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LOW TEMPERATURE ANNEALING OF THE ULTRASONIC ATTENUATION IN PRESTRAINED LiF AFTER Co^{60} GAMMA IRRADIATION AT LIQUID NITROGEN TEMPERATURE

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ABSTRACT

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The effect of γ irradiation at liquid nitrogen temperature on the low temperature internal friction of compressed LiF crystals was studied by the ultrasonic pulse method at a frequency of 10 MC/S. The internal friction is substantailly increased in compressed LiF crystals after a 5.8×10^6 r dosage of γ rays at 77°K. It was noted that this enhanced internal friction irreversibly decreases during uniform heating between 83°K to 110°K. The latter result is compared with the available data concerning annealing of electron spin resonance, optical absorption, and mechanical properties in the same temperature region. From this comparison, it is concluded that a small fraction of the Frenkel defects introduced by γ irradiation diffuse to and pin dislocations in the temperature region between 83°K and 110°K. The active pinning points are most likely H centers.

A new method of analyzing internal friction data to obtain the activation energy and jump frequency of the mobile pinning point defects is described. This was accomplished by measuring the internal friction while the specimen warmed up at a low linear rate because of the large heat capacity and low thermal conductivity of LiF. According to this analysis, the activation energy of migra-

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tion of the H center in LiF is determined to be 0.103 ± 0.004 ev.

1. INTRODUCTION

A rather clear determination of the atomistic structure of various color centers produced in the alkali halides by irradiation at low temperatures has been obtained through electron spin resonance(1),(6) and optical sbsorption(7),12) studies. the production mechanism of the F center in the alkali halides by X or γ irradiation is not yet clear, though recent studies(3),(11),(13),(14),(15),(20) have contributed to a better understanding of this problem. The annealing behavior and the conversion process of the color centers, at present, are little understood and have not received a great deal of attention.

Studies concerning the interaction between color centers and dislocations in alkali halides is an essential step towards gaining insight into this type of problem. Internal friction studies are particularly suited to this type of investigation, because the internal friction is very sensitive to the degree of pinning of the dislocation by point defects.

There are only a few investigations cited in the literature which deal with the internal friction of the alkali halides after X or γ irradiation (16),(21). Investigations carried out at low temperatures are not complete. Low temperature investigations are required before a clear understanding concerning the formation mechanism of color centers and the interaction of the latter with dislocations can be obtained in ionic crystals.

Rabin and Klick(11) suggest that vacancies are formed in the bulk of the crystal during low temperature irradiation rather than at dislocations by the ejection of multiply ionized halogen atoms from their normal lattice sites by electrostatic forces. This explanation appears to exclude the model proposed by Seitz(23) for the formation of the F center in alkali halides by irradiation. Bauer and Gordon(20) suggested the Seitz mechanism cannot operate

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at very low temperatures, but that it should hold for higher temperature irradiation. At these low temperatures they found that the dislocation can be pinned or unpinned by optical irradiation after X-ray irradiation.

They also noted that the point defects produced by X or γ irradiation at low temperatures exhibit various annealing stages during warm-up. The details of these processes are different among the various alkali halides crystals. LiF exhibits different behavior in many respects when compared to other alkali halides. For example, Bauer and Gordon(20) could not find the optical pinning and unpinning of the dislocation in LiF, yet they did in NaCl crystals.

The present investigation primarily deals with the annealing behavior of point defects formed during low temperature γ irradiation of LiF between 77°k to room temperature. The annealing behavior is followed by changes in the ultrasonic attenuation of the irradiated crystal.

2. EXPERIMENTAL PROCEDURE

LiF single crystals were obtained from the Harshaw Chemical Company, February 1962, in the form of a cleaved cube, 15 mm x 15 mm x 15 mm.

One of these crystals was compressed 2.4% by means of a machine tool vise. A pair of opposite $\{100\}$ surfaces were polished optically flat and parallel to an accuracy of 10 seconds of arc.

The distribution of slip was studied under polarized sodium light. Slip bands were barely discernible in the as-cleaved crystals. Pronounced double slip was observed in the compressed specimen. Quartz transducers were attached to the polished $\{100\}$ surfaces. The active slip planes were the (101) and $(10\bar{1})$, when the polished surfaces are designated (001).

The two X-cut quartz transducers* employed had a 10.02 MC/S resonant frequency. They each had the shape of a circular plate, 10 mm in diameter. The

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* Purchased from the Kinsekisha Laboratory, Tokyo, Japan, according to the author's specifications.

flat surfaces of the transducers were gold coated to a thickness of less than one micron. A small portion of edge of the transducer was gold plated. This portion was to act as the electrode connector to the surface to be bonded to the LiF crystal. The gold film on the unbounded surface was removed in a small semicircular arc around the portion of the edge that was gold plated thus breaking direct contact between the gold film on each surface. Silver leads were soldered to the unbounded surface and 1000 volts could be developed across the two faces of the transducer. The transducers were tightly bonded to the polished surfaces of the specimen with Dow Corning Silicone Grease 33 Heavy. This bonding agent was checked and found to exhibit no thermal hysteresis during heating and cooling between 77°K to 300°K. Reproducibility of the data is reliable as far as the bonding agent is concerned. The bonding operation was carried out in such a way that no bubbles could be detected in the bonding layer and the thickness of this layer was less than one micron. One of the transducers was used for sending ultrasonic pulses into specimen, the other for receiving the pulse echos. The transducers were encased in lead plates to protect them from Co^{60} irradiation.

Two small holes about 0.5 mm in dia. and 1.55 mm deep were cut out of the specimen to act as thermocouple wells. Two copper-constantan thermocouples were inserted into these holes and held in place with adhesive. These holes were found to have no influence upon the propagation of the sound pulses in the specimen or the internal friction of the specimen.

The composite system was enclosed in an aluminum container to make the system air and light free. As far as the specimen was concerned the irradiation and internal friction measurements were carried out in the dark (see Fig.1).

The container was mounted on an apparatus support and the tuning of the transducer was carefully checked. The entire system was placed in a glass tube container and evacuated to about 10^{-3} mm Hg pressure. This allowed the temperature of the specimen to be closely controlled. The aluminum container and its contents were removed from the apparatus support and immersed in liquid nitrogen for the Co^{60} irradiation treatment. The container and contents were then remounted without change in temperature.

Temperature changes were carried out by controlling the height of the liquid nitrogen between the glass-tube container and the surrounding glass Dewar. The rate at which the specimen warmed up was determined to be 0.2 ± 0.1 deg min^{-1}. This produced a fairly uniform temperature distribution within the specimen. With the slow warm-up rate it is not expected the data would exhibit any hysteresis from an inhomogeneous temperature distribution throughout the specimen. The latter might be expected if heating and cooling were carried out too fast.

The high voltage pulses were generated by the discharge of a high voltage condenser upon grounding through a pulse-triggered thyratron at a regular interval of 20 milliseconds. These pulses were fed to a tank circuit where they were converted to oscillatory pulses having a frequency and a width determined by the resonant frequency and Q of the circuit which contains the tank circuit, a short low-capacitance-coaxial cable, and the transducer electrode. As the length of the low-capacitance-coaxial cable connecting the pulse generator and the transducer was 1.0 meter and the frequency about 10 MC/S, it was not necessary to take into account the effect of standing waves in the coaxial cable. The pulse width and the peak-to-peak voltage of the pulse was about 3 μ sec and 600 volts, respectively.

Since the transmitting and receiving transducers were separate, the ultrasonic echos received were hardly disturbed by the transmitting circuit. The observed ultrasonic echoes were detected with a Tektronix type 545 A oscilloscope with a 53/54 L plug-in preamplifier. The ultrasonic echo patters were photographed on the Braun tube. The slope of plots of log (echo height) versus echo number is by definition a measure of the logarithmic decrement. These values were converted to attenuation units in the usual manner.

A 1 x 10^4 curie Co^{60} gamma source available at the Japan Atomic Energy Research Institute was employed for the irradiation experiments. The sample was exposed to a dose rate of 3.22 x 10^5 r/hour to a total dose of 5.8 x 10^6 r.

3. EXPERIMENTAL RESULTS

The ultrasonic attenuation of the compressed sample was measured at 10.02 MC/S ten days after it had been mounted in the experimental apparatus. The measurements were made during slow warm up from liquid nitrogen to room temperature. The attenuation after compression exhibited two relaxation peaks (25),(26), one at about 150°K and the other at 180°K at 10 MC/S (see Fig. 2). These peaks were not observable before the crystal was compressed. The 150°K peak exhibited a height of 11.6 x 10^{-2} neper cm^{-1} and the height of the 180°K peak was 12.7 x 10^{-2} neper cm^{-1}. The attenuation at 77°K was 7.7 x 10^{-2} neper cm^{-1}.

The specimen was then cooled to liquid N_2 temperature and irradiated. After irradiation the attenuation at 77°K was found to be higher than the value before irradiation, suggesting that the irradiation treatment had caused a softening of the crystal.

The attenuation upon warm-up increased between 77°K and 83°K, and began to decrease above 83°K (see Fig. 2). After reaching 93°K the sample was cooled to 83°K. The attenuation leveled off to a value of about 6.5 x 10^{-2} neper cm^{-1}.

Annealing via continuous warm-up was started again. The attenuation exhibited similar behavior between 83°K to 103°K as was observed previously between 77°K and 93°K.

The level of attenuation at 103°K was, however, much lower than that observed previously at 93°K. The specimen was held at 103°K and the attenuation was observed to decrease to almost the background level.

Upon subsequent annealing of the specimen between 103°K to 130°K the attenuation only slightly decreased (see Fig.2). During the course of annealing between 130°K to 285°K four small attenuation peaks were observed at 171°K, 199°K, 227°K and 257°K, respectively.

The specimen was annealed for four days in the dark at room temperature and then cooled to liquid N_2 temperature. The attenuation measured during warm-up from this temperature exhibited essentially the same behavior as that observed during the previous warm-up. The attenuation between 83°K to 135°K was a little higher than the previous run, the 171°K peak was higher, the 199°K and 227°K peaks were a little lower and the 257°K peak of the same magnitude.

The specimen was then annealed at 200°C for two hours and cooled again to liquid N_2 temperature. Upon subsequent warm-up the attenuation was observed to (a) be lower than in either of the two previous runs between 83°K and 185°K, and (b) exhibit about the same peaks at 227°K and 257°K.

The specimen was then annealed at 450°C for two hours and furnace cooled. Upon subsequent warm-up from 77°K, the background attenuation was found to have risen about 2.5×10^{-2} neper cm^{-1}, and the attenuation spectrum resembled that of the as-compressed state rather than the initially annealed state.

Similar results were observed for other specimens tested over the same temperature range after about 1.1% compression.

4. ANALYSIS OF THE ANNEALING PROCESS

Granato and Lücke(28) have presented a detailed theory concerning the internal friction due to bowing dislocations based upon the string model of the dislocation. They present a relation between the attenuation constant and the mean free length of dislocation L as,

$$\alpha = K_1 \Lambda L^4 \qquad (1)$$

where

$$K_1 = \frac{\Omega B \omega t_1}{\pi^3 \lambda \frac{1}{2} \mu b^2} \qquad (2)$$

and Λ is the dislocation density. In the expression for K_1, Ω is an orientation factor being of the order of one, B is a damping constant associated with dislocation motion and is in general of the order of $10^{-4} \sim 10^{-6}$ c.g.s. units, t_1 is a constant which characterizes the distribution function of dislocation loop lengths and is equal to 120 if a random distribution is assumed ω and λ are the angular frequency and wave length of the carrier wave of the exciting ultrasonic pulse, respectively, μ is an elastic constant of the crystal, and b is the Burgers vector of the dislocation.

It is assumed that point defects are introduced randomly into the bulk of the crystal by γ irradiation. At some temperature these point defects become sufficiently mobile that they begin to migrate to dislocation by the random walk process and thereby pin down the dislocation. The Granato-Lücke model is assumed to be valid during the annealing of the point defects. The Granato-Lücke theory does not predict a relaxation peak. The rapid changes in α around 83°K appear on the low temperature side of the relaxation peak observed at about 120°K in the compressed crystal. It is assumed that the point defect migration primarily affects the base level of α and any secondary effect of peak changes during pinning upon α on the low temperature side of the peak are to a first approximation negligible.

The mean free length of dislocation L at time, t, is given by

$$L = L_o/1 + c(t) \qquad (3)$$

where L_o is the mean free length of dislocation at time t = 0 and c(t) is the ratio of the concentration of point defects on the dislocation at time t which have migrated to the line in time t [illegible] the initial pinning point concentration at t = 0.

If we designate the attenuation at t = 0 as K, then

$$K = K_1 \wedge L_o^4 \tag{4}$$

and the attenuation at time t becomes

$$\alpha = K\ [1 + c(t)]^{-4} \tag{5}$$

When the variation of t_1 with the degree of pinning is assumed negligible. That is, additional pinning of the dislocation is assumed to occur randomly. If we define

$$p = K/\alpha\ , \tag{6}$$

Eq. (5) becomes

$$p^{1/4} = 1 + c(t)\quad . \tag{7}$$

It is also stated that c(t) may be given by

$$c(t) = C_{oeff}\ [1 - g(t)\ ] \tag{8}$$

where C_{oeff} is the ratio of the number of point defects effective for the pinning process per unit volume produced by the irradiation to the number of point defects per unit volume existing at dislocation at time t = 0 and g(t) is a monotomically decreasing function of t and one boundary condition is g(o) = 1.

The function g(t) is to be determined. It is assumed the jump frequency of point defects is only a function of T and not of position relative to the dislocation. Therefore at constant T, the jump frequency contained in g(t) is assumed constant. For the present investigation

$$T = T_o + \beta\ t \tag{9}$$

where T_o is the temperature at t = 0 and β is the constant warm-up rate. Therefore, in this study, g(t) is also g(T).

Granato, Hikata and Lücke(29) presented a theory concerning the rapid decrease in the internal friction during recovery from deformation, when it is assumed by Cottrell-Bilby relation(30) for the migration of point defects to dislocation applies. This theory yields the relation

$$\alpha \propto [\, 1 + \beta t^{2/3} \,]^{-4} \qquad (10)$$

where β is a constant at fixed temperature. $\beta\, t^{2/3}$ corresponds to $c(t)$ in the present paper. The Cottrell-Bilby formulation is based upon the comparatively short range elastic interaction between point defects and edge dislocations(31). Chick, Anderson and Truell(32) reported, however, that the $t^{2/3}$ time dependence for $c(t)$ in the Granato-Hikata-Lücke theory cannot be applied to the case of the alkali halides NaCl, KI and CaF_2. There is no satisfactory theory for this case.

In the present study any rapid changes in the internal friction during recovery after plastic deformation to which the above mentioned theory and experiments are concerned are regarded as complete. The point defects produced upon γ irradiation at liquid N_2 temperature are likely to be distributed at random throughout the specimen. Therefore it may be inferred that only the point defects produced by γ irradiation diffuse upon warm-up according to a random walk process throughout the bulk of the specimen. Eventually these point defects meet with the attractive potential around dislocation where they interact with and pin down the dislocation.

According to Fletcher and Brown(33), the trapping probability of a dislocation of unit length for point defects which at first are randomly distributed around and then migrate to the dislocation according to a random walk process, is approximately proportional to

$$\exp [\, -\tfrac{1}{2}\alpha_o^2 \langle b_1^2 \rangle \, t / \tau \,] \qquad (11)$$

where b_1 is the average atomic jump distance for the defect as it migrates to the dislocation, and α_o must satisfy the relation

$$\alpha_o^{-2} \simeq (R_d^2 / 2) \, [\, -\gamma + \ln (2 / \alpha_c \, r_d) \,] \qquad (12)$$

where γ is the Euler constant equal to 0.577, 2 R_d is the mean distance between dislocation and r_d is the radius of a cylindrical region around dislocation which is assumed to behave as a sink for point defects. We let

$$\zeta \equiv \tfrac{1}{2}\alpha_o^2 \langle b_1^2 \rangle \qquad (13)$$

We assume $g(t) = \exp\left(-\zeta \frac{t}{\tau}\right)$, when τ is a constant independent of time. However, we will also consider the case where τ is dependent on time t. Then the jump number t/τ must be integrated when the temperature variation of τ is noted. Since τ^{-1} rapidly approaches zero $\sec^{-1}$ as the temperature is lowered below the temperature at which the diffusion of the point defect is significant. The range of the integration, T_o to T, is relaxed 0 to T with little introduction of error as long as T_o is well below the temperature where the point defects are mobile. Using relation (9), one finds

$$g(T) = \exp\left[-\frac{\zeta}{\beta}\int_0^T \frac{dT}{\tau(T)}\right] \qquad (14)$$

The jump time $\tau(T)$ is expressed as

$$\tau(T) = \tau_o \exp(E/kT) \qquad (15)$$

where E is the activation energy for diffusion of the point defects, τ_o a constant which contains the entropy factor for a jump, and k is Boltzman's constant.

Combining Equations (15), (14), and (8) with Equation (7), differentiating the latter and taking the log of both sides, one obtains the following result

$$\ln \frac{d(p^{1/4})}{dT} = \ln \frac{\zeta C_{oeff}}{\beta \tau_o} - \frac{E}{kT} \qquad (16)$$

Therefore, if the tangent of the $p^{1/4}$ vs T curves (Fig. 3) is determined at various temperatures, the activation energy of diffusion E can be estimated from the slope of a plot of $\ln\left(\frac{dp^{1/4}}{dT}\right)$ versus T^{-1}. That is, the latter plot exhibits linear behavior. Such linear behavior would suggest that the assumption of a first order reaction expressed by Eq. (14) together with Eq. (15) is probably valid. Fig. 3 shows the temperature dependence of $p^{1/4}$ derived for various assumed values of K when the observed annealing of the internal friction (Fig. 2) is employed. K is the attenuation in the initial state minus any background. As experimental value for K, then, is roughly the difference between maximum value of the attenuation in the initial state (curve □ , T = 83°K, Fig. 2) and the attenuation value for the final state (curve □ , T = 105°K, Fig. 2). Determination of K cannot be done without error, because the very low temperature side of the relaxation peak is superposed upon the background over the temperature range 77°K to 110°K. Therefore the magnitude of the background after annealing cannot be uniquely determined. Our best estimates indicate 7.0×10^{-2} neper $\mathrm{cm}^{-1} \leq K \leq 7.5 \times 10^{-2}$ neper cm^{-1} from evaluation of the experimental data. For this reason, $p^{1/4}$ vs T curves for $K = 7.00 \times 10^{-2}$, 7.25×10^{-2}, and 7.50×10^{-2} neper cm^{-1} were drawn, as shown in Fig. 3. The $\log_{10} \frac{d(p^{1/4})}{dT}$ versus T^{-1} plots, however, yield almost a single straight line in spite of using the different values of K (see Fig. 3). From Fig. 4, E is determined to be 0.103 ± 0.004 ev.

Although $\zeta C_{oeff}/\beta \tau_o$ can be found using Eq. (16), Fig. 4 and the determined value of E, a method which does not rely strongly upon the choice of K will be employed.

From Eqs. (14) and (15), g(T) can be approximated as

$$g(T) \simeq 1 - (\zeta/\beta \tau_o) F(T) \tag{17}$$

where

$$F(T) = (kT^2/E) \exp(-E/kT) \tag{18}$$

when one uses the approximation for the exponential integral

$$E_i(-x) = \int_{-\infty}^{-x} x^{-1} \exp x \, dx \simeq \exp(-x)(x^{-2} - x^{-1}) \tag{19}$$

for $x = E/kT \gg 1$. The latter condition is always satisfied for the case under consideration. Putting Eqs. (17) and (18) into Eq. (8), and using Eq.(7), one obtains

$$\frac{\zeta C_{oeff}}{\beta \tau_o} = \frac{C(T)}{F(T)} = [\ p(T)^{1/4} - 1\ ] \frac{E}{k T^2} \exp (E / kT) = \text{const.} \qquad (20)$$

Eq. (20) depends slightly upon the valud of K since it determines the experimental value of p(T). In order that the right hand side of Eq. (20) is constant over the temperature range of interest. We may take $K = 7.42_5 \times 10^{-2}$ neper cm^{-1}. Thus we obtain $\zeta C_{oeff}/\beta \tau_o = (4.9 \pm 0.2) \times 10^3$. This value may be compared with the value of the same quantity, $(6.6 \pm 3.0) \times 10^3$ found from Eq. (16), Fig. 3 and the determined value of E.

The heating rate β was measured to be 0.2 ± 0.1 deg. min^{-1}, so that $\zeta C_{oeff}/\tau_o = 16.2 \pm 8.9\ sec^{-1}$. If one takes $b_1 \sim 2 \times 10^{-8}$ cm. $R_d^2 = 1.6 \times 10^{-8}\ Cm^2$ when the dislocation density is $2 \times 10^7\ cm^{-2}$(34), and $r_d = 1.2 \times 10^{-7}$ cm, that is three times the lattice parameter of LiF, then one obtains $\zeta = 6.0 \times 10^{-8}$ from Eqs. (12) and (13). Therefore, $C_{oeff}/\tau_o = (2.7 \pm 1.5) \times 10^8\ sec^{-1}$. If τ_o^{-1} is taken as the maximum frequency of lattice vibration of LiF crystal, namely $8.4 \times 10^{12}\ sec^{-1}$(35), one obtains $C_{oeff} \simeq 3 \times 10^{-5}$. This value of C_{oeff} is unreasonably small. C_{oeff} is most likely of the order of one to ten. Therefore, τ_o^{-1} should be of the order of $10^7\ sec^{-1}$, if the other assumptions made are approximately correct. It might be thought that such a low value for τ_o^{-1} would indicate the effective mass of the point defect is very large. If we take $\tau_o^{-1} = 1 \times 10^7\ sec^{-1}$, τ^{-1} is equal to 6 sec^{-1} at 83°K and 64 sec^{-1} at 100°K. These values seem to be reasonable.

To determine C_{oeff}/C_o, we must first estimate the density of point defects introduced into the bulk of the LiF crystal by the C_o^{60} irradiation.

The energy efficiencies for the production of a Frenkel pair in LiF by two different types of irradiation(11),(36),(37) have been reported. This data is summarized in Table 1. In this table the X-rays were produced from a tungsten target energized at 40 KV.

Table 1. The energy efficiency for the production of a Frenkel pair in LiF for various types of irradiation and different irradiation temperatures.

Radiation	Temperature	Efficiency (ev/F center)	Reference
X-rays	liq. He	620	(11)
	90°K	140	(36)
Tritium β rays	77°K	370	(37)

The photoelectric effect is the dominant mechanism by which the X-rays are absorbed whereas the Compton effect is the dominant mechanism of absorption for C_o^{60} γ -irradiation. The absorption efficiency of the radiation energy in crystals expand to C_o^{60} γ -rays is most likely considerably lower than that for X-rays under the conditions outlined in this paper. It is estimated that the C_o^{60} γ -ray is probably only one-fifth as efficient in producing F centers as X-rays. The energy efficiency is estimated to be between 700 ev and 3100 ev per F center for C_o^{60} γ -irradiation. The density of Frenkel pairs introduced by a dose of 5.8×10^6 r of C_o^{60} is thus estimated to be between 3.6×10^{18} and $1.5_7 \times 10^{19}$ cm^{-3}. Let us assume a value of 9.7×10^{18} cm^{-3}.

Let us now estimate the initial density of pinning points from Eqs. (2) and (4). To do this we take account of both the experimental conditions and the material constants of LiF. These are as follows:

$\omega = 2\pi \times 10^7 sec^{-1}$, $B = 7.0 \times 10^{-4}$ c.g.s. unit(34),(38), $\Omega = 1$, $t_1 = 120$, $\lambda = 6.8 \times 10^{-2}$cm., $\mu \simeq 5 \times 10^{11}$ dyne cm^{-2} and $b = 2.83 \times 10^{-8}$ cm. Thus, $K_1 = 1.25 \times 10^{10}$ cm^{-3}. Since $K \simeq (7.26 \pm 0.25) \times 10^{-2}$ neper cm^{-1} and if the dislocation density Λ is assumed to be 2×10^7 cm^{-2}, then L_o becomes

2.3×10^{-5} cm. Therefore, the initial density of pinning points becomes 8.7×10^{11} cm^{-3}.

According to the above calculations the ratio of the density of Frenkel pairs produced by the irradiation to the initial density of pinning points. C_o, becomes 1.1×10^7. C_o will not in general be equal to C_{oeff}, because it is possible that during production of the point defects, some are trapped or annihilated by way of diffusion without reaching dislocation. We could have estimated C_{oeff} so that it would have given a reasonable value of τ_o^{-1} or the jump frequency τ^{-1} at each temperature with which we are concerned. However, from the aforementioned estimate of the value of τ_o^{-1} and C_{oeff}, C_{oeff}/C_o becomes of the order of 1×10^{-6}. Even if one assumes that it requires 10 to 100 point defects to produce one pinning point, C_{oeff}/C_o is of the order of 1×10^{-4}. This possibly shows that most of the point defects may not disappear at dislocation, but are annihilated in the bulk of the crystal by interaction with other point defects.

5. DISCUSSION

We have compared our experimental results with those obtained by Känzig(6), Känzig and Woodruff(3), Delbeque, et al.(8), Wiegand and Smoluchowsky(36), and Johnston, et al.(42),(43),(44).

Känzig studied the pulse annealing of $H^{(3)}$, $V_k^{(1),(2)}$, $V_t^{(5)}$ and $V_F^{(4)}$ centers in LiF X-irradiation at 77°K by electron spin resonance. Känzig's results show that the H center in LiF begins to anneal at 95°K and disappears within minutes at 105°K. The V_k center also begins to anneal at 95°K and disappears within minutes or seconds at this temperature. Känzig evaluated the diffusion coefficient and activation energy for holes trapped at V_k centers which jump from fluoride pair to fluoride pair as 0.1 cm^2 sec^{-1} and 0.32 ev, respectively. This was done by a preliminary investigation concerning the kinetics of the annealing of the self trapped holes.

This annealing of the V_k center corresponds exactly with conductivity changes and the thermoluminesence behavior of LiF(8),(40) which is observed during warm up (at a rate of 2.75 deg min^{-1}) after X-irradiation at 77°K. The conductivity data exhibits a small peak which could correspond to the rapid annealing of H centers.

Wiegand and Smoluchowsky(36) made dilatometric studies of LiF which had been X-irradiated at 90°K during annealing via warm-up to room temperature. They simultaneously studied the annealing of the F and 3400A° absorption bands. They found that both types of measurement agreed with each other concerning annealing characteristics over the temperature range of 100°K to 160°K. The warm-up rate they employed was 1.0 ± 0.2°K min^{-1}. Delbeque, at al.(8) observed the same annealing behavior of the absorption bands in LiF irradiated by X-rays at liquid N_2 temperature. According to Känzig, the H and V_k centers have almost the same optical absorption band about 3400A° in LiF, possibly because they both have the similar F_2^- molecular ion structure with a trapped hole. The growth and decay of the 3400A° absorption band(8),(36) corresponds directly with the behavior of the H and V_k centers as studied by electron spin resonance. The symmetry of this absorption band as obtained from light polarization studies coincides also with that expected of H and V_k centers from electron spin resonance work.

Johnston, et al.(42),(43),(44) studied the flow stress of LiF single crystals irradiated with γ -rays at 77°K in each of the following states: (1) as irradiated at 77°K, (2) after isothermal anneals at 120°K and 165°K for 30 min., and (3) after the specimen had been warmed to room temperature. They found that the flow stress observed after treatment (1) could be irreversibly decreased to almost the magnitude of the flow stress observed for case (3) by treatment (2). The experimental results of Suzuki and Doyama on additively colored alkali halide crystals suggest that the point defect which plays the dominant role in controlling the flow stress of LiF at room temperature is the V_k center. Johnston, et al.(42),(44) suggests that the decrease of the flow stress by treatment (2) is associated with the disappearance of the V_k center. The latter exhibit tetragonal lattice distortion and hence act as a point defect to cause solution hardening. The H center also has associated with it tetragonal distortion(44). Känzig(6) exposed LiF to X irradiation at 77°K for about 100 hrs. The H center concentration due to this treatment is about one-twentieth that of the V_k center. H centers should contribute to solution hardening in a similar manner as the V_k center. The concentration ratio of H centers to V_k centers, however, will vary with both the energy and dose of irradiation.

Agreement between the published data and the present study with respect to the temperature range over which irreversible transient phenomena occur is very good. In the present study, however, the crystal was prestrained, hence a pronounced dislocation network should have been introduced. The dislocations of this network are able to act as sinks for interstitial defects. Consideration must be given to the fact that the warm-up rate used in the present study was a factor of ten less than that employed by these earlier investigators with the exception of Känzig's E S R data obtained by pulse annealing at low temperatures(6). Internal friction measurements can detect a density change of dislocation pinning points as low as 10^9 cm^{-3}(22). Känzig's data obtained by pulse annealing shows excellent correspondence between the temperature range for H center annealing and that associated with the irreversible decrease of the internal friction after γ -irradiation observed in the present study.

Consideration of these facts along with the results of the studies by Rabin and Klick(11) and by Pretzel and Petty(37) enable us to suggest the following interpreation of our data.

H, F and V_k centers are produced randomly in the bulk of the LiF crystal upon γ -irradiation at linquid N_2 temperature(37). The concentration of V_k centers is far greater than that of H centers(6). Both the V_k and H centers are believed to be stable and homogeneously distributed throughout the bulk of the crystal after γ or X irradiation at liquid N_2 temperature.

We believe only H centers are responsible for the observed low temperature irreversible recovery of the internal friction.

During warm-up the holes trapped on H centers become thermally mobile. The migration of the trapped holes will enhance the migration of the crowdion F_2^- molecule associated with the H center(3) in the temperature range between 83°K to 105°K(6). The crowdion F_2^- molecule is assumed to migrate through the crystal lattice by a random walk process. This is because the holes of the crowdion hop from one anion site to another without recombination with F centers(8),(36). We believe this because the neutral flourine atom is not likely to migrate interstially in the low temperature region under discussion. This naturally follows from the fact that the activation energy for the He atom interstitial diffusion in LiF crystal is 1.81 ev(45), and that for the migration of the Li^+ vacancy is 0.65 ev(46). The activation energy which we have already estimated is 0.103 ± 0.004 ev, a value low compared to those cited above.

The pinning point defects cannot be any point defects that can be formed by cold-work of the crystal. This can be seen from the annealing data at room temperature (Fig.5)(25).

A small fraction of the H centers may become trapped in the attractive potential field in the neighborhood of dislocations. This fraction may be of the order of 10^{-5} of the H centers formed during irradiation according to the present calculations. At the core region of the dislocation, the F_2^- molecule ion may change to either an F_2 molecule by emission of its electron, or generate a neutral F atom and an F^- ion without electron emission. The elastic interaction between the dislocation and F_2 molecules or the neutral fluorine atom which is formed at the dislocation core presumably contribute to the pinning of the dislocation. The binding energy of the point defect with dislocation must be so large that annealing treatments at 200°C do not appear to alter the degree of pinning. It might be possible, however, that pinning defects other than the H center may become effective at higher temperatures. The pinning caused by the H center is so decisive that the internal friction at about 110°K decreases almost the lowest level observed, namely after annealing of the γ -irradiated crystal at 77°K. The pinning proceeds by a thermally activated process, because the present experiment was carried out in the dark. If the hole emitted from a V_k center or H center contributes to the pinning, the pinning would not be expected to be so stable. According to Bauer and Gordon(20), they could not find any electronic pinning process in LiF at low temperatures. Thus, electronic pinning of dislocation in LiF is as yet not detected and may not even occur.

Assuming that the H center pinning process as previously noted is correct, we can construct the following model. The crowdion configuration of the H center represents a metastable state in LiF. In LiF, the overlap of the electron distribution is fairly large in contrast to the other alkali halides(47). This means that the bond of LiF contains a large valence characteristic besides its usual ionic character. This corresponds to other facts about LiF, such as that its minimum Debye temperature(35) is the highest (about 80°K) among the alkali halides, and the anisotropy in the elastic constants, C_{11} and C_{44}(38) is large ($C_{11} = 11.7 \times 10^{11}$ and $C_{44} = 6.28 \times 10^{11}$ dyne/cm^2). In the temperature region above the minimum Debye temperature, the lattice vibration may cause the metastable crowdion associated with H center to become excited into a dynamically unstable state. At lower temperatures, however, the available interstitial space for the crowdion is sufficient to accommodate it(11). The trapped holes on the H centers are simultaneously thermally excited by the lattice vibration. These two processes possibly act cooperatively and excite the migration of the H center. The successive random walk migration in the $\langle 110 \rangle$ direction preserves the crowdion configuration in a way like dynamic crowdion motion. However, the jump distance is the distance between two adjacent anions in the $\langle 110 \rangle$ direction. This process possibly has a very low energy for migration associated with the H center.

Though H centers may migrate through the crystal by the latter process, only a small portion of them, that is of the order of 10^{-5} of these produced by γ -irradiation, can reach the dislocations. The remainder which is almost all the H centers disappear within the bulk of the crystal by interaction presumably with other defects. The process controlling the disappearance of the largest portion of H center is indeed not well understood.

Känzig(6) found that the disappearance of H centers is accompanied by a decrease of the V_k center concentration. He interpreted this phenomena by suggesting that some of the V_k centers disappear by recombination with electrons emitted from H centers when the latter become F_2 molecules.

We suggest the following interpretation. Känzig's interpretation is compatible with the present results when we assume H centers interact with V_k centers during H center migration. The small portion of the H centers which are able to avoid this interaction can meet dislocation. As the V_k center density is about ten times that of the H center, those V_k centers which have not interacted with H centers are able to emit their trapped holes as free holes at a temperature slightly higher than that at which the H center becomes mobile. These holes may be consumed partly in creating V_F centers and partly during the disappearance of some of the F centers. Känzig's E S R data(6) suggests the aforementioned behavior.

The decrease of the dilation of LiF during warm-up after low temperature irradiation(36) does not predominantly occur by the trapping of H center at dislocation, but by the disappearance of H and V_k centers within the bulk of the crystal. The disappearance of the H and V_k centers softens the crystal relative to its γ -irradiated strength at 77°K(42),(44).

The vertical arrow in Fig.2 at about 77°K between the compressed but unirradiated crystal data and the plot for the irradiated crystal shows that irradiation at liquid nitrogen temperature has caused softening. The attenuation increased about 5.5×10^{-2} neper cm^{-1}. The behavior appears to be extremely strange to our common knowledge concerning γ irradiation of LiF. This remains, as yet, an unanswered problem. An investigation concerning this point is currently under investigation.

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FIGURE CAPTIONS

Fig. 1 Cooling apparatus and specimen container.

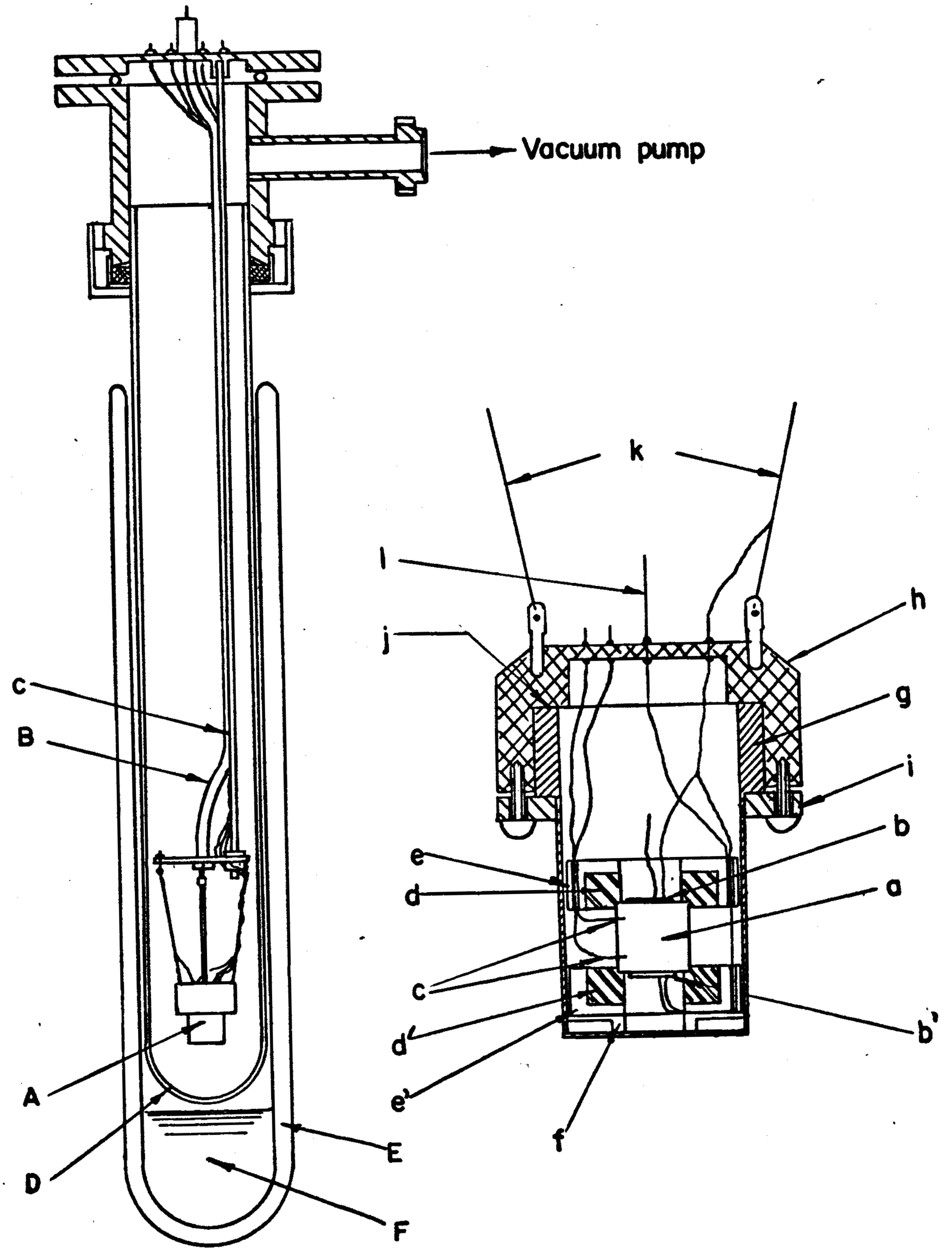
A: the alminum container for the specimen, B : two coaxial cables and leads, C : stem, D : glass tube, E : Dewar, F : liquid N_2, a : specimen, b, b' : quartz transducers, c : thermocouples, d, d' : lead shields, e, e' polyethyelene holders, f : polyethylene spacer, g : aluminum container, h : bakelite cap, i : ring to hold the cap, j: ground faces coated with DC 33 heavy grease, k : wires to serve as grounding line and hander, l : leads.

Fig. 2 Internal friction of a compressed LiF crystal versus temperature measured by warm-up process before and after gamma irradiation at 77°K, and followed by anneal at various temperatures as indicated.

Fig. 3 Temperature dependence of $p^{1/4}$ derived for various assumed values of K when annealing of the internal friction data (α_{obs} versus T) is employed.

Fig. 4 1/T dependence of $\frac{d\,(p^{1/4})}{d\,T}$ derived for various assumed values of K.

Fig. 5 annealing of the internal friction at room temperature for a compressed LiF crystal.


Vacuum pump
c
B
A
D
E
F
k
l
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h
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i
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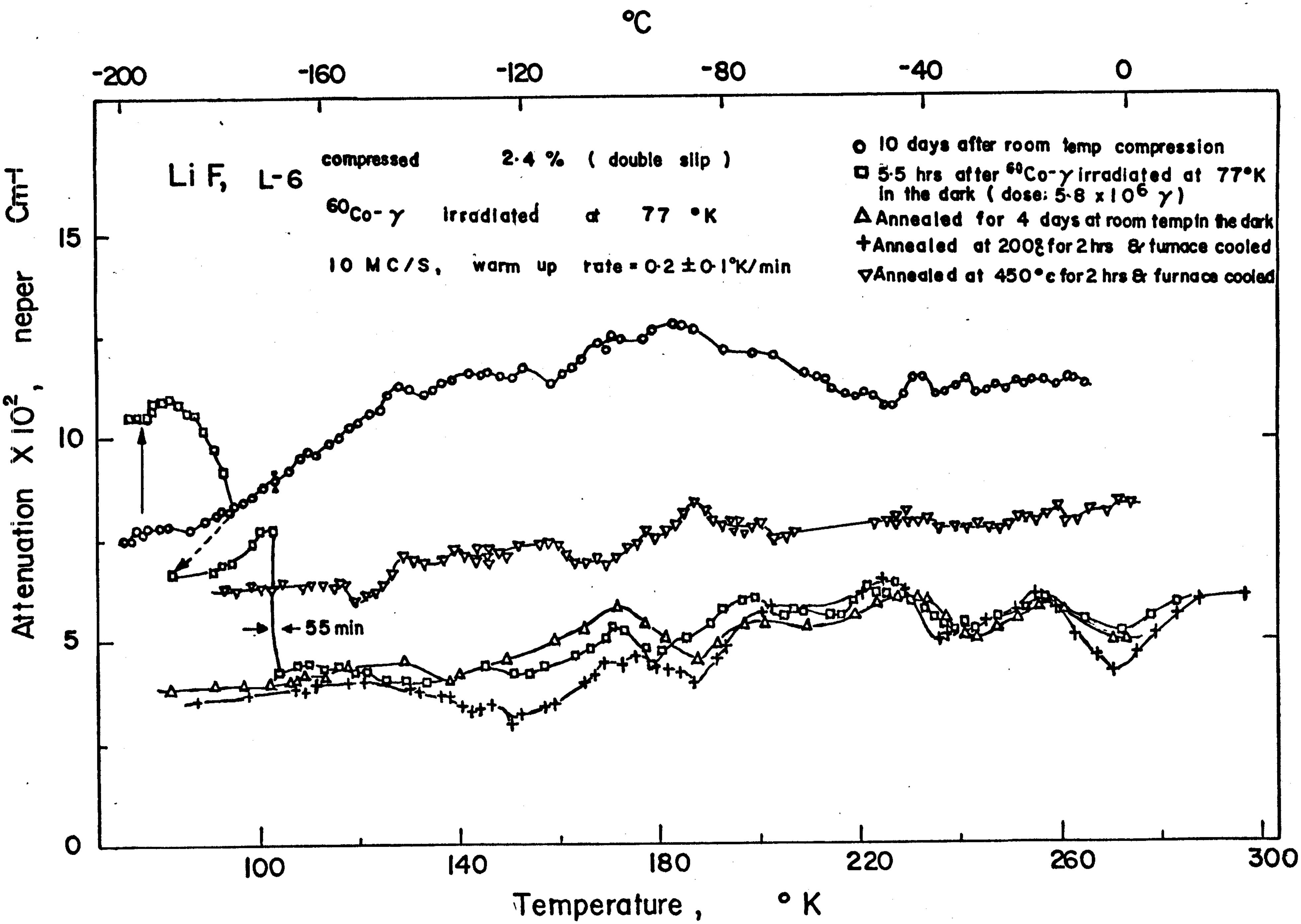
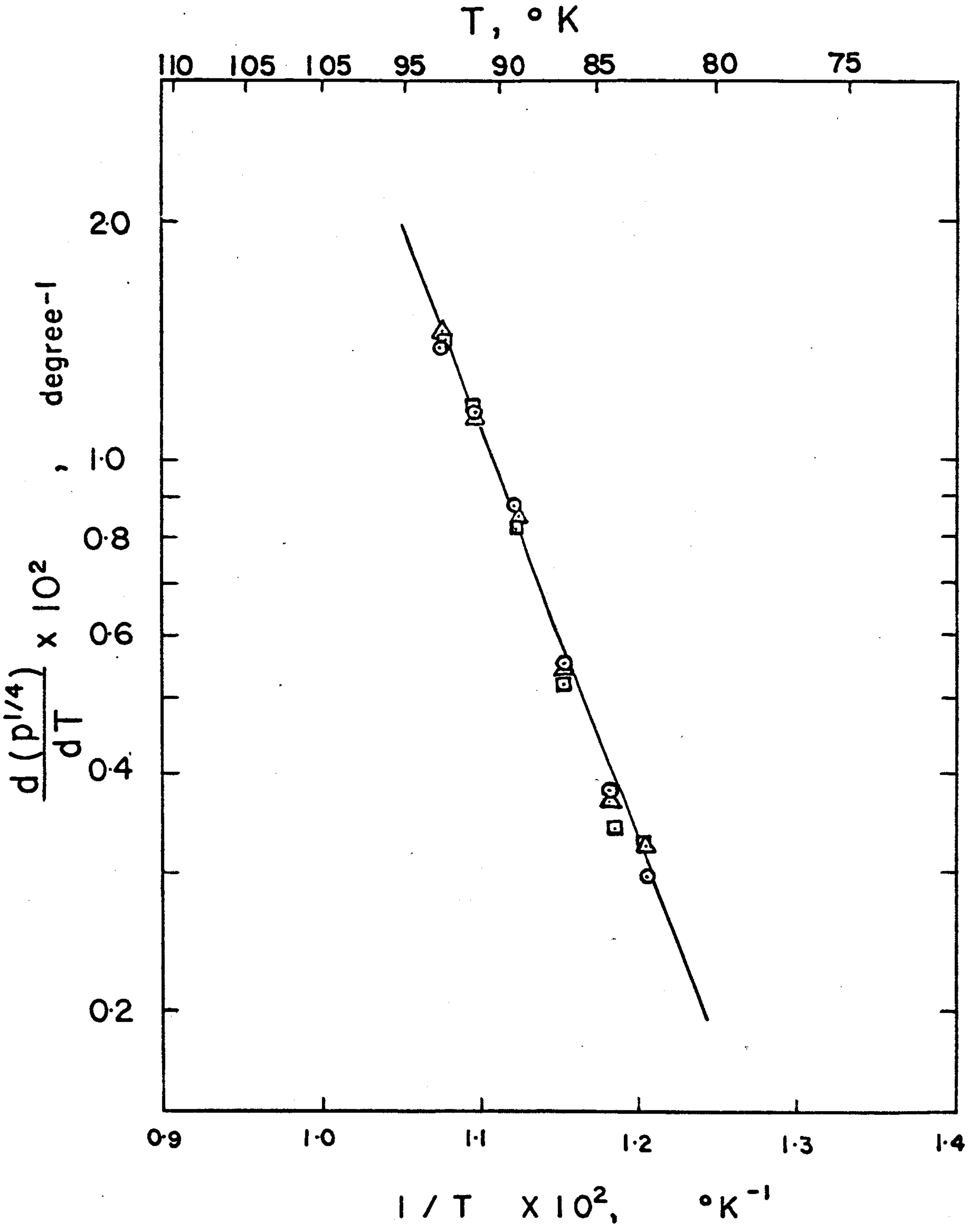
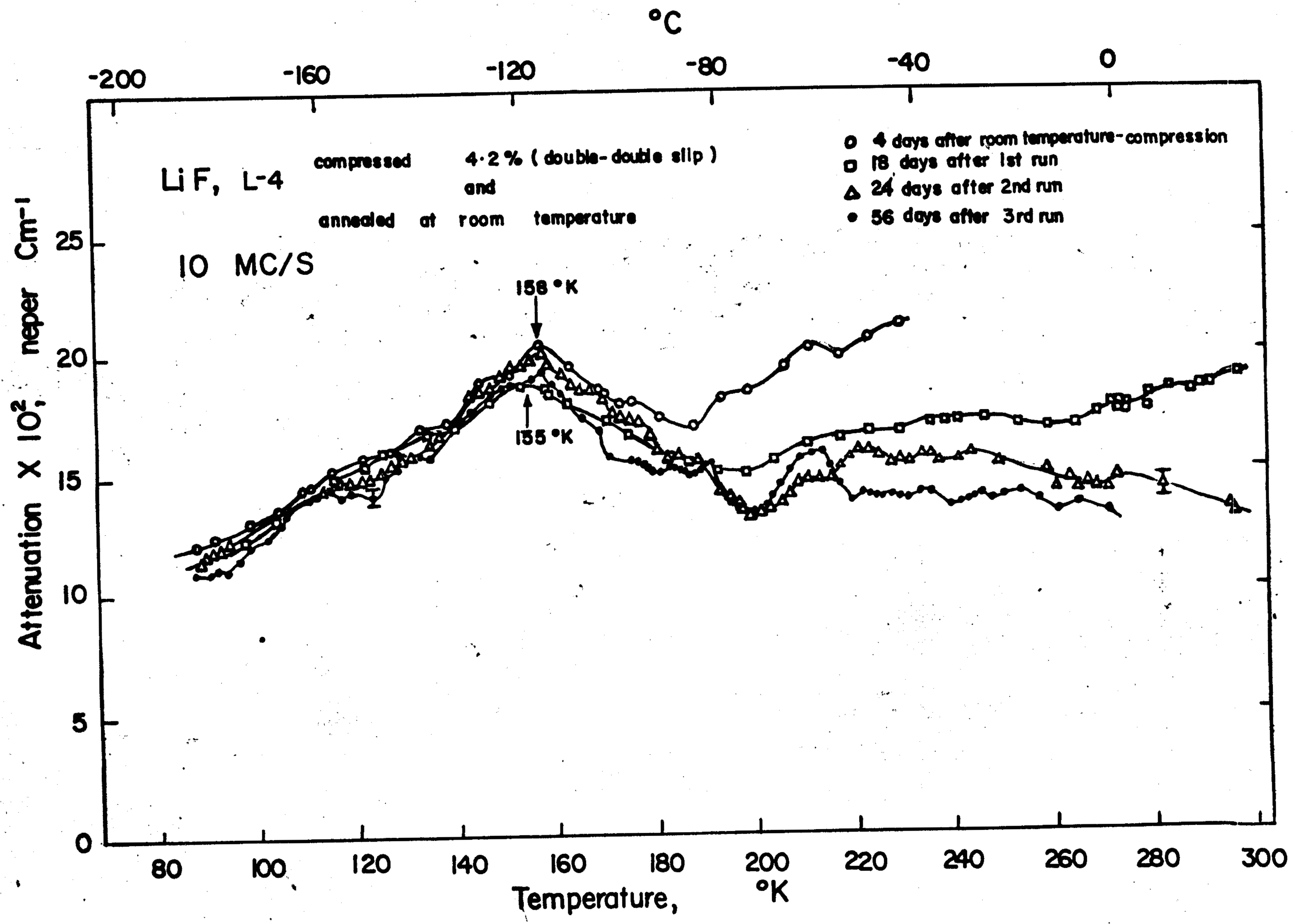
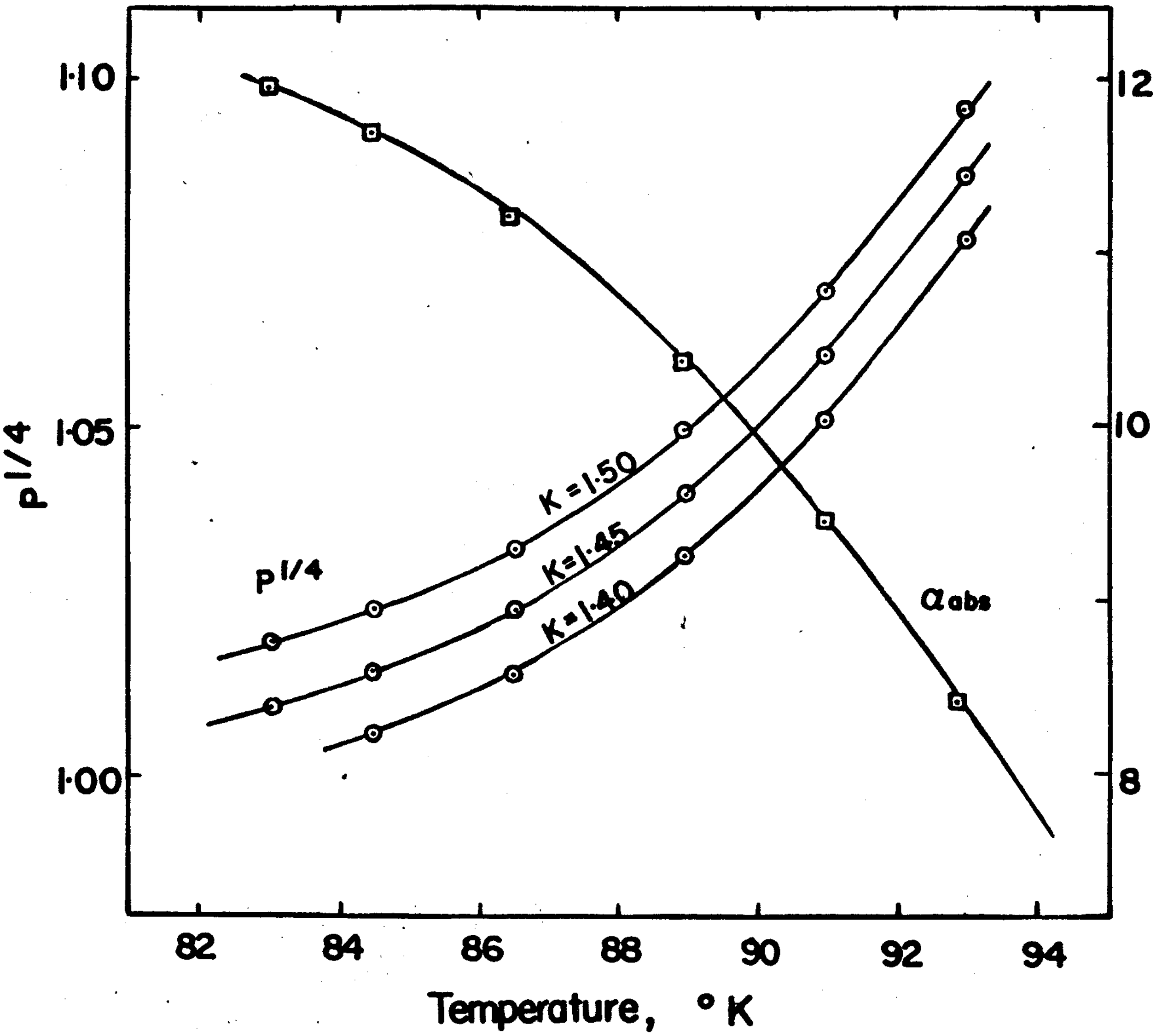
a
c
d'
b'
e'
f


°C
-200
-160
-120
-80
-40
0
Li F, L-6
compressed 2·4 % (double slip)
^{60}Co-γ irradiated at 77 °K
10 MC/S, warm up rate = 0·2 ± 0·1°K/min
○ 10 days after room temp compression
□ 5·5 hrs after ^{60}Co-γ irradiated at 77°K in the dark (dose: 5·8 x 10^{6} γ)
△ Annealed for 4 days at room temp in the dark
+ Annealed at 200°C for 2 hrs & furnace cooled
▽ Annealed at 450°c for 2 hrs & furnace cooled
← 55 min
Attenuation X 10^{2}, neper Cm^{-1}
0
5
10
15
100
140
180
220
260
300
Temperature, °K


T, °K
110
105
105
95
90
85
80
75
2·0
1·0
0·8
0·6
0·4
0·2
$\frac{d(p^{1/4})}{dT} \times 10^2$, degree-1
0·9
1·0
1·1
1·2
1·3
1·4
1 / T X 10², °K⁻¹


°C
-200
-160
-120
-80
-40
0
Li F, L-4
compressed 4·2 % (double-double slip)
and
annealed at room temperature
10 MC/S
○ 4 days after room temperature-compression
□ 18 days after 1st run
△ 24 days after 2nd run
● 56 days after 3rd run
158 °K
155 °K
Attenuation X 10², neper Cm-1
0
5
10
15
20
25
80
100
120
140
160
180
200
220
240
260
280
300
Temperature, °K


1·10
1·05
1·00
P 1/4
12
10
8
α_{abs} X 10^2, neper cm^{-1}
P 1/4
K = 1·50
K=1·45
K=1·40
α_{abs}
82
84
86
88
90
92
94
Temperature, °K