

MECHANICAL PROPERTIES OF KMgF_3 , KZnF_3 , AND KMnF_3

By

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PREFACE

This study is concerned with the investigation of the slip system of the fluoride perovskites, and of the effect of radiation damage on the strength of the perovskite compound KMgF_3 . This study also is concerned with the temperature dependence of the yield strength for the compounds KMgF_3 , KZnF_3 and KMnF_3 .

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CHAPTER I

INTRODUCTION

Many crystalline materials can be deformed both elastically and plastically. One of the aims of theoretical physics is to explain the existence and nature of these two kinds of deformation in terms of crystal structures and of the forces between atoms. The mechanical stability of solids is due to the existence of balanced forces between their constituent atoms. Attractive forces cause the atoms to adhere to one another while short-range repulsive forces prevent the atoms from approaching too closely. Normally the atoms occupy positions where these forces are balanced, but when an external force is applied this balance is upset. To restore equilibrium the atoms move slightly to nearby positions where there is a balance between the attractive, repulsive and external forces. The elastic response of a crystal to a given applied force can thus be calculated if the force law between its atoms is known.

Frenkel has estimated the shear strength of a perfect crystal by calculating the shear stress in terms of the shear modulus needed to push one plane of atoms past a second (1). The critical shear stress, σ_c , at which the lattice become unstable was found to be

$$\sigma_c = \frac{Ga}{2\pi d}$$

where G is the shear modulus, a is the interatomic spacing in the direc-

tion of the applied stress and d is the interplanar spacing perpendicular to the stress. Since a and d are of the same order the ideal critical shear stress should be of the order of $\frac{G}{2\pi}$. Experimental values of critical shear stress are usually three orders of magnitude smaller than this value.

The observed low values of the shear strength cannot be explained without the presence of imperfections that can act as sources of mechanical weakness in real crystals. It is now known that special crystal imperfections called dislocations exist in almost all crystals, and their movement is responsible for slip at very low applied stresses.

Dislocation theory has contributed to the hardening subject enormously, especially the theory of precipitation hardening by Mott and Nabarro (2), the theory of hardening due to segregation of solute atoms around a dislocation by elastic interaction proposed by Cottrell (3), the model of hardening due to segregation of solute atoms at a stacking fault by chemical interaction proposed by Suzuki (4), and short-range order hardening proposed by Fisher (5). Also tetragonal defects such as those introduced by ionizing radiation or divalent impurity vacancy pairs cause a significant strengthening of alkali halide single crystals (6). Fleischer (7) has shown theoretically that the increase in flow stress due to the strain field of tetragonal defect is proportional to the square root of the defect concentration. One method of creating tetragonal lattice distortion is by irradiation with high energy electrons. Irradiation causes this type of defect by converting a negative ion into a neutral atom, moving the atom to an interstitial position, and leaving an electron in the vacancy that now exists in the original position. This forms a Farbcentren or F center. It has been shown by

Sibley and Sonder (8) and Nadeau (9,10) that F center creation produces significant hardening of alkali halides.

While much work has been done on alkali halides very little work has been done on the mechanical strength of fluoride perovskite crystals. We report here an investigation of the slip system of the fluoride perovskites, of the effect of radiation damage on the strength of the perovskite compound KMgF_3 . We also report the temperature dependence of the yields strength for the compounds KZnF_3 , KMnF_3 and KMgF_3 .

CHAPTER II

EXPERIMENTAL PROCEDURE

Crystal Growth

The crystal growth laboratory uses two different techniques, these are the Czochralski-Kyropoulos method and the Bridgman Method. The two methods are described below:

The Czochralski-Kyropoulos Method

In this method a seed crystal is dipped into the melt and slowly pulled out. Figure 1 shows the apparatus used for pulling crystals. Sibley (6), and Hartmann (11) and Laudise (12) have given a detailed description of the system and a summary of growth theory.

For KMgF_3 a rectangular $[100]$ oriented 2.5 mm x 2.5 mm x 30 mm seed crystal was cut from a Bridgman grown single crystal. The starting materials were random crystal cuttings of Harshaw MgF_2 and Optran zone refined KF crystal pieces. The stoichiometric amounts of the starting materials were placed in the vitreous carbon crucible which was placed in the furnace. The system was evacuated to a pressure of 10^{-6} Torr. The materials were heated to 400°C under vacuum, and they were held over night at that temperature. Then argon was introduced to raise the pressure to 120 Torr. The temperature was increased until the components were molten. The KF (m.p. 850°C) (13) melts first and dissolves the solid MgF_2 (m.p. 1270°C) (13). The furnace is held at a temperature

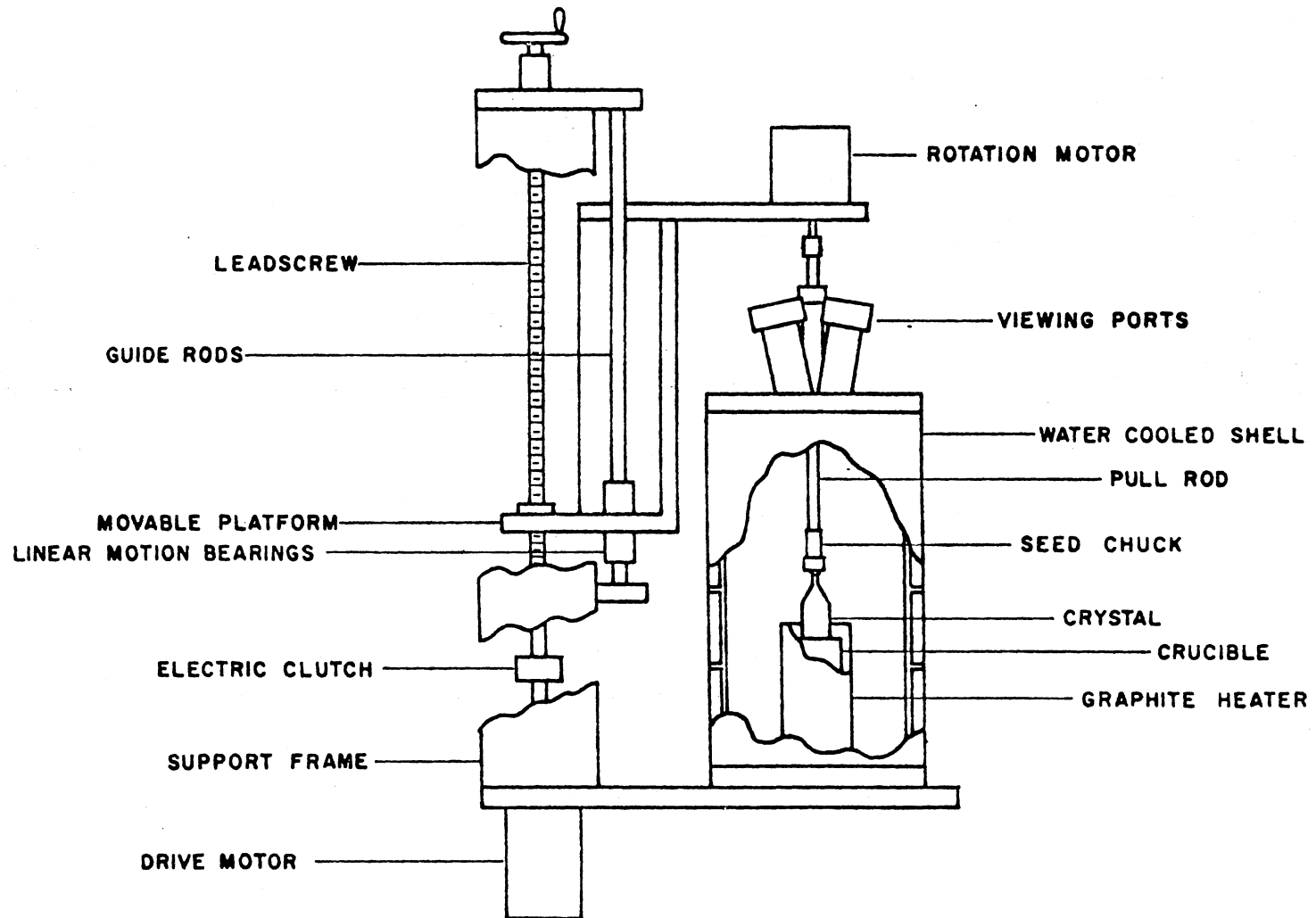


Figure 1. The Oklahoma State University Puller Apparatus

just above the melting point of KMgF_3 (1070°C) (13), and the pull rod is rotated at 30 r.p.m. After the initial polycrystalline material has melted back the pull rod is lifted at 1 to 2 mm/hr, and the furnace temperature is slowly lowered, which causes the diameter of the crystal to grow. When the crystal has grown to desired size, it is pulled free of the melt; the rotation is stopped; and the furnace is programmed down to room temperature over a period of about 20 hours. The diameter of the crystal depends on the speed with which the seed is withdrawn from the melt. One disadvantage of this method is that constant supervision is necessary during the growing period.

The Bridgman Method

Growing crystals by this method requires more time, but the system does not need constant supervision. Figure 2 shows the apparatus for this method, Butler (14), Wolf (15) and Laudise (12) give a detailed discussion of the apparatus and a summary of the growth theory.

For growing KZnF_3 crystals (m.p. 380°C) (13) a stoichiometric mixture of Optran zone-refined crystal pieces of potassium fluoride (m.p. 850°C) (13) and Optran zinc fluoride (m.p. 920°C) (13) powder was used. The materials were mixed and placed into a graphite crucible containing approximately 1 mm^3 of anhydrous ammonium bifluoride. The ammonium bifluoride decomposed at about 200°C , releasing hydrogen fluoride gas which flushed some of the adsorbed water out of the crystal. The graphite crucible was placed into the ceramic tube. Then the system was evacuated to a good diffusion pump vacuum. Then the system was heated under vacuum to a set point of 300°C and kept at this temperature overnight. In the morning argon was introduced to raise the pressure to

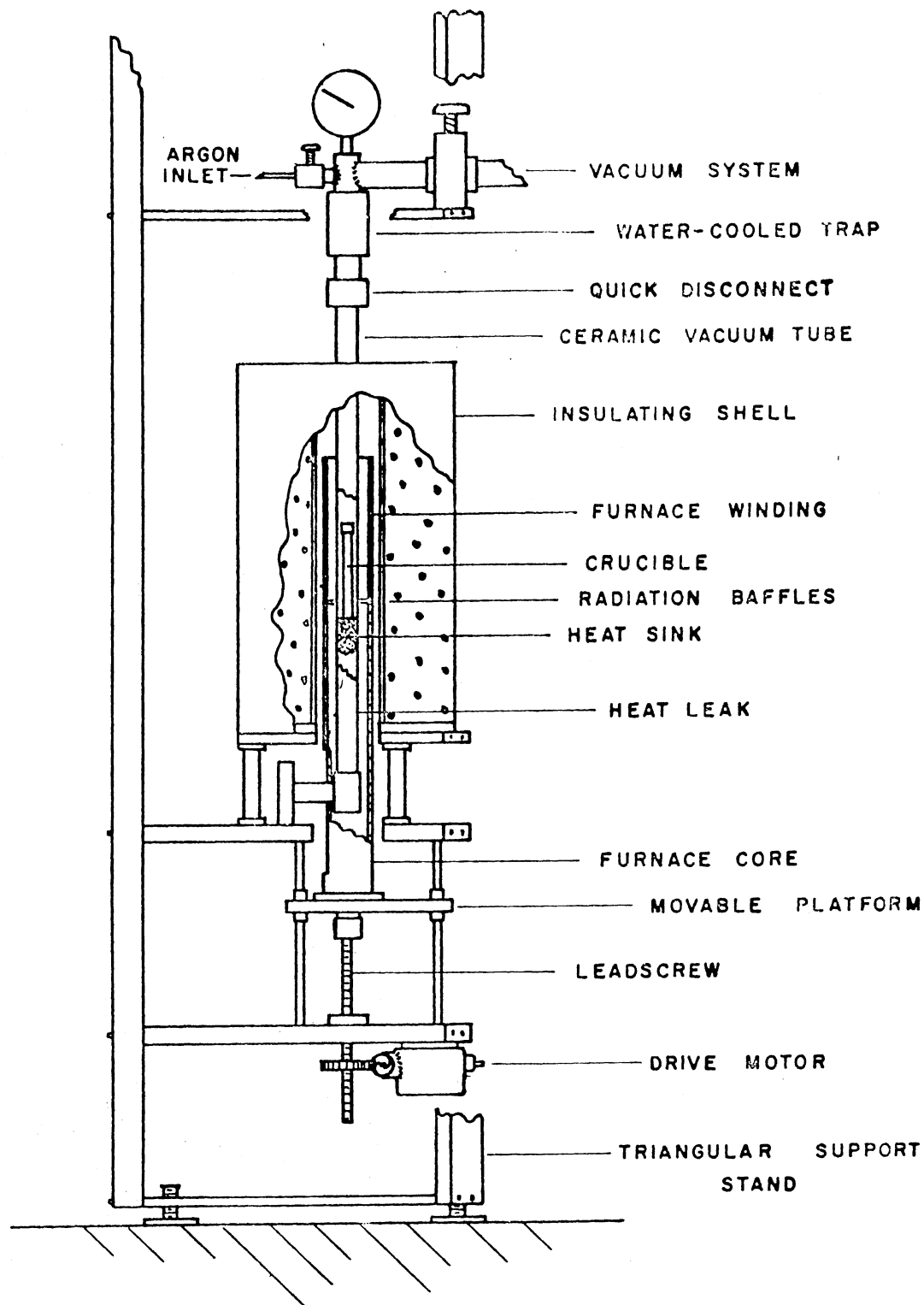


Figure 2. The Oklahoma State University Bridgman Apparatus

1500 Torr and the furnace was programmed to raise temperature up to 1100°C over a period of about 15 hours. After reaching 1100°C the system was held at that temperature for approximately five hours. For the next step the furnace cone was lifted at 1.5 cm/hr; this step solidified the melt and probably pushed the impurities to the top. After the furnace reached the top of its 13 cm pass it was lowered to the original position at the same rate. After eight to nine hours in the lower position, which remelt the material, the system then was ready to start the growth pass. Therefore, the furnace was raised at a rate of 0.15 cm/hr. After the furnace had traveled its full length, which takes approximately 90 hours, the furnace was programmed down to room temperature over a period of about 20 hours. The approximate size of crystal is 2 to 3 cm in length and 1 cm in diameter, with 15-20 gm weight.

The same method was used for growing KMnF_3 crystals (m.p. 1013°C) (16). Starting materials were Optran zone-refined crystal pieces of potassium fluoride (m.p. 850°C) (13), and manganese fluoride (m.p. 856°C) (17).

Flow Stress Measurements

There are four common different test techniques for measuring the mechanical strength of crystals (6). They are the uniaxial compression test, the four-point bend test, the dislocation rosette size test and the Vickers microhardness test. Each of these techniques is an independent method for determining the mechanical strength of a sample. Of these tests, only the Vickers microhardness test does not give the flow stress (yield point).

The flow stresses of KMgF_3 , KZnF_3 and KMnF_3 crystals were measured

as a function of temperature under uniaxial compression along the $\langle 100 \rangle$ direction on an Instron testing machine. The Instron records the applied forces on a sample as it is being compressed at a constant strain rate. The deforming apparatus is shown schematically in Figure 3. For flow stress tests above room temperature the stainless steel crosshead platen and loose anvil posts were heated with the sheathed resistance wire that was tightly wrapped around the posts as shown in Figure 3. The temperatures of each post were controlled by a Gulton West Model 20 temperature controller which used a chromel-alumel thermocouple. The actual test temperature was measured with separate chromel-alumel thermocouples which were referenced to the ice point. A Weston Schlumberger Model 4444 digital multi-meter was used to read the thermocouple E.M.F. After the temperature at crosshead and base reached the test temperature, they were held about 40 min at that temperature so that all parts of system would be in thermal equilibrium. Then the sample was set on the base, and the crosshead and base were covered with the cylindrical stainless steel shield. Each sample was held at the test temperature for 15 to 20 min, and then the sample was tested.

The flow stress samples were cut from a single crystal. Each sample measured approximately 1.5 mm x 2 mm x 6 mm. Since the sample length was at least three times the width, possible end effects were small and could be neglected (18). Samples were compressed along a $\langle 100 \rangle$ direction at a crosshead speed of 0.05 cm/min. This corresponds to a strain rate of approximately 10^{-3} sec^{-1} . Some typical stress-strain curves are given in Figure 4. The engineering flow stress, τ_e , is taken to be the value at the intersection of the tangents to the elastic and the first plastic portions of the curve as shown in Figure

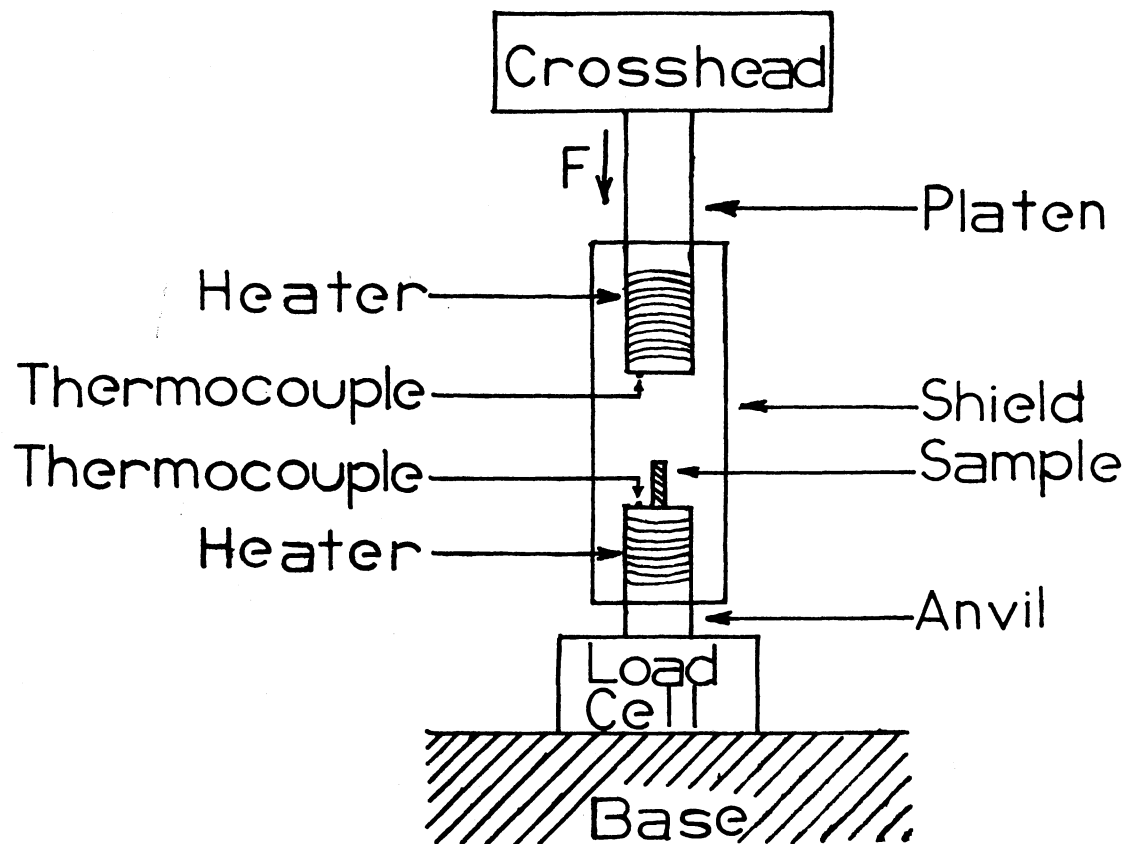


Figure 3. Schematic Representation of a Deforming Apparatus

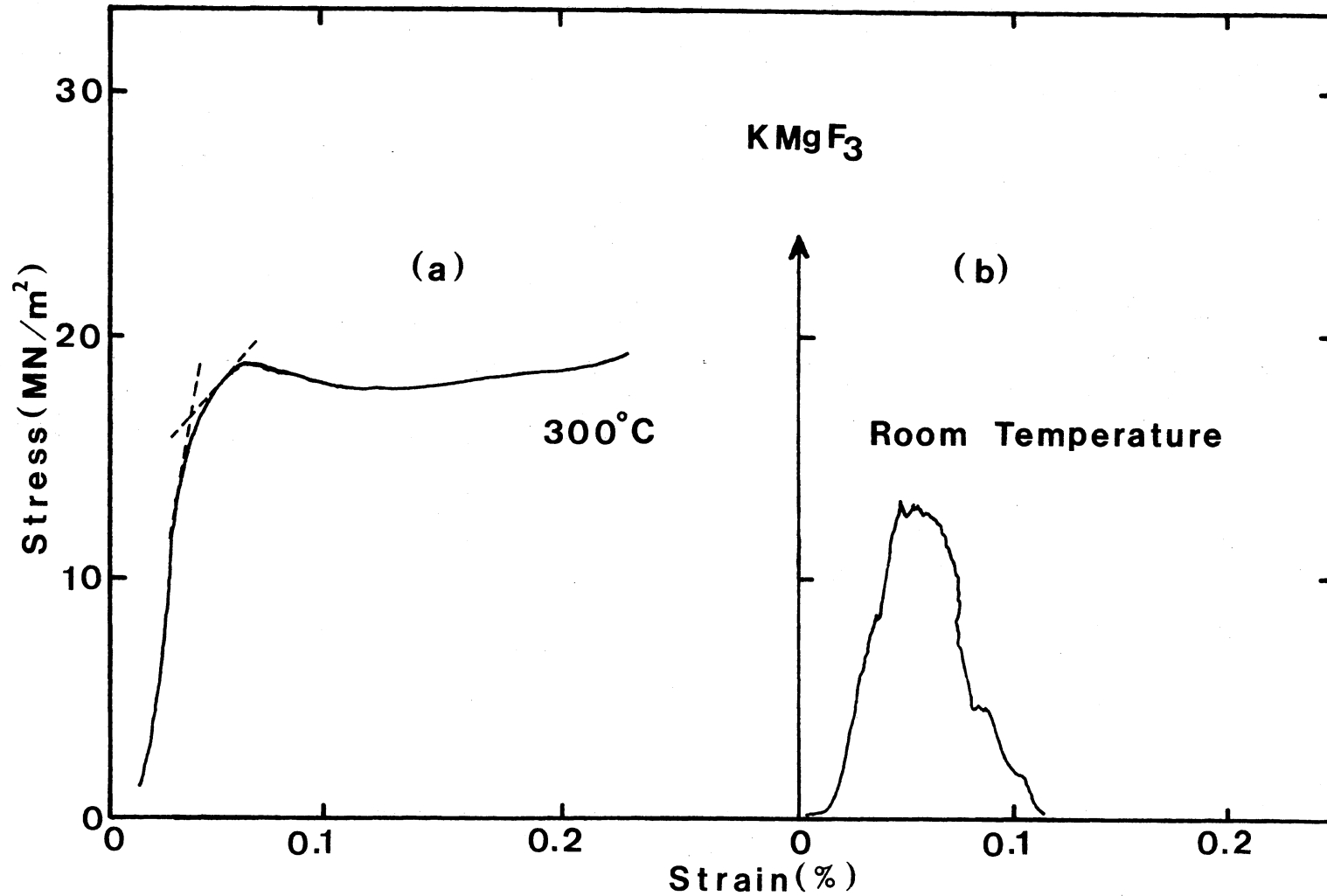


Figure 4. (a) Stress-Strain Curve for a Typical KMgF_3 Sample at 300°C. (b) A Typical Stress-Strain Curve for a KMgF_3 Sample at Room Temperature. The curve shows that the sample fractures rather than yields

4. The individual flow stresses of four or five samples were averaged to obtain the values recorded for each crystal at the test temperature. In order to compare the resolved flow stress, τ , the component of the flow stress parallel to the primary slip direction was calculated*. In KMgF_3 , KZnF_3 and KMnF_3 the primary slip is in the $\langle 110 \rangle$ direction; therefore, the resolved flow stress will equal one half the engineering flow stress, ($\tau_r = 1/2 \tau_e$).

* See results and discussion chapter.

CHAPTER III

RESULTS AND DISCUSSION

Slip System

To obtain the resolved flow stress, τ_r , it was important to find out the primary slip direction. The engineering flow stress, τ_e , is taken as the stress value at the point of intersection of tangents drawn to the elastic and the first plastic regions of the stress-strain curve as shown in Figure 4. The engineering flow stress, τ_e , is calculated by taking the applied force, F , and dividing by the cross sectional area A of the sample. The resolved flow stress, τ_r , which equals the shear stress, is calculated by resolving the applied force along the slip plane by the area of the slip plane as shown in Figure 5. The resolved flow stress can be written as:

$$\tau_r = \frac{F \sin \theta \cos \theta}{A}$$

$$\tau_r = \tau_e \sin \theta \cos \theta$$

where F is the applied force, A is the cross sectional area of the sample and θ is the angle the slip plane makes with the central axis along which F is being applied.

For KMgF_3 , a sample was compressed by a stress slightly less than the yield stress which kept the sample in the elastic region. The sample

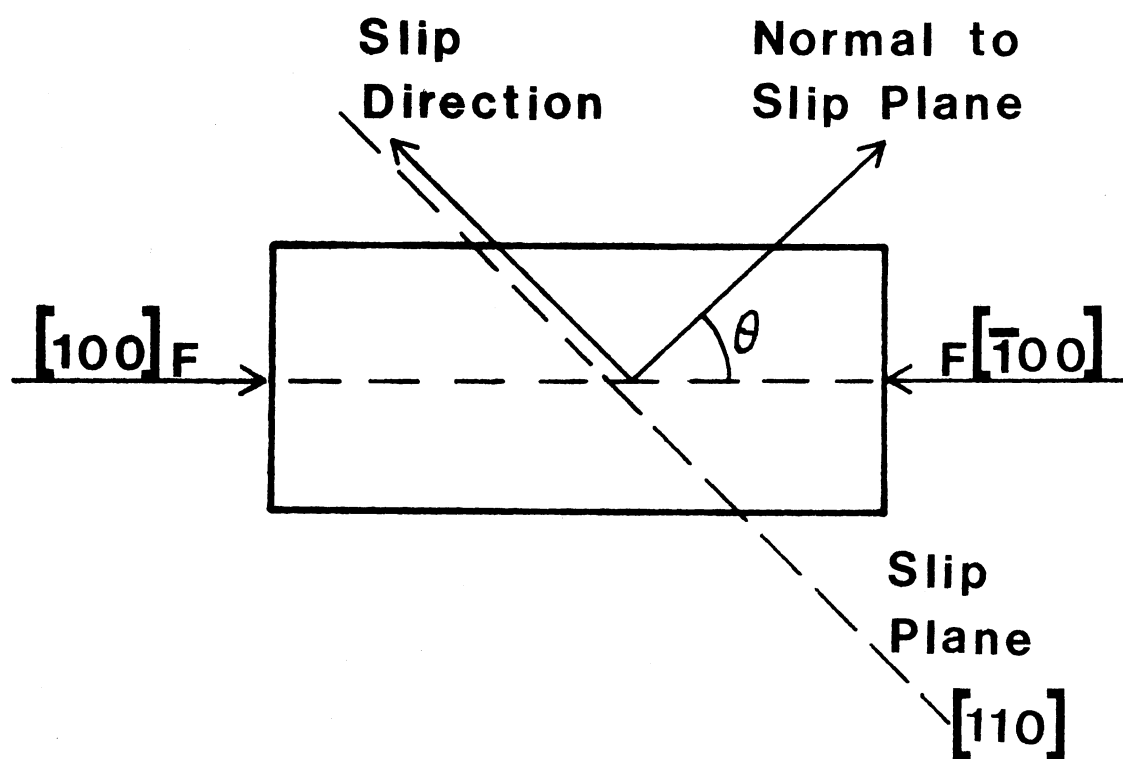


Figure 5. Schematic Representation of the Slip Planes of KMgF_3

now was weakly doubly refracting with the effective optic axis in the direction of the stress. By using sufficiently intense light source, very small amounts of double refraction was detected by the restoration of light when the sample was placed between crossed polarizers. Figure 6 is the photograph of the sample which shows the primary slip direction is in $\langle 110 \rangle$ direction which means $\theta = 45^\circ$, hence $\tau_r = \frac{1}{2}\tau_e$.

Radiation Effects

The radiation damage was tested on a plate sample of KMgF_3 to see effect of irradiation on KMgF_3 . It is well known that tetragonal defects such as divalent impurity-ion vacancy pairs and radiation-induced interstitials increase the mechanical flow stress of alkali halide crystals (6). Fleischer (7) has shown that the interaction between dislocations moving along the slip plane and isolated defects increase the resolved flow stress, τ_r . The increase is given by:

$$\Delta\tau_r = \left(\frac{G}{n}\right)C^{\frac{1}{2}},$$

where G is the shear modulus, C is the mole fraction defect concentration and n is a number which depicts the hardening effectiveness of the particular type of defect (19). Early radiation hardening studies of a number of alkali halides (9,20) show a $C^{\frac{1}{2}}$ dependence of the flow stress on F center concentration. However, the F centers alone are not the cause of the change in flow stress (9,21). The strengthening of the irradiated alkali halides is due to the halogen interstitials produced in the radiation damage process.

The resolved flow stress for all composition is directly proportional to the square root of the F center concentration. However, in

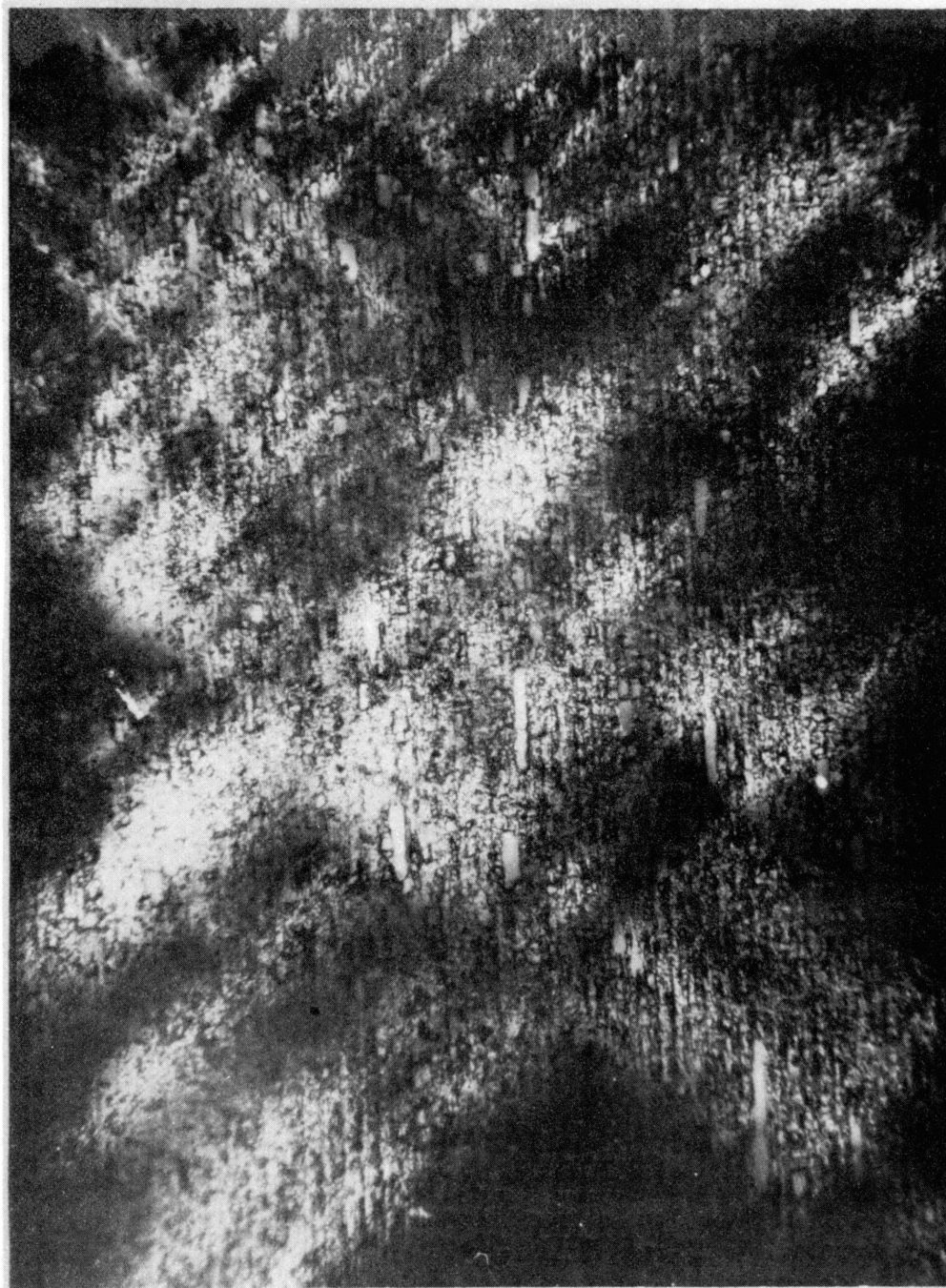


Figure 6. The Figure Shows a Photograph Taken Through Crossed Polaroids of the KMgF_3 Crystal That was Taken Through the Yield Point. The (100) axis is horizontal. The crystal shows the [110] slip planes

some of the materials a slight softening was observed for low radiation doses (9). The softening occurs during early stage coloration where few stable interstitials are thought to be produced. Recent electron microscope studies of irradiated alkali halide foils by Hobbs, Hughes and Pooley (22) indicate that interstitials produced during room-temperature irradiation either externally with 400-keV electrons or in the 100-keV microscope been cluster as prismatic dislocation loops. Hence, the hardening is not due to interactions of dislocations and individual interstitials, but rather to the interactions of dislocations and interstitial clusters. Their results indicate that the interstitial cluster in KCl are in the form of long needlelike dipole loops which lengthen with increased radiation dosage, the interstitials cluster in KI are rounded and grow radially with increase dosage, and the clusters in KBr are elongated ellipsoids.

For KMgF_3 , the plate sample was irradiated with 1.5 MeV electrons for 5 minutes with current 5 μA . The F center concentration, $N_F (\text{cm}^{-3})$, can be found from Smakula's relation (20,23) (given here for a Gaussian shaped peak),

$$N_F f = 0.87 \times 10^{17} \frac{n_o}{(n_o^2 + 2)^2} \alpha_{\text{max}} W_{\frac{1}{2}}$$

where f is the oscillator strength, n_o is the index of refraction, α_{max} is the absorption coefficient at the peak of the F band, and $W_{\frac{1}{2}}$ (eV) is the width at half maximum of the F absorption. To convert F center concentrations in cm^{-3} to mole fraction, divide by $1.59 \times 10^{22} \text{cm}^{-3}$. The measured F band had peak absorption coefficient of 130cm^{-1} and a half-width of 0.75 eV. This gives an F center concentration of 1.1×10^{18}

cm^{-3} or 70 ppm. The flow stress measurement of this irradiated sample at 573 K gives no measurable increase in flow stress. The probable reason that no increase in flow stress was observed is that, at 573 K, the interstitials are sufficiently mobile that they only interact weakly with the dislocations. In KCl at room temperature an equivalent N_F gives a large increase in the flow stress (8).

Temperature Dependence

In 1928 Taylor (24) pointed out that many sources of stress concentration should weaken a crystal stress less than a few of them, because their stress fields would overlap and partly cancel one another. In 1934 he (25) related this to the idea of dislocations and so produced the first detailed theory of work hardening. The basic idea in this was that the yield strength depends on the internal stresses opposing the movement of dislocations, these stresses being created with dislocations during plastic flow. Taylor supposed that most dislocations do not pass completely through a crystal, but, through elastic interactions with other dislocations and through obstructions provided by mosaic boundaries become pinned inside it. These dislocations cause the internal stresses which raise the yield strength (26). Considering the heat effect on dislocations, they will activate by factor $e^{-E_a/KT}$, where E_a is vibrational energy which is dependent on the melting point. The flow stress of KMgF_3 (m.p. 1070°C) (13), KZnF_3 (m.p. 880°C) (13) and KMnF_3 (m.p. 1013°C) (13) was measured as a function of temperature. The Figure 7 shows agreement between experiment and theory. Also Figure 7 shows that as temperature was raised, approximately after 350°C , the flow stress was not any more dependent on temperature and curve was

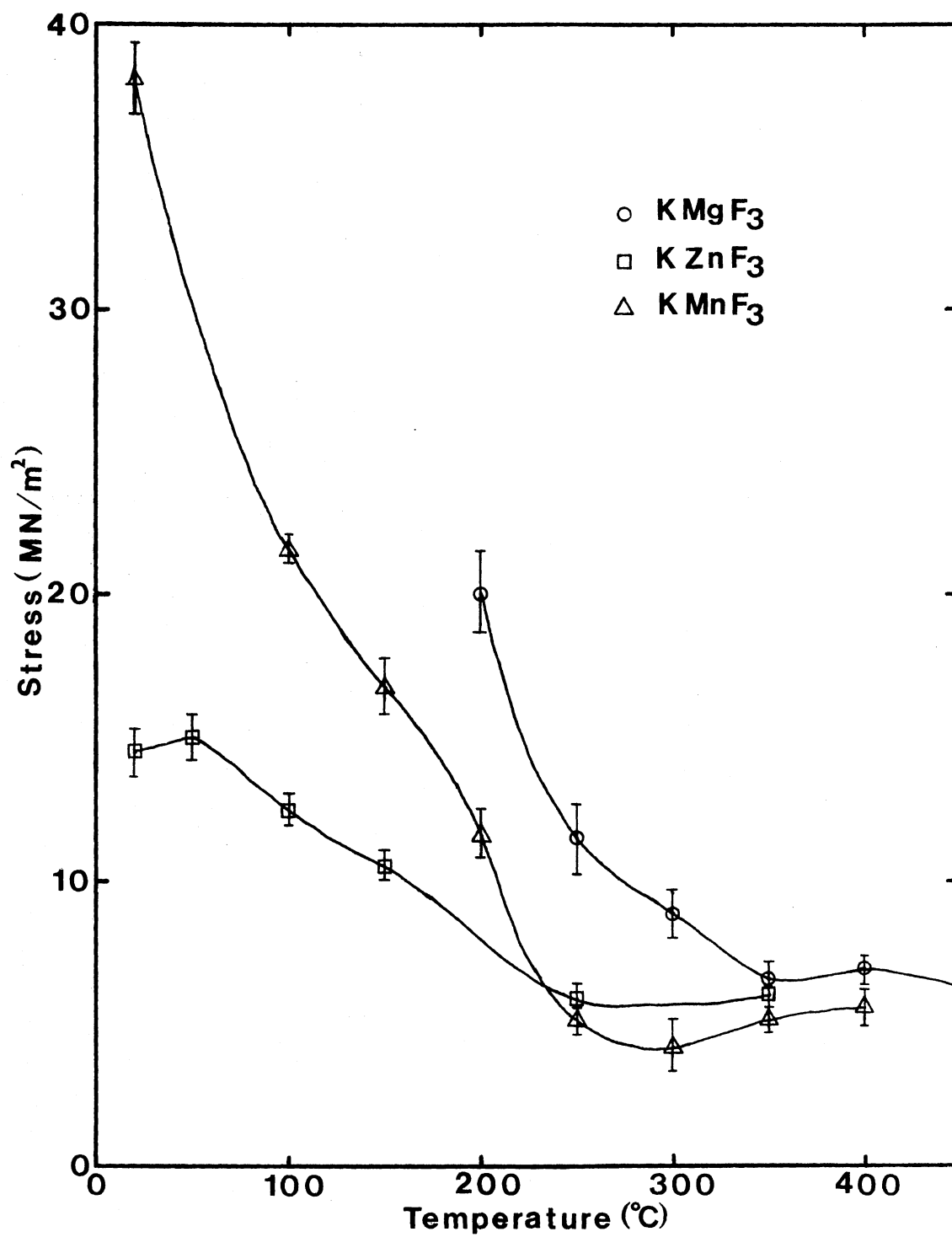


Figure 7. The Resolved Flow Stress Versus Temperature Curves for KZnF_3 , KMnF_3 and KMgF_3 Crystals are Shown

almost a straight line.

One probable reason is the precipitation of an excess component (e.g., MgF_2). At room temperature the excess may not be soluble in the lattice and precipitates to form large clusters which block the dislocations. As the temperature increases, the precipitates dissolve and the flow stress decreases until all are in solution. Then other mechanisms take over.

CHAPTER IV

SUMMARY

The slip system of the fluoride perovskites KZnF_3 , KMnF_3 and KMgF_3 was found to be in the $[110]$ plane. The flow stress of KMgF_3 irradiated at room temperature was measured at 300°C . The results showed no measurable increase in flow stress. The yield strength of KZnF_3 , KMnF_3 and KMgF_3 decreased sharply with increasing temperature up to approximately 350°C . Above 350°C the yield strength of these materials were found to be essentially independent of temperature.

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