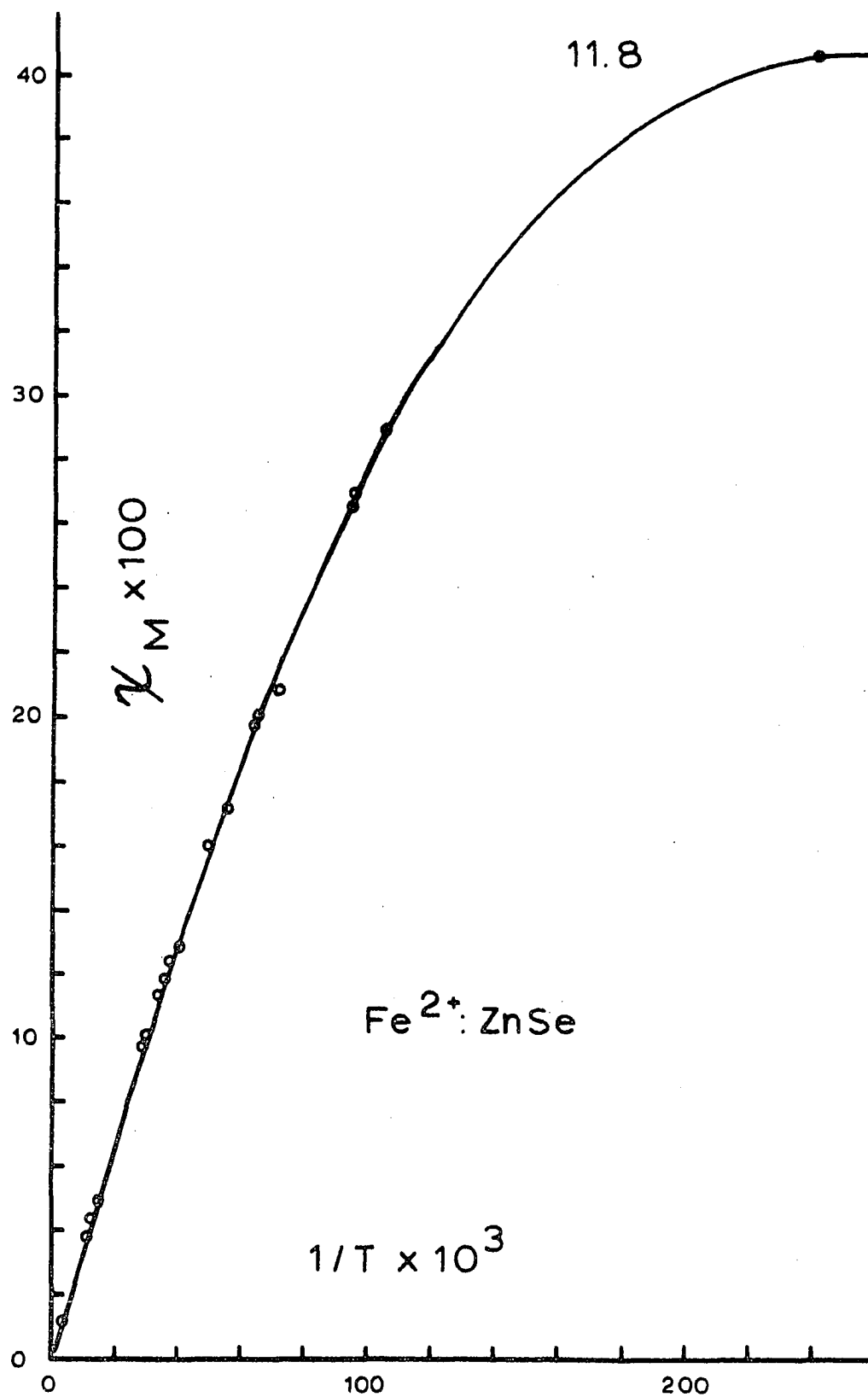


Figure 23. Measured magnetic susceptibility curve for $\text{Fe}^{2+}:\text{ZnSe}$.

and Fig. 24; for $\text{Fe}^{2+}:\text{ZnTe}$ in Table 12 and Fig. 25; for $\text{Fe}^{2+}:\text{CdTe}$ in Table 13 and Fig. 26. The determined values of K and the concentrations are $11.8 \pm 0.5 \text{ cm}^{-1}$ and $2.5 \times 10^{18} \text{ Fe/c.c.}$ for $\text{Fe}^{2+}:\text{ZnSe}$; $11.5 \pm 0.5 \text{ cm}^{-1}$ and $2.5 \times 10^{18} \text{ Fe/c.c.}$ for $\text{Fe}^{2+}:\text{CdSe}$; $15.6 \pm 0.5 \text{ cm}^{-1}$ and $7.6 \times 10^{18} \text{ Fe/c.c.}$ for $\text{Fe}^{2+}:\text{ZnTe}$; and $18.0 \pm 0.5 \text{ cm}^{-1}$ and $6.8 \times 10^{18} \text{ Fe/c.c.}$ for $\text{Fe}^{2+}:\text{CdTe}$. In assigning the best value for K , the value of the magnetic susceptibility at the liquid helium temperature was the determining factor. The measurements at this temperature were more accurate with respect to temperature because the sample was surrounded by walls in contact with liquid helium, and many measurements were made at this temperature over a period of time. The value reported was reproducible over many measurements; however, in cases where there was doubt, two values were reported. The overall accuracy in determining the value of K is less than $\pm 0.5 \text{ cm}^{-1}$ in most cases.

Fe^{2+} in a Tetrahedral Field
with a Trigonal Distortion

CdS and ZnO have trigonal distortions to the tetrahedral crystal field. CdS has such a small trigonal distortion that magnetic susceptibility $\chi_{\parallel}$ and $\chi_{\perp}$ differ only at very low temperatures. Therefore, the magnetic susceptibility curves for the tetrahedral case can be used to determine the values of S_1 and S_2 . The measured magnetic susceptibility curves are given for $\text{Fe}^{2+}:\text{CdS}$ in Fig. 27 and Tables

TABLE 11

MEASURED MAGNETIC SUSCEPTIBILITY OF $\text{Fe}^{2+}:\text{CdSe}$

$m = 74.3 \text{ mg}$ $C = 2.5 \times 10^{18} \text{ Fe/c.c.}$					
T (°K)	$1/T$ $\times 10^3$	$\chi \times 10^9$ (emu/gram)	T (°K)	$1/T$ $\times 10^3$	$\chi \times 10^9$ (emu/gram)
295.0	3.4	6.12	19.7	50.8	87.66
73.2	13.7	25.73	19.1	52.4	89.27
72.2	13.9	24.71	15.0	66.7	105.3
64.7	15.5	28.47	14.5	69.0	110.1
56.6	17.7	32.23	12.7	78.8	125.2
42.1	23.8	46.30	11.3	88.5	137.5
35.0	28.6	51.78	9.9	101.5	150.4
29.3	34.2	61.24	8.7	114.9	167.6
29.2	34.1	61.24	8.6	116.0	169.2
25.3	39.5	69.29	7.3	137.0	182.1
23.3	42.9	75.74	4.2	238.1	222.9

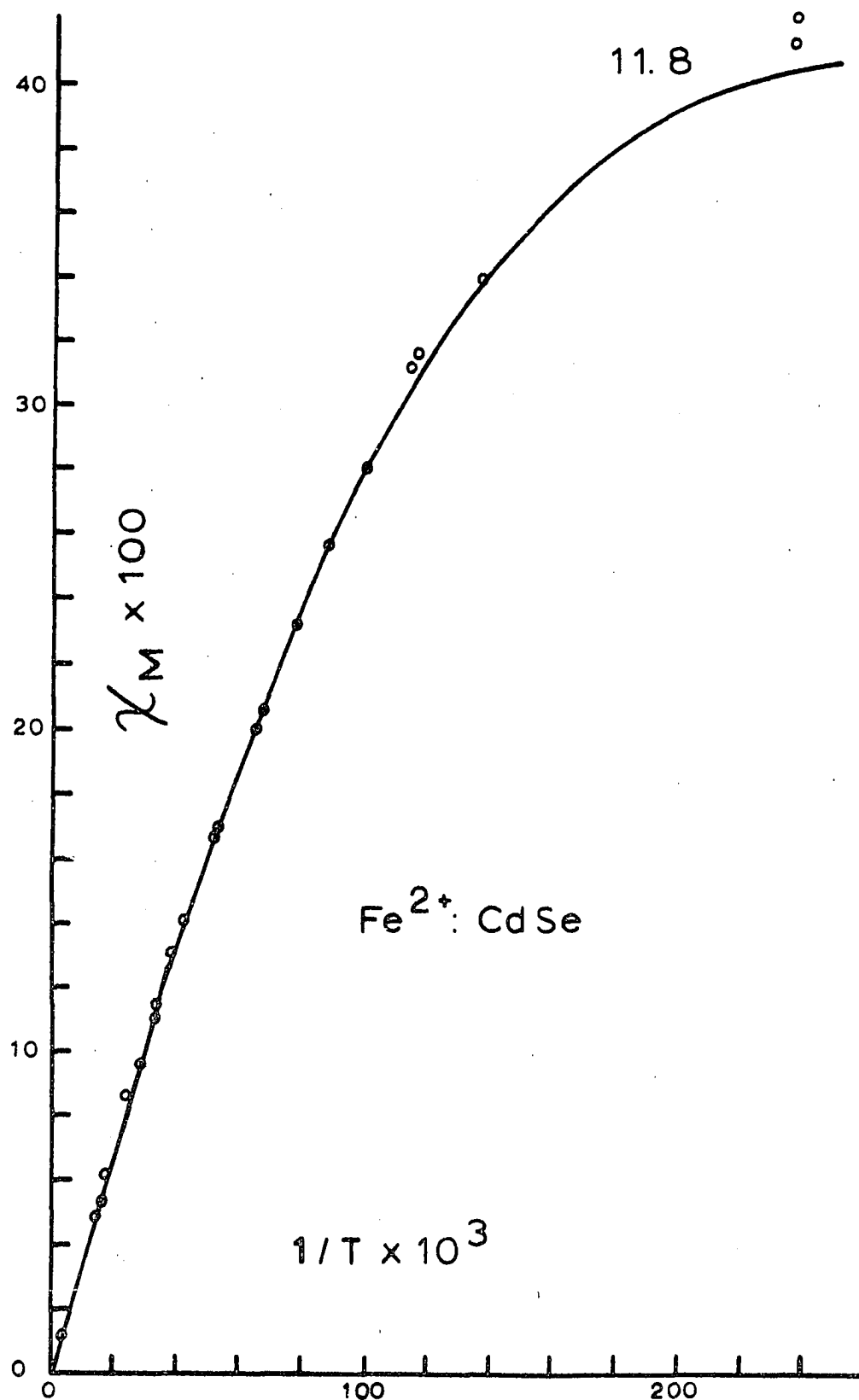


Figure 24. Measured magnetic susceptibility curve for $\text{Fe}^{2+}:\text{CdSe}$.

TABLE 12

MEASURED MAGNETIC SUSCEPTIBILITY OF $\text{Fe}^{2+}:\text{ZnTe}$

$m = 69.8 \text{ mg}$ $C = 7.6 \times 10^{18} \text{ Fe/c.c.}$					
T ($^{\circ}\text{K}$)	$1/T$ $\times 10^3$	$\chi \times 10^8$ (emu/gram)	T ($^{\circ}\text{K}$)	$1/T$ $\times 10^3$	$\chi \times 10^8$ (emu/gram)
295.0	3.4	1.84	20.2	49.5	25.95
120.0	8.4	4.58	18.0	55.6	28.20
77.3	13.0	6.74	16.6	60.2	30.78
77.3	13.0	7.16	15.8	63.3	32.07
76.0	13.2	7.16	13.1	76.3	36.58
36.5	27.4	14.96	10.5	95.2	39.48
35.4	28.3	16.28	9.2	108.7	43.51
29.9	33.4	17.24	8.2	121.2	45.12
27.1	36.9	19.18	4.2	238.1	50.28
23.8	42.0	22.08	4.2	238.1	51.25
21.8	45.9	23.04			

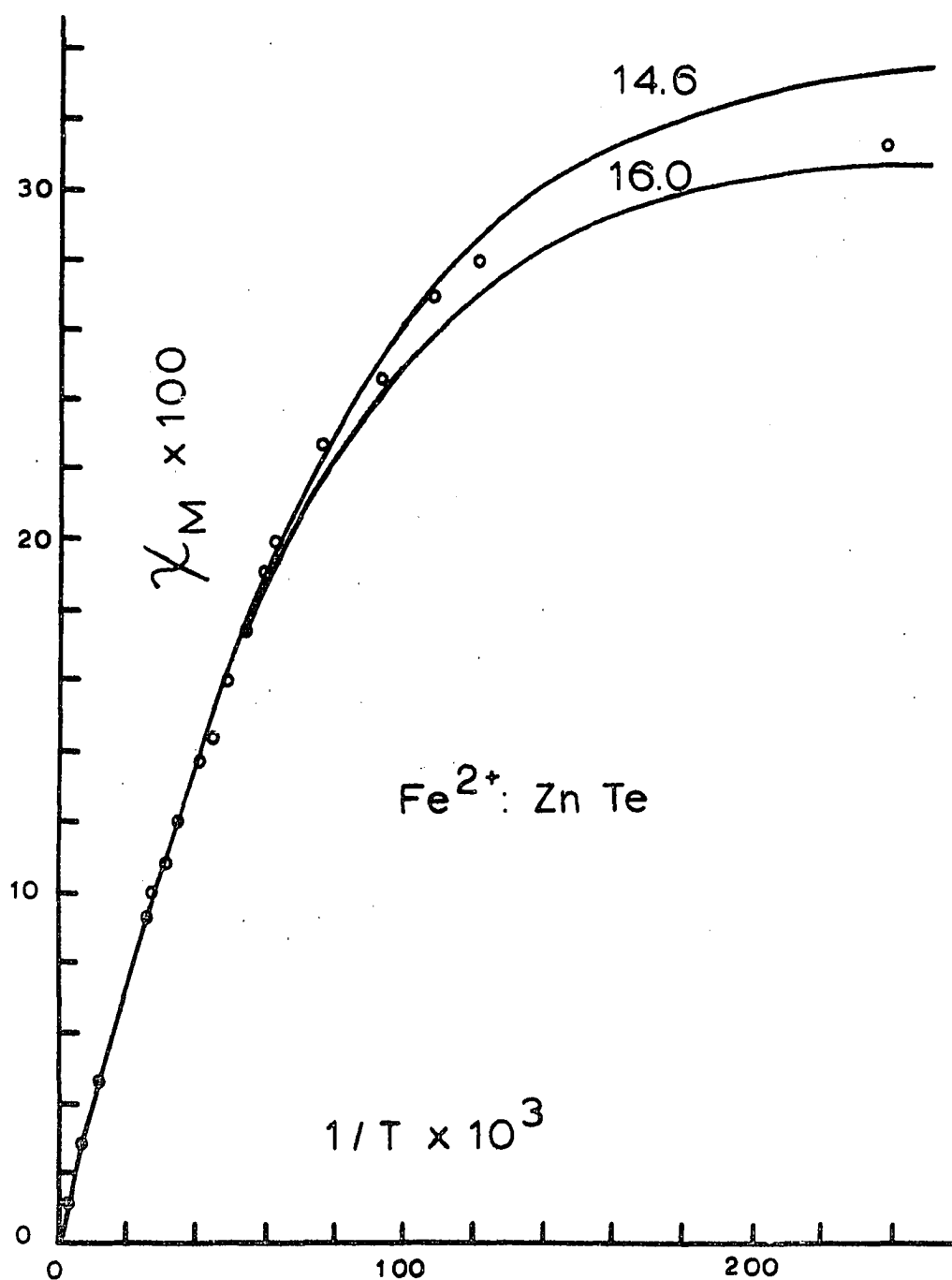


Figure 25. Measured magnetic susceptibility curve for $\text{Fe}^{2+}:\text{ZnTe}$.

TABLE 13

MEASURED MAGNETIC SUSCEPTIBILITY OF $\text{Fe}^{2+}:\text{CdTe}$

$m = 40.7 \text{ mg}$ $C = 6.8 \times 10^{18} \text{ Fe/c.c.}$					
T (°K)	$1/T$ $\times 10^3$	$\chi \times 10^8$ (emu/gram)	T (°K)	$1/T$ $\times 10^3$	$\chi \times 10^8$ (emu/gram)
295.0	3.4	1.63	26.3	38.0	17.18
77.0	13.0	6.19	20.5	48.8	21.19
72.0	13.9	6.37	18.7	53.5	21.90
55.0	18.2	8.75	12.5	80.0	28.35
41.9	23.9	11.09	10.8	92.6	30.79
37.4	26.7	12.57	10.5	95.2	31.93
35.4	28.3	13.15	9.8	101.5	32.79
32.0	31.3	14.61	8.8	113.0	33.94
31.8	31.5	14.61	4.2	238.1	39.09
31.7	31.5	14.61	4.2	238.1	39.24
26.7	37.5	17.18			

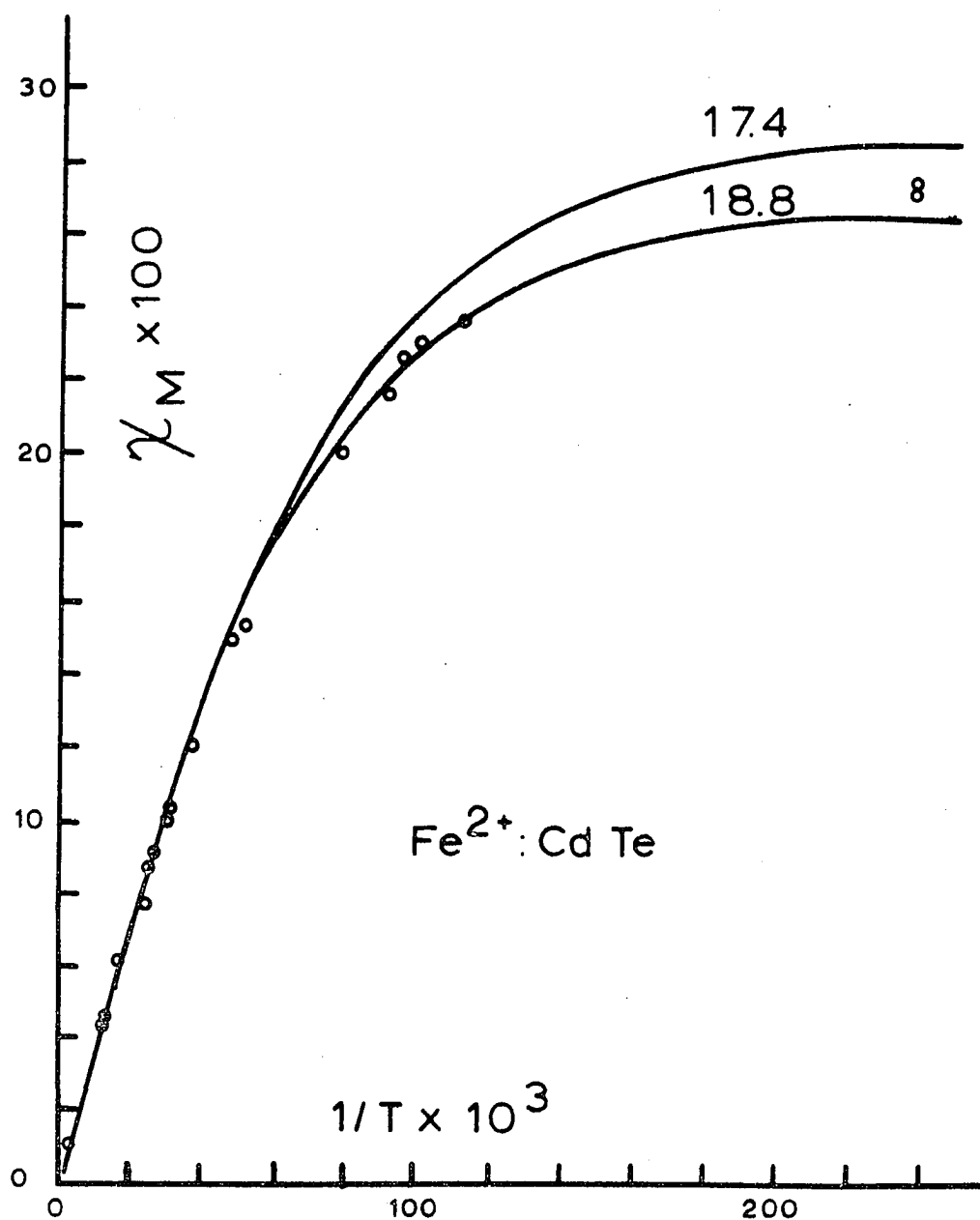


Figure 26. Measured magnetic susceptibility curve for $Fe^{2+}:CdTe$.

14 and 15.

For both $\text{Fe}^{2+}:\text{CdS}$ and $\text{Fe}^{2+}:\text{ZnS}$ we were fortunate to have crystals from Dr. Jürgen Schneider of the Physical Institute, University of Freiburg, Germany. These crystals gave the same magnetic susceptibility curves as those crystals doped in our laboratory. The results for the Schneider crystals are recorded in Tables 9 and 15.

ZnO has a very large trigonal distortion, and its effect on the electronic energy levels is such that a different magnetic susceptibility calculation must be made. The theoretical parameters are then varied to fit the measured magnetic susceptibility which is shown in Fig. 28 and Fig. 29. These measurements are recorded in Tables 16 and 17. From the magnetic susceptibility measurements it is found that $S_1 = 7.8 \text{ cm}^{-1}$ and $S_2 = 17.6 \text{ cm}^{-1}$ for $\text{Fe}^{2+}:\text{ZnO}$. The difference between S_1 and S_2 is much larger for $\text{Fe}^{2+}:\text{ZnO}$ than for $\text{Fe}^{2+}:\text{CdS}$ where $S_1 = 14.3 \text{ cm}^{-1}$ and $S_2 = 16.0 \text{ cm}^{-1}$. A summary of these measurements in the cubic crystal field is compiled in Table 19. The spin-orbit parameter λ is determined as described on page 76. The ratio λ/λ_0 indicates the reduction of λ (free ion value $\lambda_0 = -103 \text{ cm}^{-1}$) when the impurity ion is subjected to the crystal field. The parameter Dq is $\Delta/10$ of Fig. 17, and S_1 and S_2 are shown in Fig. 18.

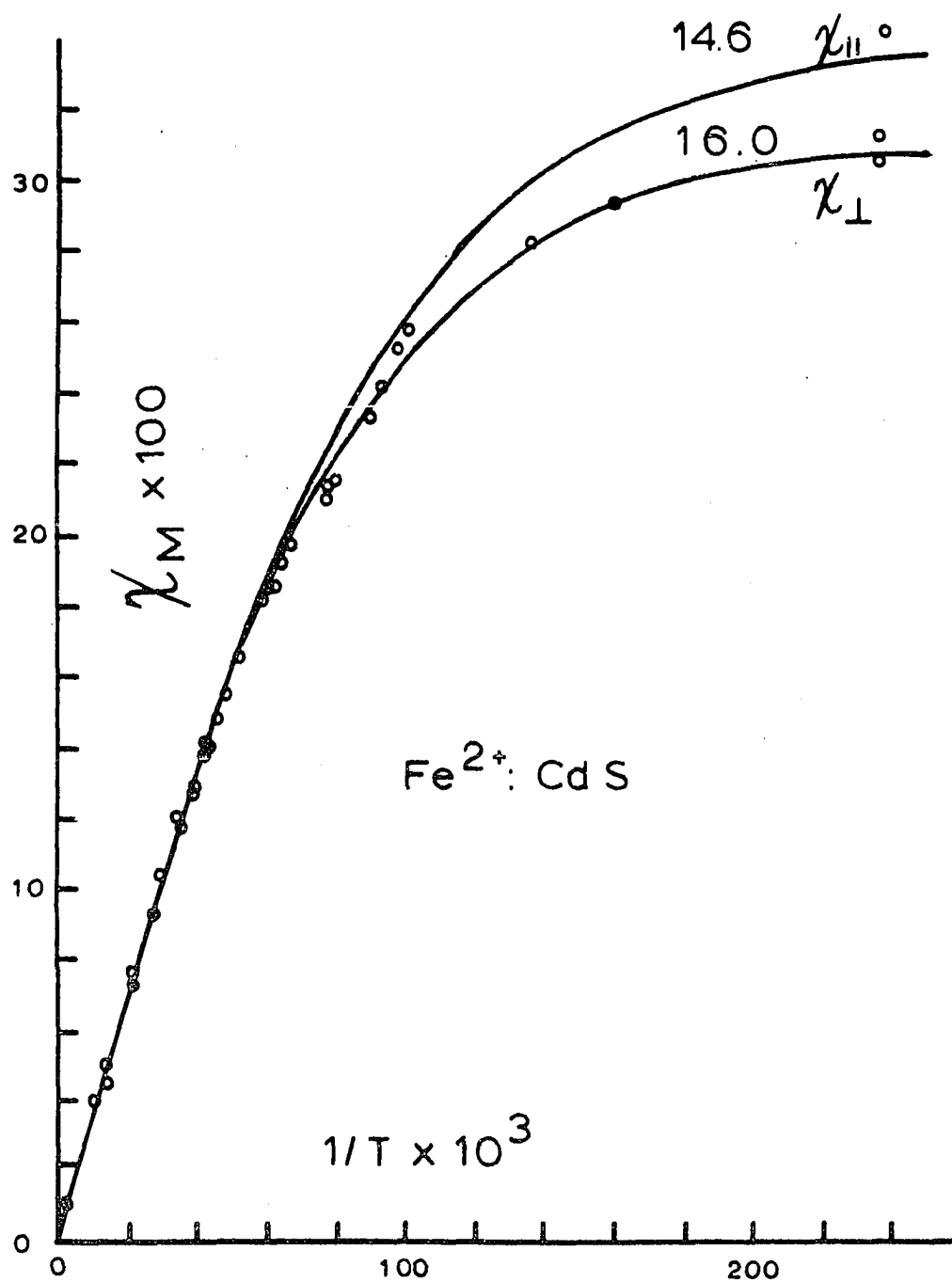


Figure 27. Measured magnetic susceptibility curve for $\text{Fe}^{2+}:\text{CdS}$.

TABLE 14

MEASURED MAGNETIC SUSCEPTIBILITY OF $\text{Fe}^{2+}:\text{CdS}$

m = 22.1 mg (our crystal)					
C = 11.8×10^{18} Fe/c.c.					
T (°K)	$1/T$ $\times 10^3$	$\chi \times 10^8$ (emu/gram)	T (°K)	$1/T$ $\times 10^3$	$\chi \times 10^8$ (emu/gram)
296.0	3.4	1.11	19.9	50.3	21.50
86.3	11.6	5.54	18.5	54.1	22.88
69.6	14.4	6.13	16.4	61.0	24.81
45.7	21.9	10.04	16.4	61.0	25.50
44.1	22.7	10.32	12.3	81.3	28.80
32.1	31.2	14.47	11.1	90.1	31.98
28.6	35.0	16.68	9.9	101.0	35.70
27.3	36.6	15.99	7.3	137.0	39.00
24.7	40.5	17.37	6.2	160.0	40.38
22.4	44.6	19.02	4.2	238.1	43.28

* All χ values reported are for $\chi_{\perp}$

TABLE 15

MEASURED MAGNETIC SUSCEPTIBILITY OF $\text{Fe}^{2+}:\text{CdS}$

$m = 97.0 \text{ mg (Schneider)}$ $C = 254 \times 10^{18} \text{ Fe/c.c.}$					
T (°K)	$1/T$ $\times 10^3$	$\chi_{\perp} \times 10^6$ (emu/gram)	T (°K)	$1/T$ $\times 10^3$	$\chi_{\perp} \times 10^6$ (emu/gram)
296.0	3.4	0.61	12.8	78.1	11.44
68.6	14.6	2.68	12.1	82.6	11.50
35.5	28.2	5.04	10.6	94.3	13.00
24.9	40.2	6.98	10.2	98.5	13.54
22.8	43.9	7.52	4.2	238.1	16.38
22.3	44.7	7.57			
20.9	47.9	7.95			
16.1	62.1	9.88	T (°K)	$1/T$ $\times 10^3$	$\chi_{\parallel} \times 10^6$ (emu/gram)
15.0	66.7	10.31			
14.5	69.0	10.58	4.2	238.16	18.37

* All χ values reported are for $\chi_{\perp}$ except for the last entry which is for $\chi_{\parallel}$. Higher Fe^{2+} concentration in the Schneider crystal allows one to measure $\chi_{\perp}$ and $\chi_{\parallel}$ at 4.2°K and find a measurable difference.

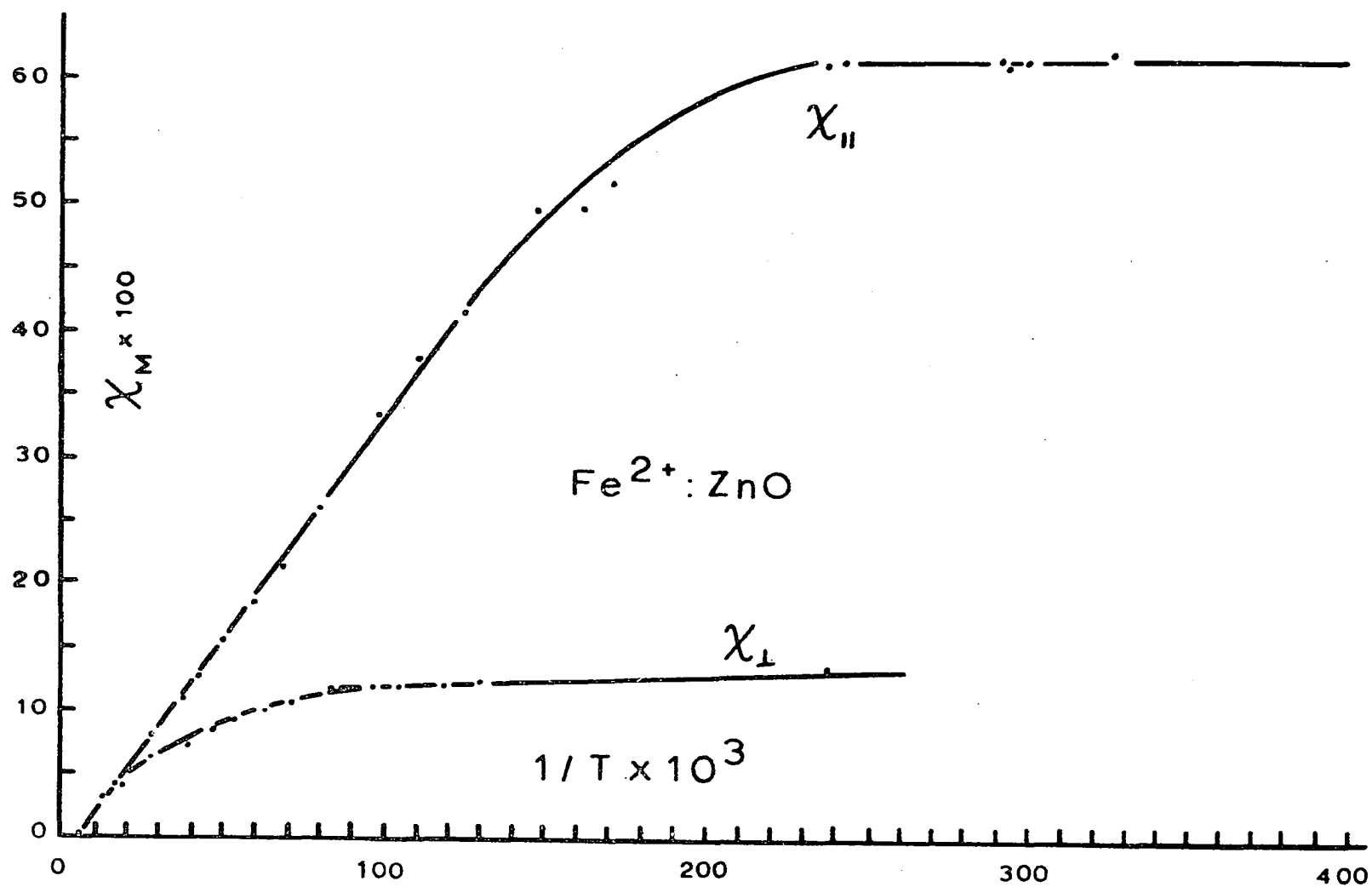


Figure 28. Measured magnetic susceptibility curve for Fe²⁺:ZnO.

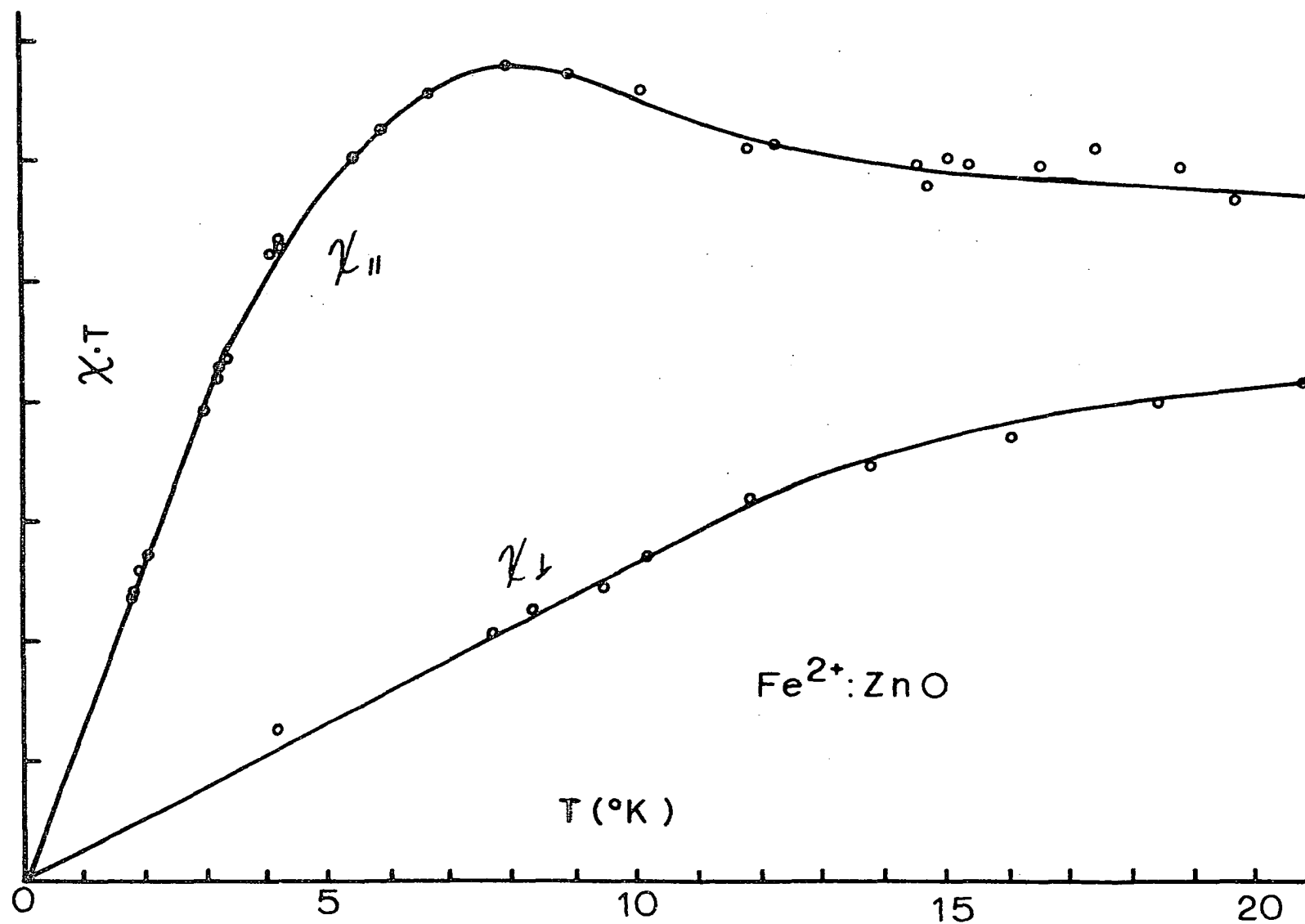


Figure 29. Measured magnetic susceptibility curve for $\text{Fe}^{2+}:\text{ZnO}$.

TABLE 16

MEASURED MAGNETIC SUSCEPTIBILITY OF $\text{Fe}^{2+}:\text{ZnO}$ ($\chi_{\parallel}$)

$m = 65.5 \text{ mg}$ $C = 2.5 \times 10^{18} \text{ Fe/c.c.}$					
T (°K)	$1/T^3$ $\times 10^3$	$\chi_{\parallel} \times 10^9$ (emu/gram)	T (°K)	$1/T^3$ $\times 10^3$	$\chi_{\parallel} \times 10^9$ (emu/gram)
298.0	3.4	0.64	11.90	84	19.61
77.3	13.0	2.74	10.20	98	22.93
50.9	19.6	3.55	9.00	111	26.54
36.2	27.6	6.50	8.00	125	30.40
32.4	30.7	6.50	6.75	148	34.49
25.8	38.8	9.72	6.15	163	36.25
25.2	39.7	8.54	5.80	172	37.71
23.3	42.9	9.67	4.20	238	44.85
21.3	46.9	10.53	4.20	238	45.66
19.8	50.5	11.76	4.12	243	45.66
18.8	53.2	12.41	3.42	292	48.88
17.5	57.1	13.16	3.40	294	48.88
16.6	60.2	13.97	3.35	299	48.88
15.4	64.9	15.04	3.06	327	49.15
15.1	66.2	15.74	2.10	476	51.03
14.8	67.6	15.42	2.02	495	51.03
14.6	68.5	15.95	1.85	538	51.03
12.3	81.3	19.34	1.80	555	51.03

TABLE 17

MEASURED MAGNETIC SUSCEPTIBILITY OF $\text{Fe}^{2+}:\text{ZnO}$ (χ_1)

$$m = 65.5 \text{ mg}$$

$$C = 2.5 \times 10^{18} \text{ Fe/c.c.}$$

T (°K)	$1/T$ $\times 10^3$	$\chi_1 \times 10^9$ (emu/gram)
298.0	3.4	0.64
72.9	13.7	2.95
61.1	16.4	3.33
33.1	28.2	5.69
25.3	39.5	6.28
21.1	47.4	7.41
18.5	54.1	7.63
16.1	62.1	8.54
13.9	71.9	9.56
11.9	84.0	9.93
10.3	97.1	10.26
9.5	105.2	10.26
8.4	119.0	10.42
7.7	130.0	10.64
4.2	238.1	11.55

TABLE 18
CONCENTRATIONS OF Fe^{2+} IN HOST CRYSTALS

Host	Mass (mg)	R $\times 10^5$	# Fe/c.c. $\times 10^{-18}$	# Fe / # Host $\times 10^6$	wt. Fe/ wt. Host $\times 10^5$
ZnO	65.5	3.0	2.5	63	2
CdS	21.1	7.7	6.1	330	3
ZnS	51.4	16.0	14.0	530	9
CdSe	74.3	3.0	2.5	140	9
ZnSe	69.7	3.0	2.5	110	1
CdTe	40.7	8.0	6.8	440	2
ZnTe	69.8	9.0	7.6	390	3
CdS (S)	97.0	300.0	254.0	12,670	115
ZnS (S)	37.5	300.0	254.0	10,050	172

$$R = \Delta\chi_g^{\text{exp}} / \Delta\chi_g^{\text{cal.}}$$

$$\# \text{ Fe/c.c.} = R \cdot (L_0/M.W.)_{\text{Fe}}$$

$$\# \text{ Fe} / \# \text{ Host} = R \cdot (L_0/M.W.)_{\text{Fe}} \cdot (L_0/M.W.)_{\text{Host}}^{-1}$$

$$\text{wt. Fe} / \text{wt. Host} = R \cdot (M.W.)_{\text{Fe}} \cdot (M.W.)_{\text{Host}}^{-1}$$

TABLE 19

SUMMARY OF EXPERIMENTAL RESULTS FOR Fe^{2+}

Host	E(opt.) (cm^{-1})	K(χ) (cm^{-1})	λ (cm^{-1})	λ/λ_0	Dq (cm^{-1})	
ZnS	2947	15.0	-88.6	0.86	314	
CdTe	2282	18.0	-85.8	0.83	245	
ZnTe	2486	15.6	-84.3	0.82	273	
CdSe	2500*	11.5	-71.4	0.69	268	
ZnSe	2738	11.8	-75.6	0.73	291	

Host	E(opt.) (cm^{-1})	K(χ) (cm^{-1})	λ (cm^{-1})	λ/λ_0	S_1 (cm^{-1})	S_2 (cm^{-1})
CdS	2550	15.0	-82.6	0.80	14.3	16.0
ZnO	3000*	17.4	-95.0	0.92	7.8	17.6

*estimated

** One can do a more refined analysis which changes the crystal field parameters, but not the energy levels. This is an example of the magnetic susceptibility accurately determining the energy levels while rather insensitive to exact model, although crystal field parameters vary considerably. Refined analyses give $\lambda = -99, -99, -96, -81, -85, -93$, and -100 for ZnS through ZnO, respectively.

CHAPTER VI

Cr^{2+} IN TETRAHEDRAL SITES

Introduction

The electronic structure of chromium, another of the iron-group transition metals, is given by $(\text{Ar})(3d)^5(4s)^1$. In the divalent state the atom loses two outer electrons leaving $(\text{Ar})(3d)^4$. Like the case of Fe^{2+} in Chapter IV, the completely filled inner core can be neglected since only the phenomena due to the four 3d electrons is under study. As previously described, crystal field theory should predict the splitting of the electronic energy levels when successively smaller perturbations are considered. The starting point is again the ground state of the free ion. The ground state of Cr^{2+} is 5D as it was in Fe^{2+} . A tetrahedral crystal field will split the 5D ground state into 5E and 5T_2 levels, except now the 5T_2 level lies lower than the 5E . The 5T_2 level is split by first order spin-orbit perturbation, and both 5E and 5T_2 levels are split by second order spin-orbit effects as shown in Fig. 30. If this were the case, then the same procedures for the measurement of the magnetic susceptibilities, as used for Fe^{2+} , would yield the positions of the electronic energy levels of the 5T_2 multiplet. It

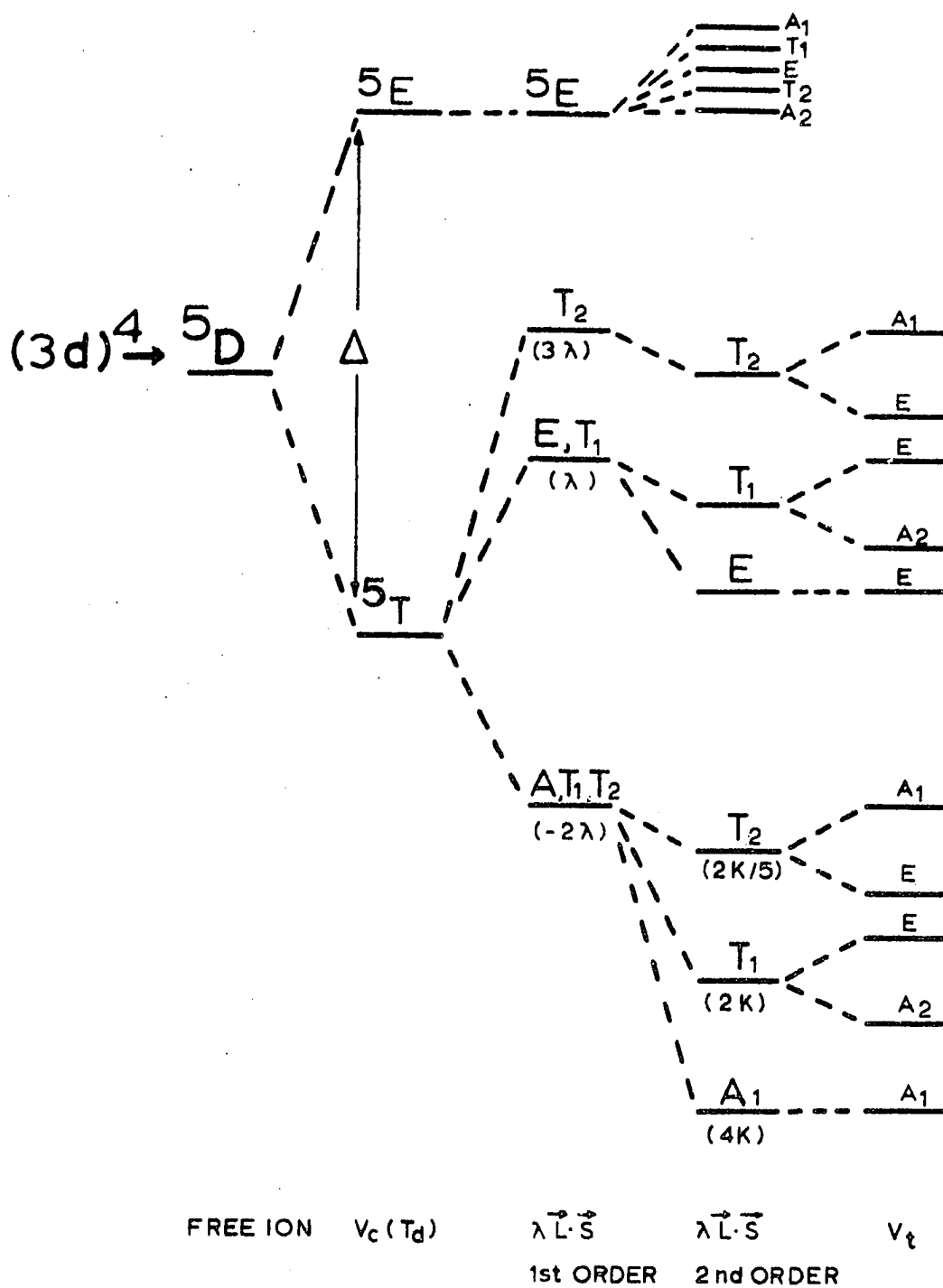


Figure 30. Energy levels of Cr^{2+} in crystal field.

could be expected that the value of λ (spin-orbit coupling parameter) and K (second-order splitting) would be quite accurately determined. However, the magnetic susceptibility measurements on Cr^{2+} doped ZnS , CdS , ZnSe , CdSe , ZnTe , and CdTe seem to agree with previous measurements using electron spin resonance^{46,47,48,49} and optical spectroscopy; that crystal field theory alone does not predict the electronic energy levels found from experiment.

Jahn-Teller Effect

The phenomena which must be considered in order to explain the experimental results is known as the Jahn-Teller effect, which may be defined⁵¹ as the intrinsic instability of an electronically degenerate complex against nuclear distortions that remove the degeneracy. This does not apply to degeneracies arising from an odd number of electrons and described by Kramers' theorem.⁵² Although the phenomena was first predicted in 1937,⁵³ Sturge⁵¹ points out that the first unambiguous evidence for its existence was reported by Bleaney and Bowers⁵⁴ in 1952. A review of Jahn-Teller effects in solids is given by Sturge⁵¹ in the "Solid State Physics" series which includes results up to 1966-1967.

The Jahn-Teller effect was not considered in magnetic susceptibility studies of Fe^{2+} in tetrahedral II-VI compounds because the optical spectra^{3,44,45} indicated that the Jahn-Teller effects are confined to the $^5\text{T}_2$ level, and the effects

on the 5E level are small if at all. The magnetic susceptibility measurements reported above for Fe^{2+} confirm that the experimental data can be explained without the inclusion of Jahn-Teller effects in the theory of the 5E manifold. Electron spin resonance data are not available for Fe^{2+} in tetrahedral sites because the ground state of the Fe^{2+} ion in this case is nonmagnetic.

For the case of Cr^{2+} in a tetrahedral site, the Jahn-Teller effect plays a significant role, as we have mentioned. This system was first studied by Morigaki and by Estle, et al in 1963. Both performed electron spin resonance experiments on $Cr^{2+}:CdS$,^{46,47,48} and Estle, et al also studied $Cr^{2+}:ZnSe$ ⁴⁹ in 1964. The interpretations of their data differed. Both attributed the results to a Jahn-Teller distortion at the impurity site, but the symmetry choices differed. Morigaki attributed his results to a distortion of trigonal C_{3v} symmetry. Estle, et al interpreted their results in terms of a tetragonal D_{2d} distortion. Sturge in his review⁵¹ points out arguments which favor a distortion of tetragonal symmetry to lift the degeneracy of the 5T_2 state. This situation is illustrated in Fig. 31. Note that after the tetrahedral crystal field is considered, the next perturbation is the reduction of symmetry at the impurity site to the tetragonal D_{2d} . Then spin-orbit interaction is considered, and one must go to the second order to split the 5E and 5B_2 states. Under second order spin-orbit splitting the 5B_2

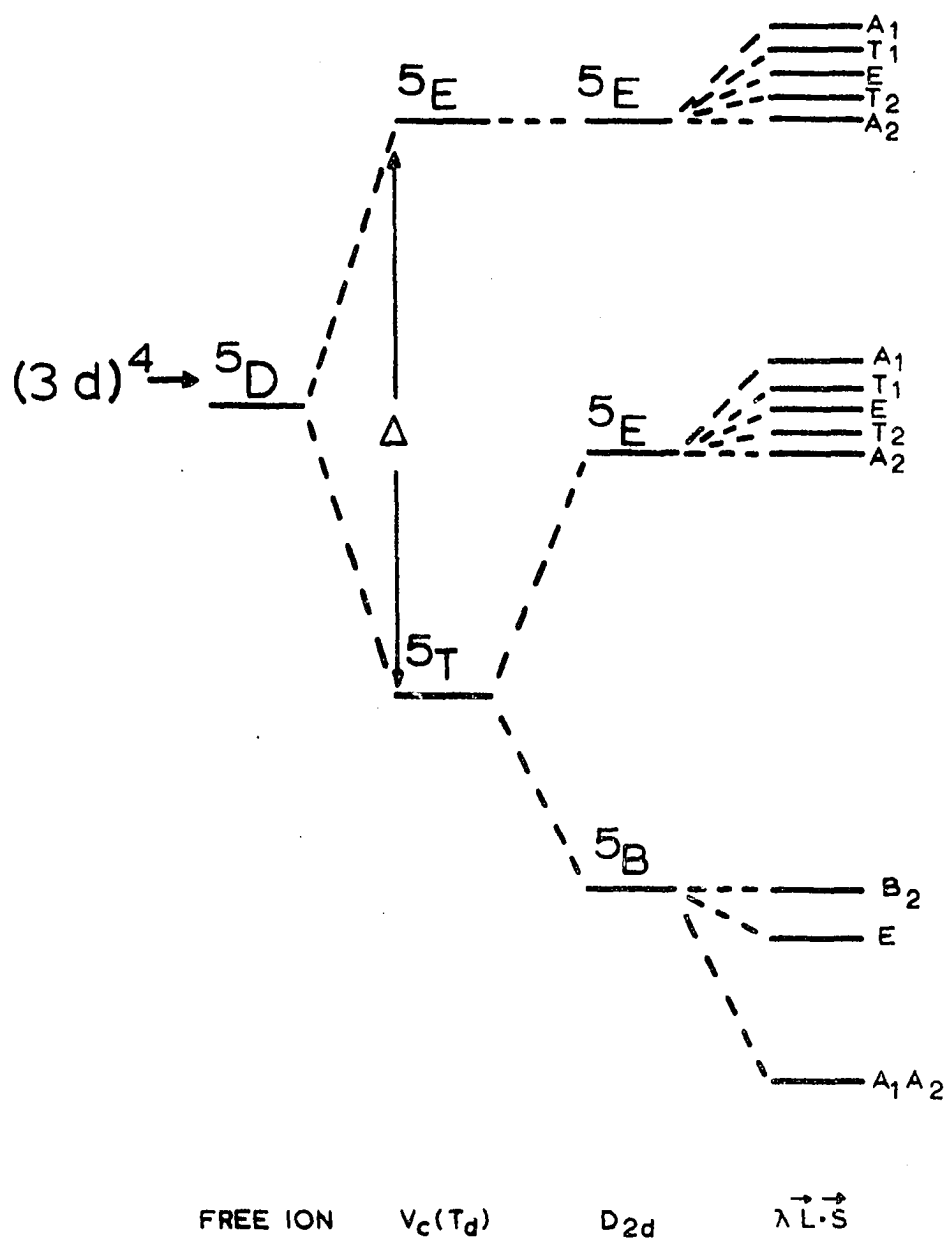


Figure 31. Energy levels of Cr^{2+} in crystal field with Jahn-Teller effect.

state goes to A_1 , A_2 , E, and B_2 states. The A_1 and A_2 ground states⁴⁸ are degenerate within this approximation; therefore, we cannot expect the magnetic susceptibility to become constant at rather low temperatures if this model is correct.

A recent paper by Vallin, Slack, and Roberts⁵⁰ also supports the choice of a tetragonal distortion since their data of the optical absorption in the far infrared (2 cm^{-1} to 120 cm^{-1}) does not detect the optical transitions predicted by Morigaki's choice of the trigonal C_{3v} distortion. Their measurements included only $\text{Cr}^{2+}:\text{ZnSe}$ in the paper, but a report at the March, 1970 American Physical Society meeting⁵⁵ indicated that work was in progress for ZnS , CdS , ZnTe , and CdTe as well.

Magnetic Susceptibility Measurements

The paramagnetic susceptibility has been measured for chromium doped ZnS , CdS , ZnSe , CdSe , ZnTe , and CdTe . As with the case of Fe^{2+} , the general features of the resulting paramagnetic susceptibility curves are similar for all of the chromium doped host crystals. However, quantitative features such as the 5E to 5B_2 splitting and the A_1 , A_2 to E splitting in Fig. 31 can be determined by careful measurements on each doped crystal. Although the theoretical calculation of paramagnetic susceptibility of Cr^{2+} in a tetrahedral site undergoing Jahn-Teller distortion has not yet been done, this problem is now being considered by Dr. C. F. Dorman at the

Oklahoma College of Liberal Arts in Chickasha, Oklahoma.

If we assume the electronic energy level splittings shown in Fig. 31 (with Jahn-Teller effect), we expect to determine the ${}^5E - {}^5B_2$ and $A_1, A_2 - E$ splittings mentioned above. The ${}^5E - {}^5B_2$ splitting we expect to be approximately 100 cm^{-1} to 300 cm^{-1} . No optical data is available here because absorption data in this range would be masked by thermal vibrations of the host crystal. The $A_1, A_2 - E$ splitting has been measured by Vallin, Slack, and Roberts⁵⁰ and found to be 7.43 cm^{-1} .

The measured paramagnetic susceptibility curves for $\text{Cr}^{2+}:\text{CdS}$ and $\text{Cr}^{2+}:\text{ZnS}$ are given in Fig. 32 and Fig. 33, respectively. We should expect to see both the ${}^5E - {}^5B_2$ splitting and the $A_1, A_2 - E$ splitting. As we can see in Figs. 32 and 33, the ${}^5E - {}^5B_2$ splitting does show up as the bend in the susceptibility at approximately 40°K . Since the $A_1, A_2 - E$ splitting has been found to be 7.4 cm^{-1} , we expect another bend or change in slope at 4°K or less. Experimentation is now being extended to lower temperatures as we have done in the case of $\text{Fe}^{2+}:\text{ZnO}$. The paramagnetic susceptibility measurements then can qualitatively determine the ${}^5E - {}^5B_2$ splitting as well as the $A_1, A_2 - E$ splitting.

The concentrations reported in Tables 5 and 23 are found by using the "spin-only" formula for the paramagnetic susceptibility as described by Van Vleck.¹ This method is remarkably accurate for this purpose, but it does not predict

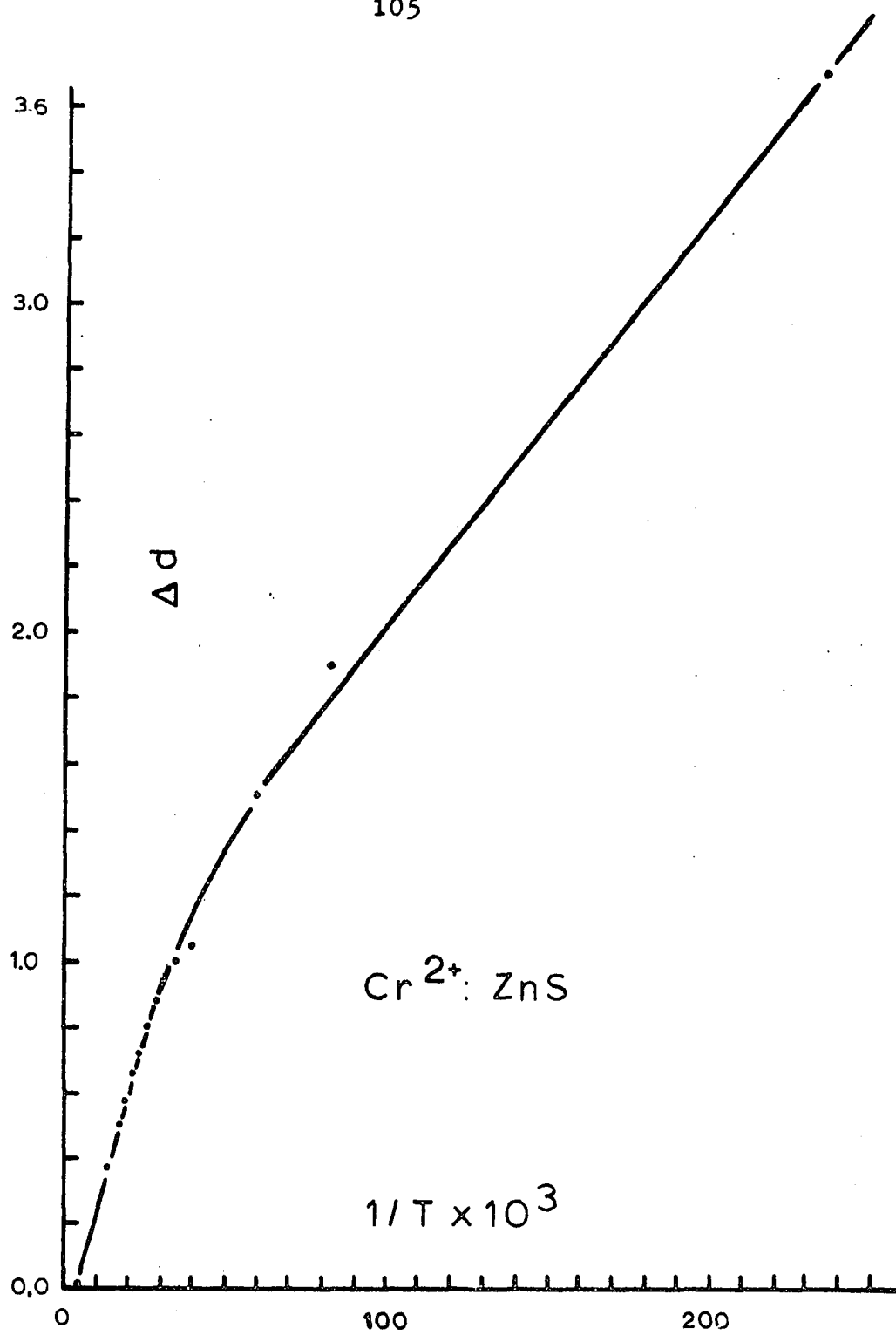


Figure 32. Measured magnetic susceptibility curve for $\text{Cr}^{2+}:\text{ZnS}$.

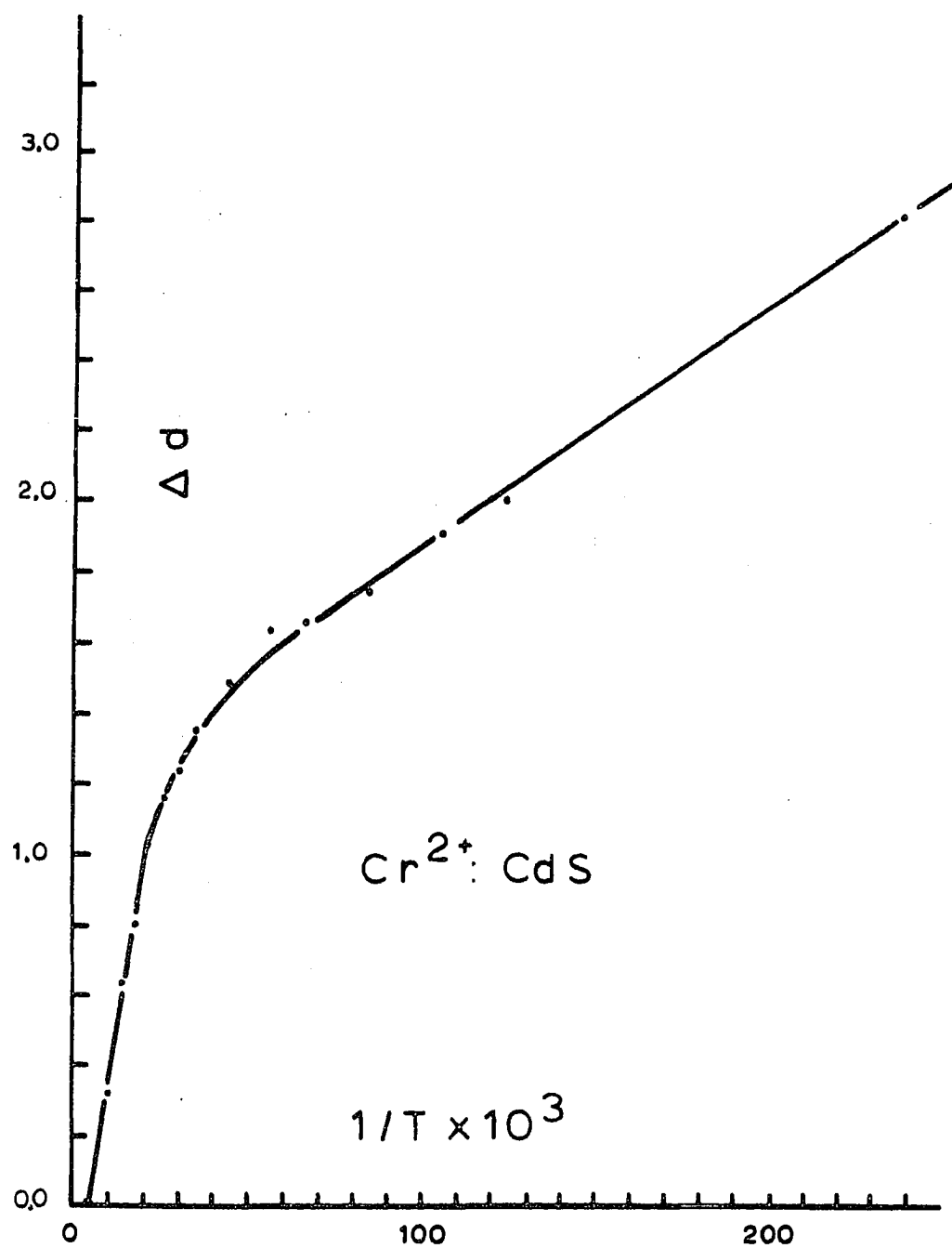


Figure 33. Measured magnetic susceptibility curve for $\text{Cr}^{2+}:\text{CdS}$.

TABLE 20

MEASURED MAGNETIC SUSCEPTIBILITY OF
 $\text{Cr}^{2+}:\text{ZnS}$ and $\text{Cr}^{2+}:\text{CdS}$

$\text{Cr}^{2+}:\text{ZnS}$			$\text{Cr}^{2+}:\text{CdS}$		
$m = 60.8 \text{ mg}$			$m = 324.3 \text{ mg}$		
$C = 0.8 \times 10^{18} \text{ Cr/c.c.}$			$C = 1.9 \times 10^{18} \text{ Cr/c.c.}$		
T (°K)	$1/T$ $\times 10^3$	Δd (LS-H-1)	T (°K)	$1/T$ $\times 10^3$	Δd (MS-H-2)
298.0	3.4	0.00	298.0	3.4	0.00
77.3	13.0	0.37	99.0	10.1	0.32
59.3	16.9	0.51	77.3	13.0	0.64
54.5	18.3	0.58	59.7	16.8	0.80
48.2	20.7	0.67	40.1	24.9	1.16
43.0	23.3	0.72	33.9	29.5	1.24
38.7	25.8	0.83	29.3	34.1	1.36
34.2	29.2	0.88	22.8	43.9	1.49
28.7	34.8	1.02	17.9	55.9	1.64
24.8	40.3	1.05	15.1	66.3	1.66
21.2	47.2	1.25	11.9	84.0	1.74
17.1	58.5	1.52	9.5	105.3	1.91
12.3	81.3	1.90	8.1	123.5	2.01
4.2	238.1	3.67	4.2	238.1	2.82

TABLE 21

MEASURED MAGNETIC SUSCEPTIBILITY OF
 $\text{Cr}^{2+};\text{ZnSe}$ and $\text{Cr}^{2+};\text{CdSe}$

$\text{Cr}^{2+};\text{ZnSe}$			$\text{Cr}^{2+};\text{CdSe}$		
$m = 100.0 \text{ mg}$			$m = 189.4 \text{ mg}$		
$C = 1.2 \times 10^{18} \text{ Cr/o.o.}$			$C = 0.3 \times 10^{18} \text{ Cr/o.o.}$		
T (°K)	$1/T$ $\times 10^3$	Δd (MS-H-1)	T (°K)	$1/T$ $\times 10^3$	Δd (MS-H-1)
298.0	3.4	0.00	298.0	3.4	0.00
77.3	13.0	0.40	77.3	13.0	0.20
46.4	21.6	0.85	44.3	22.6	0.42
37.4	26.7	1.10	31.5	31.8	0.65
36.3	27.5	1.15	28.2	35.5	0.70
33.1	33.3	1.24	23.6	42.4	0.80
27.6	36.2	1.57	20.2	49.5	1.05
25.7	38.9	1.60	14.7	68.0	1.40
23.3	42.9	1.80	13.0	76.9	1.65
21.2	47.2	2.18	11.4	87.7	1.75
17.6	56.8	2.35	8.5	117.7	2.23
12.6	79.4	3.10	7.7	129.9	2.57
4.2	238.1	10.00	6.9	144.9	2.95
			4.2	238.1	3.30

TABLE 22

MEASURED MAGNETIC SUSCEPTIBILITY OF
 $\text{Cr}^{2+}:\text{ZnTe}$ and $\text{Cr}^{2+}:\text{CdTe}$

$\text{Cr}^{2+}:\text{ZnTe}$			$\text{Cr}^{2+}:\text{CdTe}$		
$m = 113.8 \text{ mg}$			$m = 98.7 \text{ mg}$		
$C = 0.3 \times 10^{18} \text{ Gr/o.o.}$			$C = 1.2 \times 10^{18} \text{ Gr/o.o.}$		
T (°K)	$1/T$ $\times 10^3$	Δd (MS-H-1)	T (°K)	$1/T$ $\times 10^3$	Δd (MS-H-1)
298.0	3.4	0.00	298.0	3.4	0.00
20.1	49.8	0.50	77.3	13.0	0.32
16.1	62.1	0.70	48.5	20.6	0.90
12.7	78.1	0.90	44.5	22.5	1.00
10.4	96.2	1.10	39.6	25.9	1.04
9.0	111.1	1.25	36.8	27.2	1.16
4.2	238.1	2.35	31.3	32.0	1.28
			25.3	39.5	1.64
			22.6	44.3	1.95
			15.7	63.7	2.70
			11.8	84.8	3.35
			9.2	108.7	3.60
			4.2	238.1	5.10

TABLE 23

CONCENTRATIONS OF Cr^{2+} IN HOST CRYSTALS

Host	Mass (mg)	R $\times 10^6$	# Cr/c.c. $\times 10^{-18}$	# Cr / # Host $\times 10^6$	wt. Cr/ wt. Host $\times 10^6$
ZnS	60.8	9.6	0.8	32	5.1
CdS	324.3	23.0	1.9	96	8.3
ZnSe	100.0	14.0	1.2	53	5.2
CdSe	189.4	3.4	0.3	15	0.9
ZnTe	113.8	3.1	0.3	14	0.8
CdTe	98.7	14.5	1.2	78	3.2

or explain the changes in the paramagnetic susceptibility curve at low temperatures.

CHAPTER VII

Ni^{2+} IN TETRAHEDRAL SITES

Introduction

Nickel is another of the iron-group transition metals, and its electronic structure is given by $(\text{Ar})(3d)^8(4s)^2$. In the divalent state the outer two $4s$ electrons are lost, and we need consider only the magnetic phenomena arising from the eight $3d$ electrons. As previously described,^{42,56} crystal field theory predicts the splittings of the electronic energy levels are shown in Fig. 34. We note at this point that the ground state is nonmagnetic as in the case of Fe^{2+} , but here the lower energy level separations are a function of the spin orbit coupling parameter λ rather than K as in Fe^{2+} . Therefore, the determination of the spin-orbit coupling parameter λ from the measured magnetic susceptibility is more direct than in the case of Fe^{2+} .

In the calculation of the positions of the electronic energy levels using crystal field theory, the mixing of the 3P free-ion level with the lower 3F level must be considered. The 3F levels are then split by crystal field theory, and the energy level separation is given as a function of the crystal field parameter Δ or $10Dq$. Next the levels are

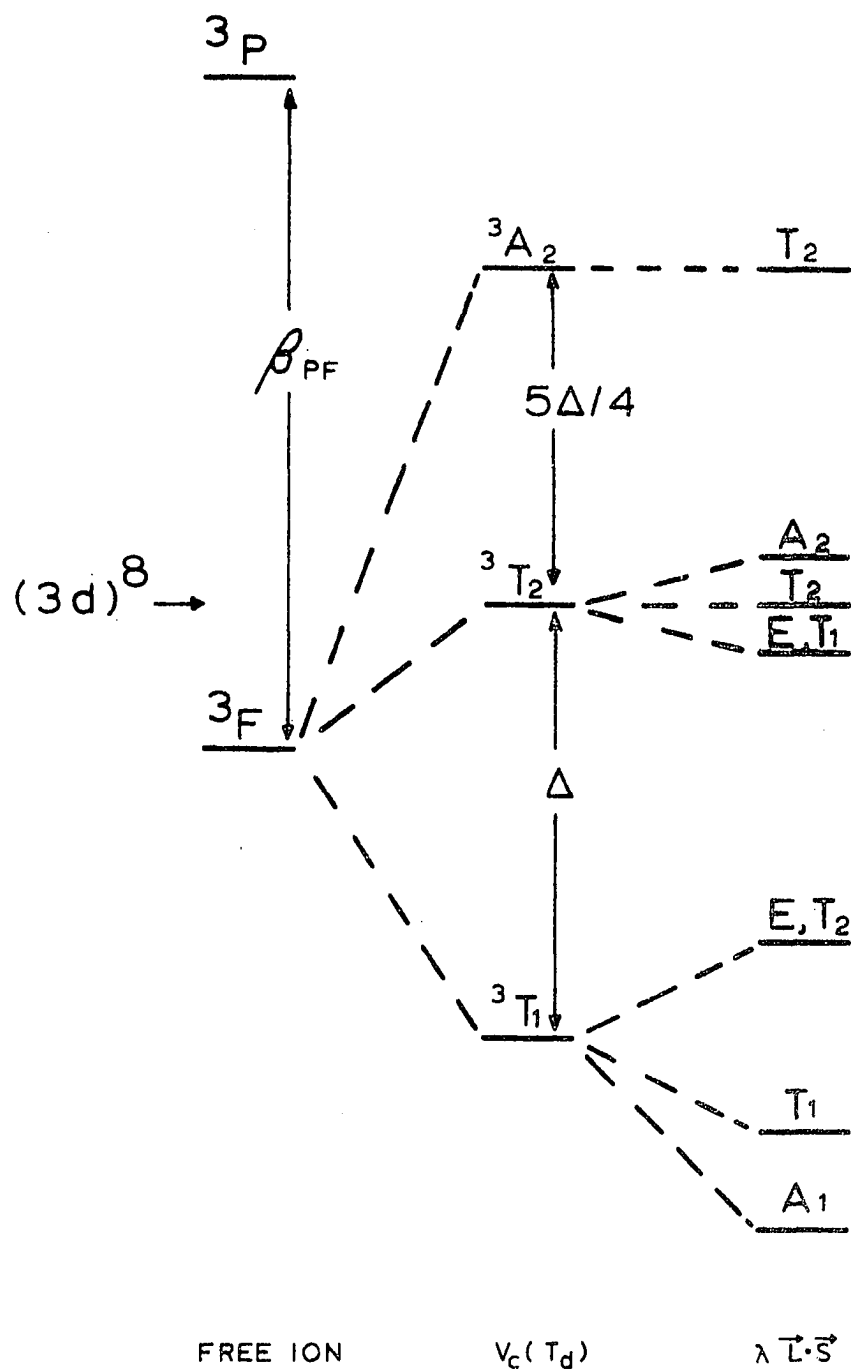


Figure 34. Energy levels of Ni^{2+} in cubic crystal field.

split by first order spin-orbit interaction. In previous studies of Ni^{2+} in ZnO ,⁴² CdS ,⁴² and ZnS ⁵⁶ it was found that λ was -175 cm^{-1} , -170 cm^{-1} , and -150 cm^{-1} respectively. The value of the parameters β pf and Δ as determined from optical spectroscopy were approximately 8880 cm^{-1} and 4440 cm^{-1} respectively. These magnetic susceptibility measurements have been extended to include Ni^{2+} in CdSe , ZnSe , and ZnTe .

The calculated magnetic susceptibility as a function of the parameter $T(^{\circ}\text{K})$ and $\lambda (\text{cm}^{-1})$ is shown in Fig. 35. The method of calculation has been reported previously^{42,56} and is similar to the approach described for Fe^{2+} in an earlier chapter.

Magnetic Susceptibility Measurements

The measured paramagnetic susceptibilities of Ni^{2+} in CdSe , ZnSe , and ZnTe are given in Table 24. The procedure was exactly as we have described for Fe^{2+} in various host crystals. In the preliminary measurements, data was taken down to 10°K . When all three crystals had been measured, and the magnetic susceptibility curves compared to theoretical curves, it was found that the experimental curve fit the theoretical curve calculated with a spin-orbit parameter of -60 cm^{-1} . This was unexpected because the value of $\lambda = -175$, -170 , and -150 for ZnO , CdS , and ZnS respectively.

Our first thought was that the doping was somehow the cause of our problem. Therefore, Ni^{2+} was doped into ZnS

TABLE 24

MEASURED MAGNETIC SUSCEPTIBILITY OF
 $\text{Ni}^{2+}:\text{CdSe}$, $\text{Ni}^{2+}:\text{ZnSe}$, and $\text{Ni}^{2+}:\text{ZnTe}$

$\text{Ni}^{2+}:\text{CdSe}$ $m = 52.4 \text{ mg}$ $C = 5.0 \times 10^{18}$ Ni/o.c.		$\text{Ni}^{2+}:\text{ZnSe}$ $m = 56.4 \text{ mg}$ $C = 15.4 \times 10^{18}$ Ni/o.c.		$\text{Ni}^{2+}:\text{ZnTe}$ $m = 59.5$ $C = 4.3 \times 10^{18}$ Ni/o.c.	
T (°K)	Δd LS-H-1	T (°K)	Δd LS-H-1	T (°K)	Δd LS-H-1
298.0	0.00	298.0	0.00	298.0	0.00
77.3	0.85	112.5	1.90	77.3	0.28
50.5	1.35	77.3	3.30	46.7	0.80
47.9	1.55	68.2	3.60	39.9	0.95
44.0	1.68	59.2	4.25	34.5	1.25
38.8	1.80	37.3	5.75	30.1	1.42
32.4	1.93	36.0	5.73	27.6	1.77
29.1	1.98	32.9	6.07	24.3	1.80
26.4	2.00	29.0	6.15	20.2	1.95
21.6	2.00	25.4	6.25	16.5	1.85
17.6	2.00	19.2	6.65	13.6	1.90
15.6	2.00	16.9	6.70		
13.5	2.00	11.8	7.00		
11.6	2.00	9.7	7.00		

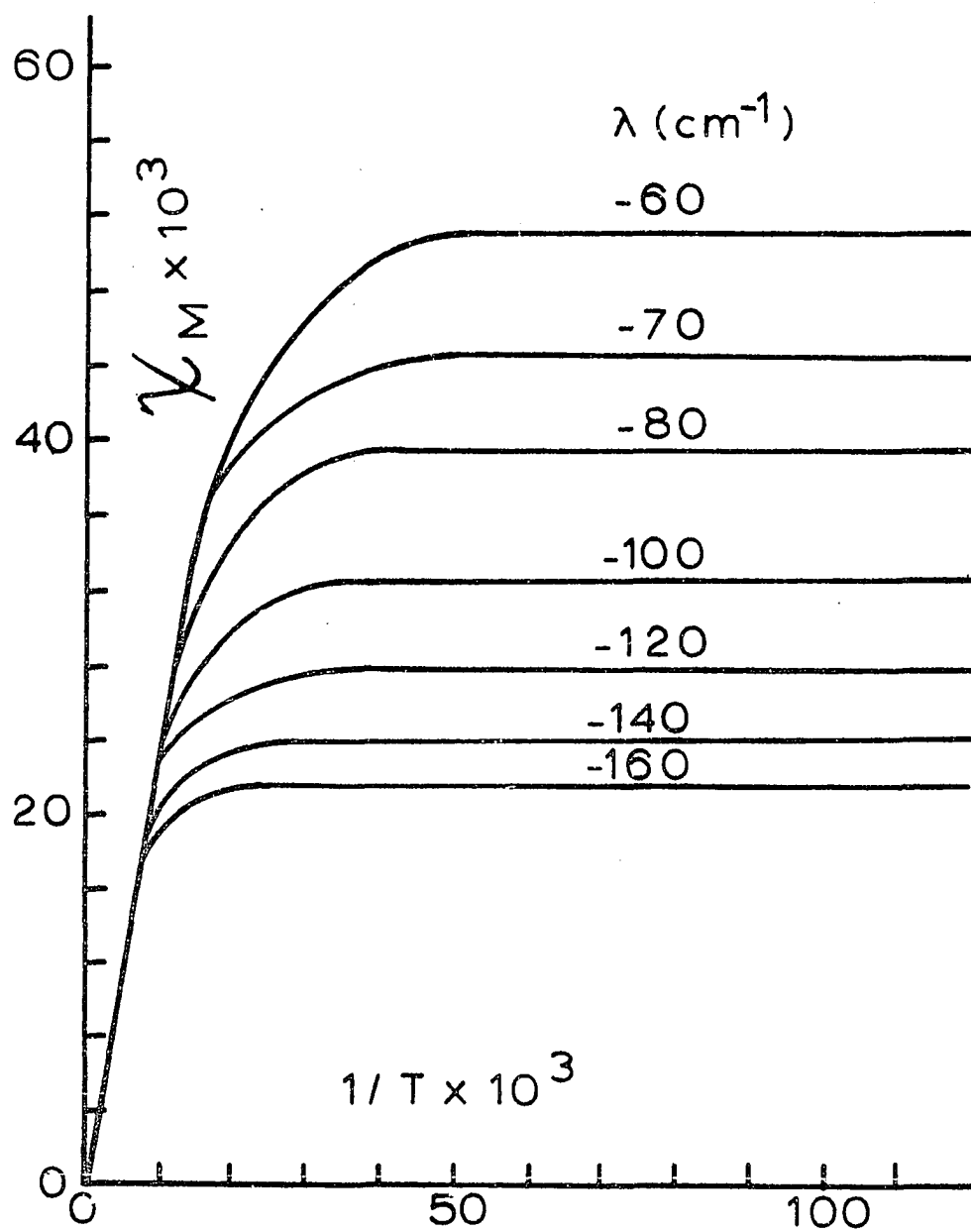


Figure 35. Calculated χ_M vs. $1/T$ (Ni^{2+}).

and then the magnetic susceptibility measured as a check on the doping procedures. It was found that the magnetic susceptibility measurements gave $\lambda = -150 \text{ cm}^{-1}$ as before. Then we doped Ni^{2+} into a new set of host crystals. We again found that the paramagnetic susceptibility increased with a decrease in temperature until the paramagnetic susceptibility become constant with further decrease in temperature. The new magnetic susceptibility curves again indicated a spin-orbit coupling parameter of -60 cm^{-1} .

At this point our experiments seem to be self-consistent, and the procedures of doping the crystals and measuring the magnetic susceptibility give previous results when Ni^{2+} is doped into ZnS. However, the spin-orbit coupling parameter for ZnSe, CdSe and ZnTe seems to be approximately one-half the value of λ in ZnO, CdS and ZnS which in turn is approximately one-half the free-ion value of $\lambda = -340 \text{ cm}^{-1}$.

Dr. Jürgen Schneider of the University of Freiburg in Germany is interested in doing infrared spectroscopy measurements on these crystals. We hope that future measurements will lend evidence to support or deny the unusually low spin-orbit coupling parameter which our magnetic susceptibility measurements indicate for Ni^{2+} in the selenides and tellurides. Concentrations of the Ni^{2+} ion in the host crystals as determined from magnetic susceptibility measurements are given in Table 25.

TABLE 25

CONCENTRATIONS OF Ni^{2+} IN HOST CRYSTALS

Host	Mass (mg)	R $\times 10^5$	# Ni/c.c. $\times 10^{-18}$	# Ni / # Host $\times 10^6$	wt. Ni / wt. Host $\times 10^5$
ZnS	53.5	29.6	27.0	1067	17.8
ZnSe	56.4	16.9	15.4	684	6.9
CdSe	52.4	5.5	5.0	267	1.7
ZnTe	59.5	4.7	4.3	231	1.4

CONCLUSIONS

The sensitivity of a Faraday balance has been improved by more than an order of magnitude, and its range of magnetic susceptibility measurements has been extended to temperatures lower than 1.8°K . The Faraday balance was then applied to the study of transition metal ions in II-VI compounds in 16 different cases.

The techniques of doping transition metals in II-VI compounds are reported for the crystals studied in this work. The magnetic properties of two other crystals grown from a different method are studied and compared to crystals doped in our laboratory to gain confidence in the doping techniques.

Magnetic susceptibility measurements of seven iron doped crystals were studied which led to the determination of the positions of the lower lying levels of the impurity ion. The five crystals of tetrahedral symmetry doped with iron had K values of 15.0 cm^{-1} , 18.0 cm^{-1} , 15.6 cm^{-1} , 11.5 cm^{-1} , and 11.8 cm^{-1} for $\text{Fe}^{2+}:\text{ZnS}$, $\text{Fe}^{2+}:\text{CdTe}$, $\text{Fe}^{2+}:\text{ZnTe}$, $\text{Fe}^{2+}:\text{CdSe}$, and $\text{Fe}^{2+}:\text{ZnSe}$, respectively. CdS and ZnO host crystals possess a trigonal distortion, and S_1 , S_2 are found to be 14.3 , 16.0 cm^{-1} and 7.8 , 17.6 cm^{-1} for $\text{Fe}^{2+}:\text{CdS}$ and $\text{Fe}^{2+}:\text{ZnO}$, respectively.

The magnetic susceptibility data for the Cr^{2+} doped II-VI compounds seems to support the electronic energy level scheme predicted by considering a Jahn-Teller distortion

which reduces the symmetry of the lattice site to D_{2d} . Although the calculated magnetic susceptibility is not available at this writing, the qualitative features are very encouraging and experimentation is in progress to detect lower levels by magnetic susceptibility measurements at temperatures less than 4.2°K .

The magnetic susceptibility measurements for Ni^{2+} doped crystals were expected to be very straightforward. Indeed, the crystals were doped with Ni^{2+} ions, and the results were consistent for three complete series of doped crystals. When the measured magnetic susceptibility was fit to the theoretical curves; however, it was found that the spin-orbit parameter was approximately -60 cm^{-1} . This was unexpected since the spin-orbit parameter for $\text{Ni}^{2+}:\text{ZnS}$ is -150 cm^{-1} which, in turn, is approximately one-half the free ion value of -340 cm^{-1} . Therefore, optical absorption experiments are now being conducted by Dr. Jürgen Schneider to confirm or deny these unusual values for λ .

Magnetic susceptibility studies of transition metal ions in II-VI compounds have proven to be quite fruitful and have obtained information difficult to obtain from either electron spin resonance or far infrared spectroscopy.

REFERENCES

1. J. H. Van Vleck, Theory of Electric and Magnetic Susceptibilities, (Oxford University Press, London, (1932)).
2. A. B. P. Lever, Inorganic Electronic Spectroscopy, (Elsevier Publishing Company, Amsterdam, 1968).
3. G. A. Slack, S. Roberts, and J. T. Vallin, Phys. Rev. 187, 511 (1969).
4. W. H. Brumage, C. R. Quade, and C. C. Lin, Phys. Rev. 131, 949 (1963).
5. C. P. Poole, Jr., Electron Spin Resonance, (Interscience Publishers, New York, 1967).
6. L. F. Bates, Modern Magnetism, (Cambridge University Press, London, 1963), 4th edition, p. 122.
7. P. W. Selwood, Magnetochemistry, (Interscience Publishers, New York, 1964). 2nd edition, p. 11.
8. M. Faraday, Experimental Researches, Vol. III, (Taylor and Francis, London, 1855), pp. 27 and 497.
9. P. Curie, Ann. Chim. Phys. 5, 289 (1895).
10. J. W. Stout and M. Griffel, J. Chem. Phys. 18, 1449 (1950).
11. R. L. Powell, M. D. Bunch, and R. J. Corruccini, Cryogenics: 1, 139 (1961).
12. R. B. Scott, Cryogenic Engineering, (D. Van Nostrand Company, Princeton, New Jersey, 1959).

13. F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, NBS Monograph 10, (1960).
14. M. Aven and J. S. Prener, eds., Physics and Chemistry of II-VI Compounds, (North-Holland Publishing Company,
15. F. A. Kroger, The Chemistry of Imperfect Crystals, (North-Holland Publishing Company, Amsterdam, 1964).
16. W. Van Gool, Principles of Defect Chemistry of Crystalline Solids, (Academic Press, New York, 1966).
17. R. Pappalardo and R. E. Dietz, Phys. Rev. 123, 1188 (1961).
18. H. A. Weakliem, J. Chem. Phys. 36, 2117 (1962).
19. J. M. Baranowski, J. W. Allen, and G. L. Pearson, Phys. Rev. 160, 627 (1967).
20. T. L. Estle and W. C. Holton, Phys. Rev. 150, 159 (1966).
21. C. B. Burgett, Luminescence and Photoconductivity in Copper Doped Zinc Sulfide, (Unpublished Ph. D. thesis, Dept. of Physics, University of Oklahoma, 1969).
22. L. Holland, Vacuum Deposition of Thin Films, (John Wiley and Sons, Inc., New York, 1956), p. 110.
23. J. D. Strong, Procedures in Experimental Physics, (Prentice-Hall, Inc., New Jersey, 1938), p. 151.
24. W. H. Brumage and J. P. Mahoney, J. Chem. Phys. 48, 5733 (1968).
25. A. N. Nesmenanov, Vapor Pressure of the Elements, Academic Press, New York, 1963).
26. G. Herzberg, Atomic Spectra and Atomic Structure, (Dover Publications, New York, 1944) p. 132.

27. H. A. Bethe, Ann. Physik 3, 133 (1929); English translation, Consultants Bureau, New York, 1958.
28. C. J. Ballhausen, Crystal Field Theory, (McGraw-Hill Book Company, New York, 1962).
29. J. L. Prather, Atomic Energy Levels in Crystals, (U.S. Government Printing Office, Washington, D. C., 1961).
30. Ref. 13, 119.
31. R. W. G. Wyckoff, Crystal Structures (Interscience Publishers, New York, 1953), p. 108.
32. Ref. 1, p. 182.
33. G. H. Slack, S. Roberts, and F. S. Ham, Phys. Rev. 155, 170 (1967).
34. Ref. 23, p. 135.
35. W. Low, Paramagnetic Resonance in Solids, (Academic Press, New York, 1960), p. 28.
36. D. S. McClure, Electronic Spectra of Molecules and Ions in Solids, (Academic Press, New York, 1959), p. 81.
37. Ref. 32, p. 35.
38. W. Low and M. Weger, Phys. Rev. 118, 1119 (1960).
39. W. Low and M. Weger, Phys. Rev. 118, 1130 (1960).
40. E. B. Wilson, J. C. Decius, and P. C. Cross, Molecular Vibrations, (McGraw-Hill Book Company, New York, 1955), p. 340.
41. M. Tinkham, Group Theory and Quantum Mechanics, (McGraw-
42. W. H. Brumage and C. C. Lin, Phys. Rev. 134, A950 (1964).

43. J. P. Mahoney, C. C. Lin, and W. H. Brumage, J. Chem. Phys. 50, 2263 (1969).
44. G. A. Slack, F. S. Ham, and R. M. Chrenko, Phys. Rev. 163, 335 (1967).
45. G. A. Slack and B. M. O'Meara, Phys. Rev. 163, 335 (1967).
46. K. Morigaki, J. Phys. Soc. Japan 18, 733 (1963).
47. K. Morigaki, J. Phys. Soc. Japan 19, 187 (1964).
48. W. Low, ed., Paramagnetic Resonance, Vol. 1, (Academic Press, New York, 1963), p. 144.
49. T. L. Estle and W. C. Holton, Phys. Rev. 150, 159 (1966).
50. J. T. Vallin, G. A. Slack, and S. Roberts, Solid State Comm. 7, 1211 (1969).
51. F. Seitz, D. Turnbull, and H. Ehrenreich, eds. Solid State Physics, vol. 20 (Academic Press, New York, (1967), p. 92.
52. H. Kramers, Proc. Acad. Sci. Amsterdam 33, 959 (1930).
53. H. A. Jahn and E. Teller, Proc. Roy. Soc. A161, 220 (1937).
54. B. Bleaney and K. D. Bowers, Proc. Phys. Soc. (London) A65, 667 (1952).
55. J. T. Vallin, G. A. Slack, and S. Roberts, Bull. Am. Phys. Soc. (3) 15, 290 (1970).
56. J. P. Mahoney, Magnetic Susceptibilities of Ni^{2+} Doped ZnS Crystals, (Unpublished Masters thesis, Dept. of Physics, University of Oklahoma, 1967).