

THERMAL CONDUCTIVITY OF POTASSIUM MANGANESE
FLUORIDE AT LIQUID HELIUM TEMPERATURE
AND NEAR THE NEEL TEMPERATURE

By

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CHAPTER I

HISTORICAL DEVELOPMENT AND THEORETICAL CONSIDERATIONS

Introduction

Heat is usually transported through a solid by two different processes--phonons and free electrons. When heat is introduced into a crystal a certain amount of energy is transferred to the atoms and the disturbance of the first excited atoms is propagated to the next atoms as the process is continued through the crystal. This propagation of the perturbation of the atomic motion in the crystal can be considered as due to quantized waves traveling in the crystal. Each one of these quanta is called a phonon. This is dominant mechanism for transporting heat in dielectrics. The second manner of transporting heat is by means of free electrons. This latter mechanism occurs in metals although even in metals some of the heat is carried by phonons. In semiconductors and alloys both processes are present. Experiments show that the heat transport is proportional to the temperature along the specimen (1), and from this observation the heat conductivity is defined as

$$\lambda = \frac{\dot{Q} L}{A \Delta T} \quad (1)$$

where \dot{Q} is the rate of flow of heat along the specimen, A is the cross section and ΔT is the difference of temperature over the length L .

Heat transport by lattice waves in solids depends on the anharmonicities of the lattice forces, on the imperfections of the crystal lattice and on the boundary conditions (2). In metals and semimetals the thermal conductivity depends also on the mobility of free electrons. The sources of thermal resistance may vary from one material to another (2).

Determination of thermal conductivity of potassium manganese fluoride, KMnF_3 , is interesting because KMnF_3 is an antiferromagnetic material and its nearly cubic structure gives rise to low anisotropy and to predominance for nearest neighbor interaction (3). It is attractive too because many experiments have been done on the properties of KMnF_3 , but only few to obtain the thermal conductivity at low temperature, and none to determine the thermal conductivity at liquid helium temperature.

This work will consist of a brief review of some of the theories of thermal conductivity in crystalline dielectric matter at low temperature, the determination of the thermal conductivity of KMnF_3 at liquid helium temperature and near the Neel temperature, and the conclusions about the behavior of the thermal conductivity dependence on temperature in this temperature region.

Historical Development of Thermal Conductivity in Solids Dielectrics

Eukens in 1911 measured the thermal conductivity of a large number of solids at liquid air and at room temperature (4). He observed that the conductivity of single crystals increased with decreasing temperature above the boiling point of liquid air ($\sim 80^\circ\text{K}$). Debye explained this behavior by assuming that heat flows through a dielectric solid transported by traveling elastic waves with the same spectrum as in a

continuous medium. The scattering of these waves gives rise to thermal resistance. This scattering may be expressed in terms of the mean free path, which is defined as the distance that a wave travels before it reduces its intensity to $1/e$ of its initial value. Thermal conductivity thus is given in Debye's approach by

$$\lambda = \frac{1}{4} \Lambda C_v v$$

where C_v is the specific heat per unit volume, v is the wave velocity and Λ is the free path. The mean free path is limited by scattering of the waves due to fluctuation in density, which arises from the anharmonicity of the lattice vibrations, and it is inversely proportional to the absolute temperature. This explanation was in agreement with Eucken's measurements. Peierls in 1929 and in 1935 developed a theory in which he treated the solid as a crystal lattice of atoms rather than a continuous medium. In this theory the normal modes are quantized, and the quanta are called phonons. In accord with Peierls' theory, the thermal conductivity λ is written as

$$\lambda = \frac{1}{3} \Lambda C_v v. \quad (2)$$

At sufficiently high temperature, the specific heat is independent of the temperature T , and Λ is inversely proportional to T . Then, assuming that v is constant, the thermal conductivity is inversely proportional to T

$$\lambda \sim \frac{1}{T}.$$

If we define the thermal resistance R_T by $\lambda = 1/R_T$, according to

the Peierls' theory the thermal resistance is given by

$$R_T = a T^{\nu} \exp\left(-\frac{\theta}{2T}\right) + bT \quad (3)$$

where a , ν and b are constant and θ is the Debye temperature (4).

To test the behavior of dielectric crystals at low temperature, de Haas and Biermasz (5) measured the thermal conductivity in the region of liquid helium for KBr and KCl. They found that thermal resistance diminished rapidly from 90° K to 10° K and increased strongly at lower temperature. They investigated the dependence of the thermal resistance on thickness and found that thermal resistance was not inversely proportional to thickness (6). For temperatures higher than 0.50θ where C_v was constant, λ was proportional to $1/T$. And from $\lambda \sim C_v v \Lambda$ they assumed that the free path Λ was proportional to $(C_v v)^{-1} \lambda$ for values of $T > 0.50 \theta$. For values of $T < \theta$, C_v decreases while $\lambda \sim \frac{1}{T}$. This means that Λ increases at lower temperature. For values of T lower than the one for which λ has a maximum, the value of λ was found to be of the same order of the thickness of the rod. This was in agreement with the fact that for this temperature regime the thermal conductivity is dependent on the thickness. At the lowest helium temperature $\lambda \sim T^3$, as well as C_v . For still lower temperature the increasing resistance was caused by reflection of the waves by the walls of the sample. They concluded that the hypothesis of the reflection of elastic waves by the wall of the sample or from the mosaic crystals made it possible to explain the phenomena of variation of thermal conductivity at that temperature.

In 1938, Casimir (7) considered the case when the free path is very long compared with the dimension of the crystal. He compared the flow of

heat in a cylindrical crystal, at a temperature lower than the one for which the scattering of elastic waves by the boundaries is important, with the flow of electromagnetic energy in a cylinder. He deduced a prescription for thermal conductivity at temperatures lower than that one where the dimensions of the crystal are comparable with the free path. The Casimir formula is

$$\lambda = \frac{F}{\pi R^2} \frac{dT}{dz} = R P A_c^{3/2} 2.31 \times 10^3 T^3 \quad (4)$$

This formula applies for temperature lower than the one corresponding to λ maximum. λ maximum usually occurs at a value of T between $\theta/20$ and $\theta/30$ (1). Then we can write that Casimir's formula applies for temperatures T , such that

$$T < T_{\lambda \max} \sim \frac{\theta}{20}$$

The Casimir formula was deduced for cylindrical rods with circular cross section of radius R . When the cross section is a square, R is changed in the formula by $0.56 d$; d is the side of the square. F is the flow of energy per second through a crystal with cylindrical shape of radius R , and with a gradient temperature dT/dz in the z direction. A_c is a constant that can be calculated from the specific heat when it is written

$$C = A_c T^3,$$

P is an adimensional factor of the order of unity and for anisotropy bodies it may be written

$$P = \frac{2\alpha^2 + 1}{(2\alpha^3 + 1)^{2/3}}$$

where alpha is the ratio between the longitudinal and transverse velocity of sound. For values of α between 1 and 2, $P \sim 1.4$. A_c can be calculated for a material if its Debye temperature is known. When the material is isotropic $P = 1.4$ can be used. Casimir's formula may now be written $\lambda = B R T^3$ where B is a parameter containing P and A_c . This formula is called the T^3 law, and it shows λ as a function of B , R and T ; and for B , λ is a function of the Debye's temperature. Casimir made experiments on SiO_2 and KCl , and concluded that his theoretical considerations led to a fairly satisfactory interpretation of the experimental facts (7).

In 1958 P. G. Klemens wrote in detail about thermal conductivity. In this paper, the thermal conductivity for non-metal crystals, due to the lattice vibrations at high temperature is given by a formula deduced by Leibfried and Schloemann (2)

$$\lambda \sim \frac{24}{10} \frac{4^{1/3}}{\gamma^2} \left(\frac{C^3}{h}\right) M a^3 \frac{\theta}{T} \quad \text{for } T \gg \theta \quad (5)$$

where C is the specific heat at high temperature, γ is a parameter determined from the thermal expansion, a^3 is the volume per atom, M is the mass per atom, θ is the Debye's temperature and T is the absolute temperature.

For thermal conductivity limited by umklapp processes at low temperature, Klemens deduced the following expression:

$$\lambda \sim \frac{7.05}{4.8^2} \left(\frac{k_B}{h}\right)^3 aM \frac{T^3}{\theta} e^{-\frac{\theta}{\alpha_1 T}} \text{ for } T \ll \theta \quad (6)$$

and making the proportionality an equality, he gave as a formula for thermal conductivity, at low temperature, limited by umklapp processes, the following one:

$$\lambda = A_0 \lambda_0 \left(\frac{T}{\theta}\right)^3 e^{-\frac{\theta}{\alpha_1 T}} \text{ for } T \ll \theta \quad (6)$$

where α_1 is a numerical constant of the order of unity; α_1 depends upon the details of the zone structure and upon the dispersion of the lattice waves near the boundaries, A_0 is a constant, which if it is derived from formula (6) gives $A_0 = 0.5$, and $\lambda_0 = \lambda(T') \frac{T'}{\theta}$ for $T' = T > \theta$. Then, the final formula given by Klemens for λ is

$$\lambda(T) = 0.5 \lambda_0 \left(\frac{T}{\theta}\right)^3 e^{-\frac{\theta}{\alpha_1 T}} \text{ for } T \ll \theta. \quad (7)$$

Substances having the same parameter should have a reduced thermal conductivity $\frac{\lambda(T)}{\lambda_0}$ such that when it is plotted as a function of T/θ there should be one curve (2).

The thermal resistance is decreased rapidly by umklapp process at low temperature, and after the thermal resistance reaches a minimum it is again increased by external boundaries. At the lowest temperature the size of the sample acts to produce a lower thermal conductivity. Each resistive process contributes additively to the total resistance, and the total thermal resistance of a dielectric crystal can be written as

(2)

$$R_T(T) = DT^3 + F(T) + BT^{-3} e^{-\frac{\theta}{\alpha_1 T}} \quad (7)$$

where $D T^3$ is due to the size effect, $F(T)$ arises from static imperfections and $B T^{-3} e^{-\frac{\theta}{T}}$ is the effect of umklapp processes.

The thermal conductivity does not decrease more rapidly than inversely with temperature because of imperfections. For point defects it is inversely proportional to T , whereas it can decrease more slowly or even increase with other imperfections. Then, when the thermal conductivity changes faster than linearly an important fraction of the resistance may be attributed to umklapp processes at low temperature. When the sample is almost free of imperfections the behavior of thermal conductivity is given by the formula

$$\lambda(T) \sim B T^3 e^{-\frac{\theta}{T}}$$

At the lowest temperature, when the size effect is the most important, and the crystal is almost free of imperfections, the thermal conductivity is given by

$$\lambda = D T^3$$

Exponential variation of the thermal conductivity has been found by Berman (3), White and Woods (8), by Wilkinson and Wilks (9), by Webb and Wilks (10) and by Berman, Foster and Ziman (11).

Theoretical Considerations

To study thermal conductivity in a crystal we consider it, in a first approximation, as a composed of atoms bound together with Hooke's forces. Then, we solve the motion for the crystal lattice in its normal

modes. Solving the motion in its normal modes, where $\omega_{\underline{k}j}$ is the quantized normal mode or phonon corresponding to the wave vector \underline{k} and to the polarization index j , the Hamiltonian of the system is (12)

$$H = \sum_{\underline{k}j} (N_{\underline{k}j} + \frac{1}{2}) \hbar \omega_{\underline{k}j} \quad (8)$$

where $N_{\underline{k}j}$ is the total number of quantized normal modes or phonons with the wave vector \underline{k} , and $\hbar\omega_{\underline{k}j}$ is the energy of the phonon $\omega_{\underline{k}j}$.

The velocity of a wave packet with wave vector \underline{k} is given by the group velocity

$$(v_{\underline{k}j})_i = v_{\underline{k}j} \cdot e_i = \frac{\partial \omega_{\underline{k}j}}{\partial k_i}$$

where e_i is an unit wavevector and k_i is the component of \underline{k} in the direction of e_i . The number of phonons per unit volume in an isolated system of volume V in equilibrium at temperature T is (13)

$$n_{\underline{k}j}^0 = \frac{1}{V} \left[e^{\frac{\hbar\omega_{\underline{k}j}}{k_B T}} - 1 \right]^{-1}$$

The heat flow in the system at position \underline{r} is

$$\dot{Q} = \sum_{\underline{k}j} n_{\underline{k}j}(\underline{r}) \hbar\omega_{\underline{k}j} v_{\underline{k}j} \quad (9)$$

where $n_{\underline{k}j}$ is the density of phonons in the system with a non-uniform temperature distribution. The net flow of heat in a system in equilibrium is zero, and if we write $\delta_{\underline{k}j} = n_{\underline{k}j} - n_{\underline{k}j}^0$, the flow of heat may be written

$$\dot{Q} = \sum_{\underline{k}j} \delta_{\underline{k}j} \hbar\omega_{\underline{k}j} v_{\underline{k}j} \quad (9)$$

The equation of Boltzmann for the phonon distribution is

$$\left(\frac{\partial n_{\underline{k}j}}{\partial t}\right)_{\text{scatt.}} = \underline{V}_{\underline{k}j} \cdot \nabla T \frac{\partial n_{\underline{k}j}}{\partial T} \quad (10)$$

If the concept of relaxation time is introduced, the scattering expression may be written (14) as

$$\left(\frac{\partial n_{\underline{k}j}}{\partial t}\right)_{\text{scatt.}} = - \sum_i \frac{1}{\tau_i} (n_{\underline{k}j} - n_{\underline{k}j}^0) \quad (11)$$

Substituting this expression of the scattering into Boltzmann's equation, and assuming that the system is not far from equilibrium, such that

$$\frac{\partial n_{\underline{k}j}}{\partial T} = \frac{\partial n_{\underline{k}j}^0}{\partial T}$$

the Boltzmann equation may be written as

$$\frac{\partial n_{\underline{k}j}}{\partial t} = - \nabla T \cdot \underline{V}_{\underline{k}j} \tau \frac{\partial n_{\underline{k}j}}{\partial T} .$$

Here $\frac{1}{\tau} = \sum_i \frac{1}{\tau_i}$ and the flow of heat may be expressed by

$$\dot{Q} = - \sum_{\underline{k}j} \nabla T \cdot \underline{V}_{\underline{k}j} \tau h \omega_{\underline{k}j} \frac{\partial n_{\underline{k}j}}{\partial T} \underline{V}_{\underline{k}j} .$$

In the last equation the thermal conductivity is a tensor for anisotropic systems, and it is defined from the formula for heat flow as

$$\lambda_{\alpha\beta} = \sum_{\underline{k}j} (\underline{V}_{\underline{k}j})_{\alpha} (\underline{V}_{\underline{k}j})_{\beta} \tau h \omega_{\underline{k}j} \frac{\partial n_{\underline{k}j}}{\partial T} \quad (12)$$

allowing to write the flux of heat as a function of the thermal conductivity tensor in the following form

$$\dot{Q} = -\nabla T \cdot \lambda_{\alpha\beta} \quad (13)$$

When the system is isotropic, the thermal conductivity reduces to

$$\lambda = \sum_{\underline{k}_j} \frac{V}{k_j} v_{\underline{k}_j}^2 \cos^2 \phi \tau \hbar \omega_{\underline{k}_j} \frac{\partial n_{\underline{k}_j}^0}{\partial T} \quad (14)$$

and $\dot{Q} = \lambda \nabla T$ (13) for isotropy, where ϕ is the angle between the group velocity and ∇T . When the distribution of discrete states may be approximated to a continuous distribution, the sum in formula (14) may be changed to the integral over \underline{k} . Making this change, the thermal conductivity is given by (14) as

$$\lambda = \sum \frac{V}{6\pi^2} \int_0^{k_{\max}} \tau \hbar \omega_{\underline{k}_j} \frac{\partial n_{\underline{k}_j}^0}{\partial T} v_{\underline{k}_j}^2 k^2 dk_j \quad (14)$$

where k_{\max} is the effective radius of the first Brillouin zone. If the acoustic approximation is used, which means that $\omega = v k$, this equation is Debye's equation for isotropic solids, and the thermal conductivity is expressed by

$$\lambda = \frac{1}{2\pi^2 v} \int_0^{\omega_{\max}} \tau \frac{\hbar \omega}{K_B T^2} \frac{e^x}{(e^x - 1)^2} \omega^2 d\omega \quad (15)$$

where $x = \frac{\hbar \omega}{K_B T}$, ω_{\max} is the Debye's maximum for ω , and v is the sound velocity.

Antiferromagnetism

The magnetic moment of one atom or ion may be expressed by

$$\mu = \gamma \hbar J = -g \mu_B J \quad (16)$$

where $\hbar J$ is the total angular momentum of the atom or ion. This total angular momentum is the sum of the orbital angular momentum $\hbar L$ plus the spin angular momentum $\hbar S$, γ is the ratio between the magnetic moment and the angular momentum and the g factor is

$$g = \frac{J(J+1) + S(S+1) - L(L+1)}{2 J(J+1)} \quad (17)$$

Usually antiferromagnetics (AFM) are characterized by the property of having the spins ordered in an antiparallel arrangement but no net magnetization below certain temperature (15). This temperature is called the Neel temperature. KMnF_3 is an exception to this, but the magnetization vanishes at 81°K while the order vanishes at 88°K .

The fact that AFM have spin order and no magnetization suggests that electron spins are ordered in a special form in which the field of one electron acts on the other electrons, and conversely. To explain this behavior it is assumed that the atoms of an AFM possess magnetic moment, and that a negative exchange coupling is operating among them (17). In the crystalline antiferromagnetic model an arrangement of the atomic magnetic moments is assumed in such a way that they point upward and downward in an alternating manner when the temperature is sufficiently low.

The susceptibility of AFM crystals has a maximum at a temperature close to the Neel temperature (T_N) (16). Below this temperature AFM are

magnetically anisotropic. At temperatures higher than T_n the susceptibility obeys the Curie-Weiss law

$$\chi = \frac{C}{T + \theta} \quad \text{for } T > T_n \quad (18)$$

where χ is the magnetic susceptibility and C is the Curie parameter. If the Curie temperature is defined as that one where the extrapolated paramagnetic susceptibility is ∞ , we may say that θ is a value equal to $-T_c$ in the Curie law $\chi = \frac{C}{T - T_c}$.

With this model of AFM the crystal may have two or an even number of sublattices. For each sublattice with spin pointing up there is one pointing down. It has been postulated that there is an energy directing the magnetization along certain definite crystallographic axes called the magnetocrystalline anisotropy energy (15).

The operator expressing the energy of the interaction between the electron spins of the atoms localized in a crystal may be written as the Hamiltonian of the system (18)

$$H = - \sum_{ij} J_{ij} \underline{S}_i \cdot \underline{S}_j \quad (19)$$

The exchange interaction in the crystal is equivalent to an interatomic potential (17)

$$V_{ij} = - \frac{1}{2} J (1 + 4 \underline{S}_i \cdot \underline{S}_j) \quad (20)$$

where \underline{S}_i and \underline{S}_j are respectively the spin angular moments of the atoms i and j measured in units of h . J is the exchange integral. In an antiferromagnet, J is negative and denotes, in the case of compounds, predominantly the coefficient of indirect exchange coupling, that is, the

coupling via the intermediary of a negative ion such as F^- .

The magnetization for the two sublattices is equal when there is no applied field, and the magnetization of each sublattice is called the saturation magnetization M_0 , which is equal to

$$M_0 = \frac{1}{2} \mu_B N g S B_s(y_0) . \quad (21)$$

N is the number of magnetic atoms per unit volume, g is the g factor; for an electron spin g is 2,00, μ_B is the Bohr magneton and it is equal to $\frac{e\hbar}{2mc}$, S is the spin angular momentum number, B_s is the Brillouin function and y_0 is equal to

$$y_0 = G M_0 S g \frac{\mu_B}{K_B T} .$$

parameter defined from the exchange field, K_B is the Boltzmann constant at T is the Kelvin temperature.

The solution for the spins motion in crystal lattice of an antiferromagnetic compound with only two sublattices may be written as (19)

$$\hbar\omega = - \mu_B \sqrt{H_e^2 (1-f(k)^2) + H_a (2H_e - H_a)} \quad (22)$$

Where H_a is a fictitious magnetic field introducing the anisotropy and H_e is the exchange field such that $J S = - 2 \mu_B H_e$. In this prescription, J is the negative exchange integral and μ_B is defined from the ratio between the magnetic moment of an atom with its spin S : $\underline{\mu} = 2\mu_B S$. When k is small $f(k) = 1 - \gamma k^2$. Neglecting anisotropy the solution is

$$\hbar\omega = \pm 2 \mu_B H_e \sqrt{2\gamma} k \quad (23)$$

This result gives ω depending linearly on k for small values of k ,

which is different from the similar case for ferromagnetism.

The approximated dispersion relation from Equation (22) of ω has the form given in Figure 1.

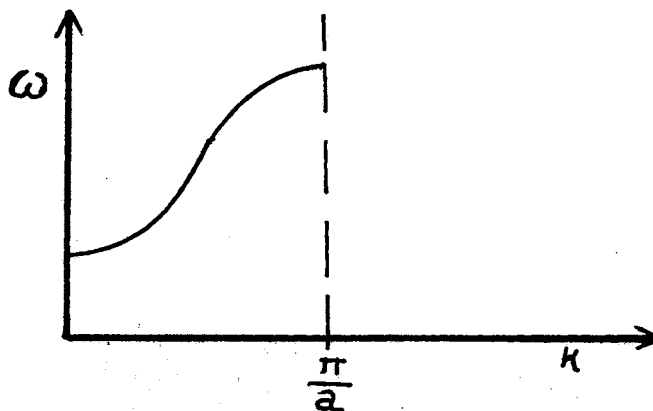


Figure 1. Dispersion Relation of One Spin Wave in an Anti-ferromagnet

The elementary excitations of a spin system have a wave like form; and, when they are quantized, are called magnons. A spin wave calculation determines the way in which the excited states deviate from a perfectly ordering (16).

Akhiezer and Shishkin (20) have studied the thermal conductivity of ferromagnetic dielectric materials and found that, at low temperature, the thermal conductivity in unbounded ferromagnetic dielectrics, which contain no impurities is determined by the interaction of spin waves with other and with phonons. They showed that when the Curie Temperature T_c is lower than the Debye temperature θ_D , the thermal conductivity is

rather proportional to $e^{\frac{T_c}{4T}}$ than to $e^{\frac{\theta_D}{2T}}$. They gave a prescription for thermal conductivity due to phonons and another one for thermal conductivity due to magnons.

The prescriptions for λ_f and λ_m are:

$$\lambda_f \sim \frac{T_c \theta_D^2}{\hbar a \omega^2} \left(\frac{T}{\theta}\right)^5 e^{\frac{T_c}{4T}}; T_c \ll \theta_D \quad (24)$$

$$\lambda_m \sim \frac{T_c^3}{\hbar a \omega^2} \left(\frac{T}{T_c}\right)^{7/2} e^{\frac{T_c}{4T}}. T \ll \theta_D \quad (25)$$

Akhiezer and Bar'yarkhatar (21) have studied the thermal conductivity of ferroelectrics at low temperature based in the mutual scattering of spin waves. They deduced the following formula for thermal conductivity at low temperature

$$\lambda = \frac{T^2}{\hbar^2} \left(\frac{2}{3} C_s + \frac{1}{3} C_l\right) \frac{1}{a^3 A_1}. \quad (26)$$

Where a is the lattice constant, C_s and C_l are, respectively, the heat capacity of the spin waves and of the lattice. A_1 is a value depending

on $T e^{-\frac{\theta_D}{T}}$ γ .

When

$$\theta_D \gg T_c$$

$$\lambda \approx \frac{4}{g} \frac{T}{\hbar a} e^{-\frac{\pi^2 T_c}{2T}} \quad (27)$$

They pointed out that when $\theta_D \gg T_c$ and $T \ll \frac{\theta_D^2}{T_c}$, spin waves play an essential role in the heat conduction. If $\theta_D \gg T \gg \frac{\theta_D^2}{T_c}$ the heat is conducted by phonons.

Gurzhi (22) has studied the thermal conductivity in dielectric and ferrodielectrics. He used the Debye approach $\lambda = C_v \Lambda v$ and obtained at very low temperature that λ is proportional to T^3 for dielectrics. For a temperature range from T_1 to T_2 , he obtained

$$\lambda = \frac{\theta_D}{Mv} \frac{d^2}{a^4} \left(\frac{T}{\theta_D}\right)^8 \quad (28)$$

Where T_1 is the temperature at which Λ_{pp}^N , the free path for phonon-phonon normal process, is of the same order of length that the one of the sample: $\Lambda_{pp}^N \approx d$. T_2 is the temperature at which $\Lambda^v = \frac{d^2}{\Lambda^N}$. Λ^v is the effective mean free path which characterizes the volume collisions with loss of momentum. The value d is the transverse dimension of the sample, M is the mass of the unit cell, v is the sound velocity and a is the lattice constant. At higher temperature he considered the usual decrease of thermal conductivity due to umklapp processes in the exponential form and in the $1/T$ law due to imperfections.

To work with magnons, he started considering the spin waves as the basically responsible for heat transport in ferrites at low temperature. The following formulas were deduced for him at very low temperature

$$\lambda = \frac{T_c}{\hbar} \frac{d^2}{a^3} \left(\frac{T}{T_c}\right)^2 \times \left\{ \begin{array}{l} \left(\frac{\mu M_o}{T_c}\right)^2 e^{-\frac{\beta \mu_o M_o}{T}} ; T_1 \ll T \ll \mu_B M_o \\ \left(\frac{\mu M_o}{T_c}\right)^2 ; \mu M_o \ll T \ll \left(\frac{\mu_B M_o}{T_c}\right)^{4/7} \\ \left(\frac{T}{T_c}\right)^{7/2} ; T_c \left(\frac{\mu_B M_o}{T_c}\right)^{4/7} \ll T \ll T_2 \end{array} \right. \quad (29)$$

Where μ_B is the Bohr magneton, M_o is the saturation magnetic moment and β is the anisotropy constant.

At higher temperatures than T_2 , it was considered that the thermal conductivity decreases exponentially if the sample was sufficiently pure.

Gurevich and Roman (23) studied the thermal conductivity of ferrites at low temperatures and the entrainment of phonons and magnons. They considered the flow of heat in ferrites at low temperature determined by the flows of phonons and magnons. This flow is limited by scattering at the crystal defects and at the boundaries, and by the transfer processes. The relaxation time concept of phonons and magnons is used in this deduction. It was considered that magnon-magnon and phonon-phonon interactions were much stronger than the interactions causing thermal resistance. Equilibrium distributions, with velocities v_m and v_p , for magnons and phonons were established in the magnon and phonon subsystems as a result of the latter interactions. Then, it is considered that at a given temperature and at a magnons and phonons concentration, the interaction between magnons and phonons change to be stronger than the interaction causing thermal resistance. One of the systems, the magnon or phonon, is accelerated or decelerated by the other, and a single velocity

v determined by the balance of momentum is established. The temperature region where this happens is called the entrainment temperature. They examined specifically the thermal conductivity, with entrainment of magnons and phonons, in the case of losing momentum due to the scattering of phonons or magnons by defects.

One general formula was deduced for the thermal conductivity of ferrites, this is

$$\lambda = \frac{T}{\mu} \frac{\left(\frac{2}{3} C_m + \frac{1}{3} C_p\right)^2}{\left(\frac{n_m}{z_{md}} + \frac{N_p}{z_{pd}}\right)} \quad (30)$$

Where T is the Kelvin temperature, μ is the effective mass of one magnon $= \frac{h^2}{2T_c a^2}$, C_m is the magnon heat capacity, C_p is the phonon heat capacity, n_m is the number of magnons per unit volume, N_p is the number of phonon per unit volume, z_{md} is the relaxation time of magnons in the interaction causing momentum losses and z_{pd} is relaxation times of phonons in the interactions causing momentum losses.

They defined a temperature $T_1 = 2\mu v^2 \approx \frac{\theta^2 D}{T_c}$ and considered the case when $T \ll T_1$. For this region temperature, the thermal conductivity is determined by the magnons. When $T \gg T_1$, λ is determined by phonons.

They also showed that when $T \ll T_1$ the interaction between magnons and phonons is more probable. A very important result of this study is that when there is entrainment the curve $\lambda = f(T)$ has a minimum at the beginning of the region temperature, and then the thermal conductivity increases with temperature; while when there is not entrainment it decreases monotonically.

Gurevich and Roman (24) also studied thermal conductivity of anti-ferromagnetics at low temperature. They considered two cases: $T_N \gg \theta_D$ and $T_N \ll \theta_D$. It was found that the thermal conductivity depends on the kind of magnetic impurities in the crystal.

The prescriptions deduced for them are:

$$\lambda = \frac{T_N^2}{T_{\text{afic}}}. \quad \text{For diamagnetic impurities and } T_N \ll \theta_D. \quad (31)$$

$$\lambda = \frac{T_N}{T_{\text{fac}}} \frac{T^3}{T_N^3}. \quad \text{For paramagnetic impurities and } T_N \ll \theta_D. \quad (32)$$

When both kinds of impurities are present in the antiferromagnet, the thermal conductivity is

$$\lambda = \frac{T_N}{T_{\text{fac}}} \left(\frac{T}{T_N}\right)^3. \quad \text{For } T < T_2 \quad (32)$$

and

$$\lambda = \frac{T_N}{T_{\text{afic}}} \frac{1}{T}. \quad \text{For } T > T_2 \quad (31)$$

T_2 is the temperature where λ reaches the maximum and c is the total concentration of impurities.

Potassium Manganese Fluoride (KMnF_3)

Potassium manganese fluoride, KMnF_3 , is an antiferromagnetic compound with Neel temperature $T_n = 88^\circ\text{K}$. This compound has a divalent manganese ion Mn^{+2} with five d electrons. Mn^{+2} is a S state ion, which, according to Berman, Olof and Knox (25) allows to expect a slight dis-

tortion from its cubic perovskite structure. But it is known that perovskite structure is itself unstable. These two facts make the study of KMnF_3 more interesting. At room temperature potassium manganese fluoride has a cubic perovskite structure with lattice constant $a = 4.186 \text{ \AA}$. In addition to the Neel temperature transition at 88°K , it has been shown a second magnetic transition at 81.50°K . Below this temperature of 81.50°K it exhibits a weak ferromagnetism caused by canting of the spins. Also, it is known that the cubic room temperature structure changes to an orthorhombic phase at 184°K with tetragonal pseudocells with values of $c/a > 1$, and at 84°K there is another tetragonal pseudocell too, but with $c/a < 1$ (25). Monoclinic pseudocells have been reported at lower temperature and between 88 and 105°K .

Thermal conductivity of KMnF_3 between 15°K and 300°K has been measured by Suemune and Ikawa (26) finding an anomalous decreasing in the temperature dependence of the thermal conductivity at the Neel temperature. They also found an anomalous decreasing of the thermal conductivity for another antiferromagnetic material with perovskite structure, KCoF_3 , at its Neel temperature of 144°K . These anomalous minima in the thermal conductivity were attributed to the phonon-magnon scattering (26).

In determining the specific heat of KMnF_3 between 70°K and 300°K , anomalous values of the specific heat have been found (27,28). A maximum of the specific heat at 83°K has been attributed to an antiferromagnetic ordering of the manganese ion below this temperature. Another maximum at 179°K is supposed to be due to the crystal structure change.

Khlyustov and his coworkers (28) found three temperatures where the specific heat of this material has anomalous values. They found that at

85.75 °K there is second kind transition which was attributed to the antiferromagnetic ordering. The anomaly at 95.13 °K was a first kind transition with changing of the structure, and the anomalous behavior at 191.13 corresponded to the changing of the space symmetry group in the crystal.

Goldrich and Birman (29) showed in a theoretical way that only eight space groups can arise in the perovskites by second order phase transitions without changing the unit cell.

Using the neutron scattering technique it has been found that the phase transition at 184 °K is a result of the softening of Γ_{25} phonon mode at the [111] zone boundaries, and it has been shown that the two transitions at 84 °K and 184 °K are a result of the soft phonon instability (30).

Figure 2 is a sketch of the unit cubic cell of KMnF_3 at room temperature. Figure 3 illustrates the unit cell in the orthorhombic phase.

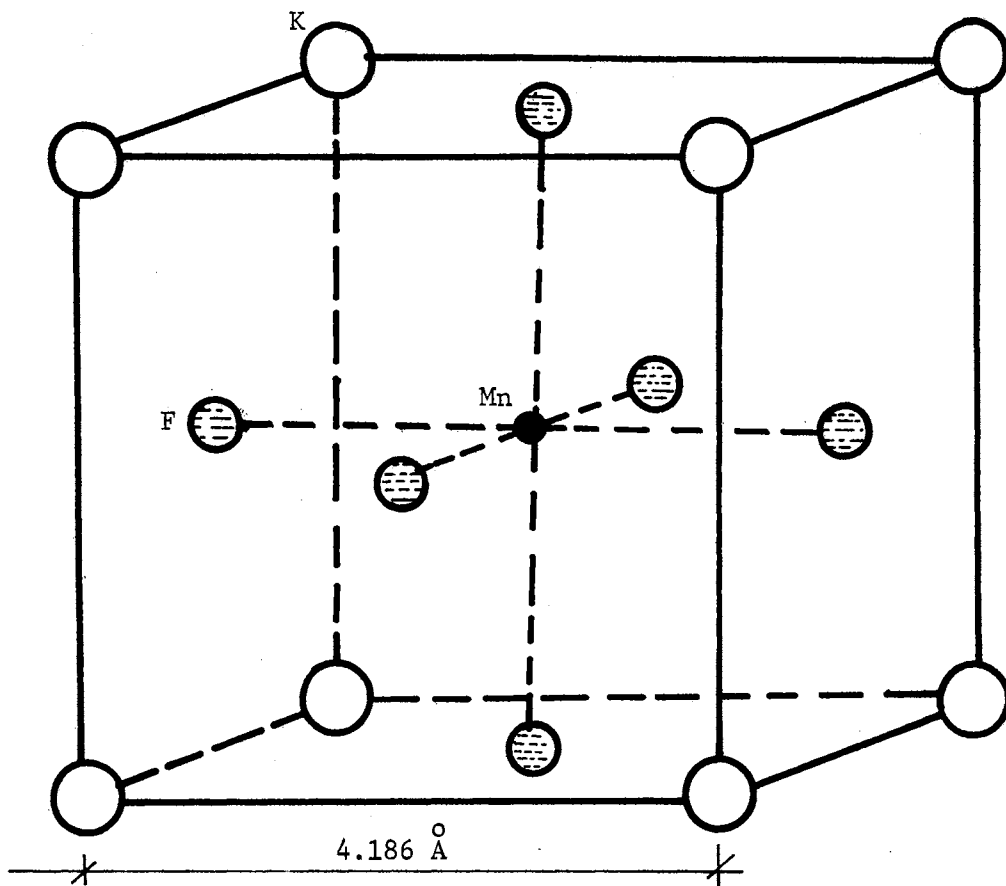


Figure 2. Unit Cubic Cell of KMnF_3 at Room Temperature

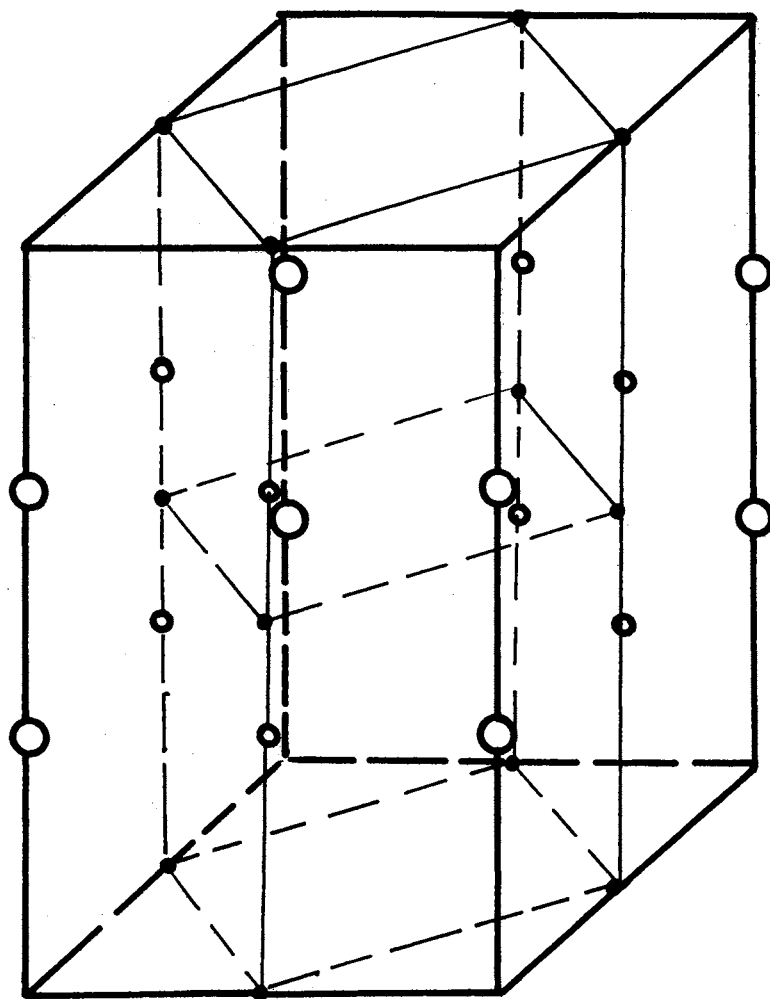


Figure 3. Unit Cell of Potassium Manganese Fluoride in the Orthorhombic Phase

- — Potassium
- — Fluorine
- — Manganese

CHAPTER II.

EXPERIMENTAL

The Sample

The sample was a crystal of potassium manganese fluoride grown at Oak Ridge National Laboratory by C. R. Riley using the Stockbarger technique. The dimensions of the sample were 10.00 mm. in length, 2.58 mm. in width and 1.50 mm. in thickness. The sample color was a soft pink. The dimensions were obtained after cutting a little bigger piece in order to have a more uniform cross section. The sample was oriented by X-ray diffraction so that the 10 mm. length was parallel to a $\langle 100 \rangle$ axis.

The Apparatus

The measurements were made by using a steady-state heat flow method. The complete apparatus consisted of a cryostat and a sample holder. In addition there was the necessary equipment to evacuate the sample holder and to produce low temperatures by evaporating cryogenic liquids such as nitrogen and helium. AuF_e -chromel thermocouples were used to measure temperature. These emf's were monitored by a potentiometer. Figure 4 shows a schematic diagram of the cryostat and sample holder. The cryostat contains four chambers. They are: an exterior vacuum chamber to isolate the next interior chamber from the room temperature, a second chamber with a cylindrical hole on its top to put liquid nitrogen in it, another interior vacuum chamber to isolate the inner chamber from the

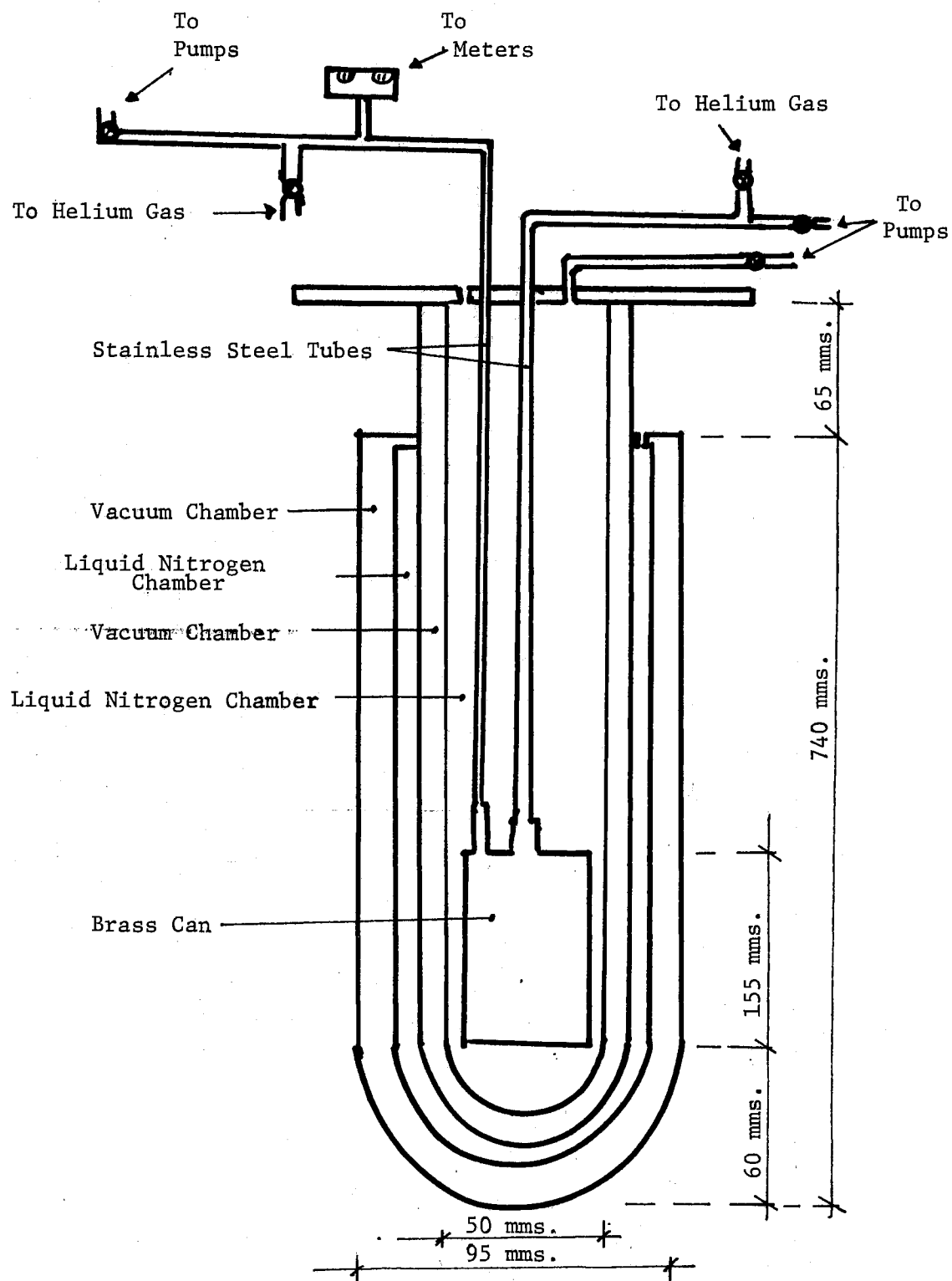


Figure 4. Cryostat and Sample Holder

last nitrogen one and the inner chamber where is placed the sample holder. In this chamber may be put liquid helium or liquid nitrogen in accord with the temperature that we need in the sample. The latter chamber may be kept in contact with the ambient by a hole or may be sealed and connected to the pumping system. This cryostat is a glass dewar used to pre-cool and to keep the sample holder can cool.

A detail of the sample holder is shown in Figure 5. It is essentially a small brass vacuum can containing a heat sink, an ambient heater and the holder for the sample. This can has on its top a vacuum seal, and from this top emerge two stainless steel tubes. One of these is to take out the cables going to the meters and to the power sources. This tube is used to evacuate the brass can too. The second tube is used to pump out the variable heat leak. This heat leak is used to increase the range in temperature that measurements can be made with a given cryogenic liquid. At the bottom of this tube there is a clamp to fix the sample. Over the clamp there is an aluminum flange where is fixed a cylindrical aluminum heat shield for heat radiations. Then the tube passes through the aluminum flange and just over the flange the electric ambient heater is placed around the tube. Above this the tube has an internal copper cylindrical heat sink. A heat leaking chamber is left between the heat sink and the wall of the tube. The chamber may be evacuated or may be filled with some gas. The set heat sink-heat leak works as a heat transfer cylinder from the inside of the brass can to the cooler in the inner chamber of the dewar. The latter heat transfer cylinder is connected to the exterior pumping system or to a connector to transfer gas into the cylinder when it is necessary. To measure the sample is fixed to the clamp in the sample holder. Indium is used to

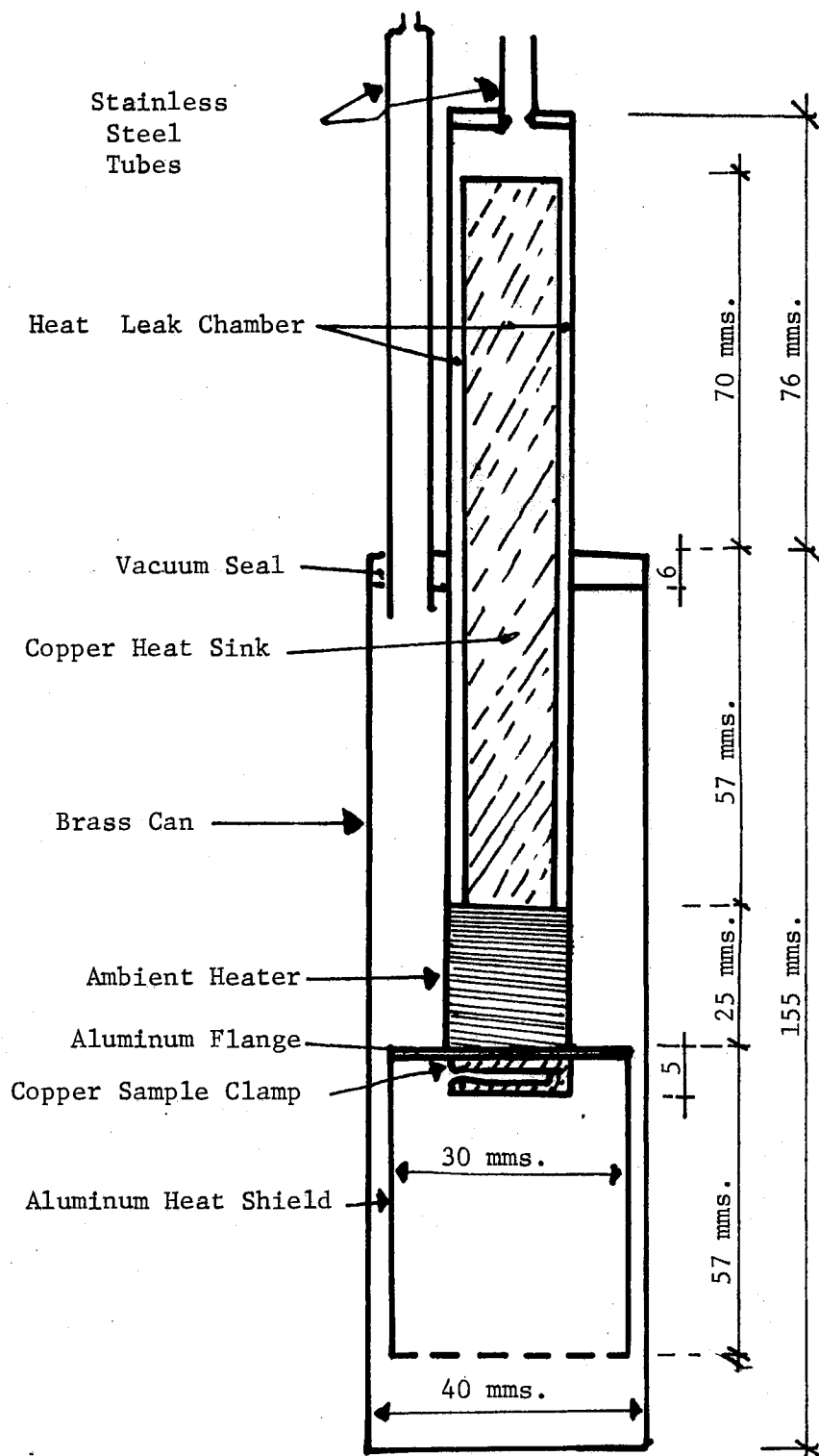


Figure 5. The Sample Holder

have a better thermal contact between the clamps and the piece of KMnF_3 . Then the ends of the thermocouple are put in contact with the sample leaving some distance apart between the thermocouple clamps. The thermocouple used in this experiment was one built with one chromel wire and one AuFe wire. It is interesting to point out that the thermocouple was connected in such a mode that allowed to measure ΔT directly. This kind of connection has the advantage that the values of ΔT obtained do not depend on the difference of temperature between the sample and the ice bath reference. Figure 6 shows a detail of this connection.

Finally, the gradient heater is fixed to the bottom of the sample. The ambient heater plays the role of raising the temperature of the sample and keeping this temperature. The gradient heater is used to transform electric power in thermal energy which flows through the sample in the form of heat. Then this heat out of the brass can through the sink.

Technique

The sample, with the clamps to measure the temperature T and the gradient temperature ΔT , was fixed to the holder sample. The distance between the clamps for ΔT was 5.10 mms. The sample cross section was 3.87 mm^2 . Once the sample holder was inside of the dewar, and the can evacuated, the next step consisted of filling the corresponding outer chamber with liquid nitrogen. Then, liquid helium was transferred to the inner dewar. With the evacuated brass can leak tested, and without any electric current in the ambient heater, the power was turned on in the gradient heater. After this it was necessary to wait for about three hours to allow the system to reach thermal equilibrium. Then, the

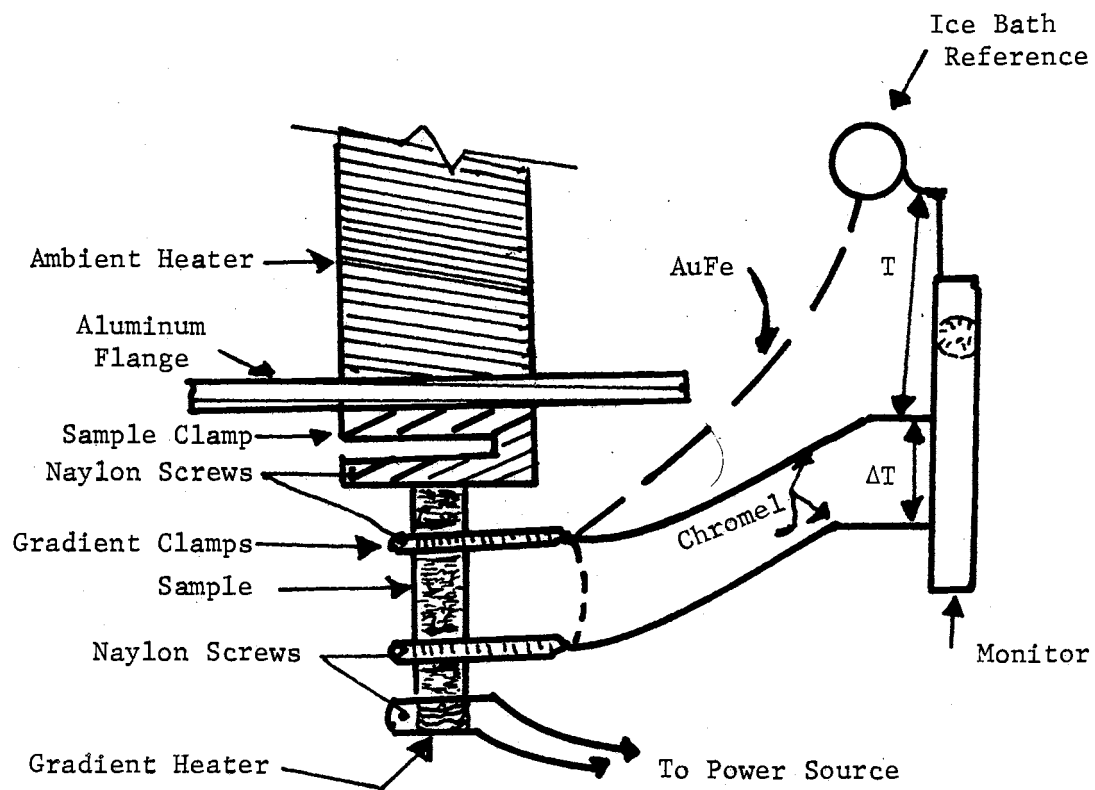


Figure 6. Detail of the Sample Holder With the Sample

first measurements were initiated at liquid helium temperature. It was observed that thermal equilibrium was reached in a relative short time, which allowed all the points at liquid helium temperature to be taken in two days. Fifteen points were taken from 5.15 °K to 22.50 °K. The measurement at each point was made in the following way: taking a reading of temperature with power in the gradient heater and another reading for temperature gradient, then turning the power off in the heater, wait for equilibrium and take again one reading for temperature and other for gradient.

To work at the Neel temperature liquid nitrogen was transferred into the inner dewar instead of liquid helium. By pumping out the liquid nitrogen, it was possible to reach a temperature of 46.35 °K. At this temperature the second run began. The same method of putting first power in the gradient heater, and then measuring with zero power was used. Twenty seven points were taken from 46.35 °K to 188.00 °K, but, in two months. At sixty three degrees some problems in getting stability forced a change in the procedure. Up to the last named temperature I could wait for equilibrium, and when the temperature was changing at a very slow rate I could read the temperature and change to read ΔT . A subsequent reading showed that the first reading of temperature was right. Now, nothing was stable, nor the temperature neither ΔT . It was necessary to read the temperature when it was almost in equilibrium and to turn to observe the temperature gradient changing until it took a limit value or began very small oscillations around a value. Then taking this value for ΔT , I returned to re-read the value of the temperature, and when it was almost the same that the one before; I took this temperature value as a right one. Tables V and VI show a sample of this

behavior in the results of the experiment.

The Result of the Experiment

The results of the experiment are shown in Tables I and II. In these tables the temperature is given in degrees Kelvin and the corresponding thermal conductivity is given in milliwatt per degree and per centimeter. The same result is shown in a graph where the thermal conductivity has been plotted as a function of the Kelvin temperature. This graph is drawn in a log-log scale. In addition, for a better understanding of the results the formula used to determine the thermal conductivity is shown. The values obtained during the experiment to be used in the formula are written in other two tables numbers III and IV. Tables V and VI are a sample of the variation of delta T going to a limit.

TABLE I
THERMAL CONDUCTIVITY OF KMnF_3 AT
LIQUID HELIUM TEMPERATURE

Point Number	T $^{\circ}\text{K}$	λ $\frac{\text{mw.}}{\text{cm.}^{\circ}\text{K}}$
1	5.19	112.0
2	5.67	137.0
3	6.21	170.0
4	7.09	198.5
5	7.48	219.0
6	8.33	266.0
7	9.15	284.0
8	11.50	299.0
9	12.46	299.0
10	12.82	292.0
11	14.07	295.0
12	15.30	273.0
13	17.50	253.0
14	18.56	232.0
15	22.25	186.0

TABLE II
THERMAL CONDUCTIVITY OF KMnF_3 NEAR THE NEEL TEMPERATURE

Point Number	T °K	λ
		$\frac{\text{mw.}}{\text{°K cm.}}$
16	46.35	81.0
17	50.40	73.0
18	55.10	65.0
19	55.40	64.0
20	61.00	59.0
21	74.25	52.5
22	79.05	50.8
23	80.50	50.6
24	81.10	50.8
25	81.95	50.9
26	83.25	50.2
27	86.40	50.4
28	86.86	50.2
29	88.25	50.0
30	88.70	50.0
31	89.90	50.8
32	97.50	51.6
33	101.50	52.6
34	107.70	54.0
35	113.20	54.0
36	120	54.20
37	126	54.30
38	135	55.00
39	149	56.40
40	168	58.00
41	188	62.00

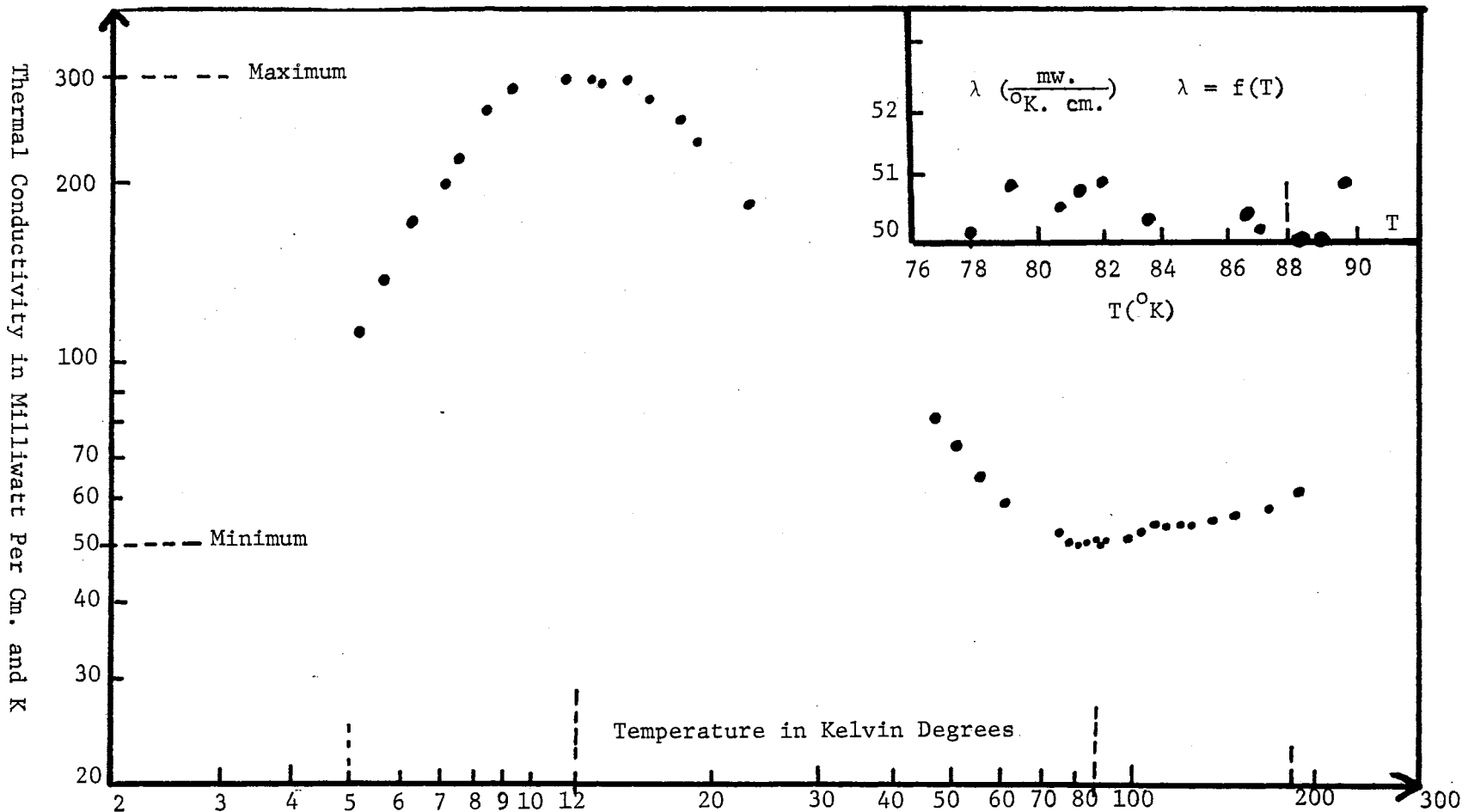


Figure 7. Thermal Conductivity of KMnF_3 Vs. Temperature From 5.15 K. to 188 K. Inset Shows the Thermal Conductivity Near T_n

TABLE III
 EXPERIMENTAL DATA TO CALCULATE THERMAL CONDUCTIVITY (λ)
 AT LIQUID HELIUM TEMPERATURE

Point Number	T °K	\dot{Q} mW	E_p μV	E_o μV	$\frac{\partial E}{\partial T}$ $\frac{\mu V}{\circ K}$	ΔT °K	λ $\frac{mw.}{\circ K \text{ cm.}}$
1	5.15	0.285	0.10	-0.34	13.43	0.0334	112.0
2	5.67	1.590	1.96	-0.16	13.82	0.1532	137.0
3	6.21	2.120	2.35	-0.01	14.25	0.1645	170.0
4	7.09	2.088	2.05	0.02	14.75	0.1380	198.5
5	7.48	2.670	2.32	-0.08	14.95	0.1600	219.0
6	8.33	3.700	2.66	-0.21	15.36	0.1820	266.0
7	9.15	2.088	1.12	-0.41	15.83	0.0964	284.0
8	11.50	0.795	0.70	0.13	16.34	0.0348	299.0
9	12.46	1.144	0.93	0.09	16.57	0.0508	299.0
10	12.82	1.144	0.99	0.12	16.63	0.0520	292.0
11	14.07	1.144	0.98	0.12	16.80	0.0555	295.0
12	15.30	1.146	0.04	0.11	16.90	0.0595	273.0
13	17.50	1.147	1.14	0.13	16.98	0.0595	253.0
14	18.56	1.147	1.30	0.20	16.99	0.0650	232.0
15	22.25	1.151	1.54	0.14	17.30	0.0810	186.0

TABLE IV
 EXPERIMENTAL DATA TO CALCULATE THERMAL CONDUCTIVITY (λ)
 NEAR THE NEEL TEMPERATURE

Point Number	T °K	\dot{Q} mW	E_p μV	E_o μV	$\frac{\partial E}{\partial T}$ $\frac{\mu V}{^\circ K}$	ΔT °K	λ $\frac{mw.}{^\circ K \text{ cm.}}$
16	46.35	0.5216	2.07	0.56	16.455	0.0858	81.0
17	50.40	0.0736	0.64	0.44	16.606	0.1330	73.0
18	55.10	0.5284	2.08	0.24	16.808	0.1080	65.0
19	55.40	0.5240	2.03	0.20	16.821	0.0108	64.0
20	61.00	0.5272	2.13	0.14	17.077	0.0117	59.0
21	66.65	0.8220	3.46	0.22	17.335	0.1860	58.0
22	74.25	0.8258	2.43	-0.19	17.665	0.0201	52.5
23	79.05	0.8345	3.91	0.03	17.870	0.0218	50.8
24	80.50	0.8355	4.06	1.20	17.940	0.0218	50.6
25	81.10	0.8360	4.02	0.11	17.961	0.0218	50.8
26	81.95	0.8400	4.00	0.02	18.040	0.0220	50.9
27	83.25	0.8350	4.00	0.05	18.050	0.0220	50.2
28	86.86	0.8410	3.88	-0.15	18.174	0.0224	50.2
29	88.25	0.8395	3.98	-0.02	18.260	0.0221	50.0
30	88.70	0.8385	3.98	-0.10	18.280	0.0224	50.0
31	89.90	0.8400	3.84	-0.17	18.328	0.0218	50.86
32	97.50	0.8450	3.75	0.30	18.630	0.0217	51.60
33	101.50	0.8465	3.49	-0.50	18.78	0.2122	52.60
34	107.70	0.8450	3.58	-0.35	19.02	0.2060	54.00
35	113.20	0.8535	3.30	-0.20	19.192	0.2060	54.0
36	120.00	0.8535	2.94	-1.10	19.415	0.2070	54.2
37	126.00	0.8560	3.18	-0.90	19.615	0.2080	54.3
38	135.00	0.8595	3.00	-1.10	19.861	0.2062	55.0
39	149.00	0.8645	2.45	-1.66	20.215	0.2031	56.4
40	168.00	0.8690	2.90	-1.27	20.670	0.2010	62.0

TABLE V
 VARIATION OF $\Delta T \frac{\partial E}{\partial T}$ GOING TO A LIMIT VALUE AT 88.25 K

t	$\Delta T \frac{\partial E}{\partial T}$	t	$\Delta T \frac{\partial E}{\partial T}$
Minutes	mw	Minutes	mw
0.0	3.90	58.0	3.99
3.0	3.90	59.0	3.99
4.0	3.90	59.0	3.99
7.0	3.90	61.0	3.99
10.0	3.90	66.0	3.99
12.0	3.90	69.0	3.99
13.0	3.94	71.0	3.99
18.0	3.94	72.0	4.01
21.0	3.97	79.0	4.01
25.0	3.97	90.0	4.01
31.0	3.99	91.0	4.03
35.0	3.99	92.0	4.03
36.0	4.01	92.0	4.02
39.0	4.01	94.0	4.03
40.0	4.01	100.0	3.93
42.0	4.01	104.0	4.01
43.0	4.01	108.0	4.01
55.0	3.97	112.0	4.01
57.0	3.96		

TABLE VI

VARIATION OF $\Delta T \frac{\partial E}{\partial T}$ GOING TO A LIMIT VALUE AT 88.25 K
WITH $P = 0$ IN THE GRADIENT HEATER

t	$\Delta T \frac{\partial E}{\partial T}$
Minutes	mw
0.0	0.54
4.0	0.23
6.0	0.10
11.0	0.00
23.0	-0.02
24.0	-0.02
26.0	-0.04
34.0	-0.04
35.0	-0.01
41.0	-0.02
42.0	-0.02
43.0	-0.02
49.0	-0.02
54.0	-0.02
62.0	-0.02

The formula used to calculate the thermal conductivity is

$$\lambda = \frac{\dot{Q}}{\Delta T} \cdot \frac{L}{A} \quad (32)$$

where P is power flowing through the crystal, L is the separation between the clamps connected with the thermocouple to measure ΔT , A is the cross section of the sample and ΔT is the temperature difference between the clamps. ΔT is determined by the following prescription

$$\Delta T = \frac{E_p - E_o}{\frac{\partial E}{\partial T}} \quad (33)$$

where E_p is the electromotive force generated in the thermocouple by the difference of temperature between the clamps when there is some power in the gradient heater, E_o is the emf when there is no power in the gradient heater and $\frac{\partial E}{\partial T}$ is the relation between temperature and electromotive force for this thermocouple.

In this experiment the ratio L/A was a constant equal to 13.50 cm^{-1} and the measurement concerned only with the power P, the temperature and the values to obtain ΔT .

Discussion of the Results

From the observation of the tables and the graph showing the results, it may be pointed out that five of the six points taken between $5.19 \text{ }^\circ\text{K}$ and $8.33 \text{ }^\circ\text{K}$ are on a straight line. This line shows a relation between the thermal conductivity and the Kelvin temperature, in which the thermal conductivity is almost proportional to T^2 rather than to T^3 . This line may be represented by

$$\lambda = 3.35 T^2 + 30.00 . \quad (34)$$

where the thermal conductivity is given in milliwatts per Kelvin degree and per centimeter and the temperature in Kelvin degrees.

The last equation for thermal conductivity gives a deviation less than 8% from the values obtained in the experiment for these five points between 5.19 and 8.33 °K.

The thermal conductivity shows a maximum at 11.50 and 12.46 °K. The value of the maximum is 299.00 milliwatt per Kelvin degree and per centimeter. Choosing the maximum at 12 °K, the Debye temperature may be estimated in 264 Kelvin degrees. This value is the result of multiplying twelve times twenty three.

The points taken between 17.50 and 61.00 °K are also on straight line. It is necessary to point out that no points were taken between 22.50 and 46.35 °K. The equation

$$\lambda = \frac{4600}{T} - 19 \quad (35)$$

represents the relation between the thermal conductivity and the Kelvin temperature from 17.50 to 61.00 °K. The thermal conductivity is given in milliwatt per Kelvin degree and per centimeter and the temperature is given in Kelvin degrees.

1. From 5.19 K to 8.33 K, the thermal conductivity is proportional to T^α , with $\alpha \sim 2$. This result is more in accord with the prediction of Gurzhy (22) for thermal conductivity in ferroelectrics at very low temperature, where, $\lambda \sim T^2$, than the prediction of Casimir (7) for dielectrics or the Gurevich and Roman (24) prediction for antiferromagnets. They predict a T^3 law in this temperature region. It may be necessary to

go to lower temperature than 5.15 K to observe this T^3 behavior. The magnitude of the conductivity is much smaller than would be expected if the heat conduction were due entirely to phonons with mean free path determined by the sample boundaries. This indicates a strong phonon scattering mechanism in this regime. Two possibilities are spontaneous "twinning" due to the structural phases transitions and magnon-phonon interactions. These can not be distinguished in the present experiment. Wolf (31) is experimenting with a diamagnetic perovskite, $KZnF_3$, which has the same cubic structure at room temperature and almost the same constant lattice that $KMnF_3$. He has found higher values of the thermal conductivity in this temperature region and a higher maximum than the one found in this experiment.

2. The behavior $\lambda \sim f(1/T)$ is in accord with the prediction of Gurevich and Roman (24) for antiferromagnets with diamagnetic impurities.

3. The thermal conductivity has a broad minimum in the vicinity of the Neel temperature 88 K. A careful search was made for evidence of magnetic critical scattering. No structure was observed indicating that this minimum is probably not magnetic in origin. A source for the minimum may be the resonance scattering of the soft phonon modes. This point should be investigated.

Summary

The thermal conductivity of a small sample of potassium manganese fluoride, $KMnF_3$, has been measured in the temperature range from 5.19 K to 188 K. A maximum was found at 12 K. The value of this maximum was $300 \frac{mW}{K \cdot cm}$. At lower temperatures than 8.33 K, the thermal conductivity, λ , behaved like $\lambda \sim f(T^2)$. The low values of the thermal conduc-

tivity are attributed to a strong phonon scattering mechanism rather than to the effect of the sample boundaries.

From 17.50 K. to 61 K., the thermal conductivity behaved proportional to $1/T$, which corresponds to the scattering of phonons and magnons by impurities.

From 80 K. to 90 K., was found an almost temperature independent behavior of the thermal conductivity. A minimum of $50 \frac{\text{mW.}}{\text{K. cm.}}$ was found at the Neel temperature 88 K. This minimum is probably not magnetic in origin.

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