other, longer period, oscillations due to pockets of the Fermi surface on the Brillouin zone boundaries.

CONCLUSIONS

From the nature of the variation of the oscillatory magnetoresistance with orientation of the magnetic field it is concluded that the Fermi surface for HgSe has protrusions in the $\langle 111\rangle$ directions of k space. These protrusions, however, are small in height and the Fermi surface is not much deformed from a spherical shape. The existing theories adequately describe the temperature dependence of the amplitudes of the magnetoresistance oscillations in HgSe, and this temperature dependence yields values for the cyclotron effective masses of conduction electrons in good agreement with those deduced from optical reflectivity data. The variation of effective mass with conduction electron density is in accord with energy band models proposed for materials that have the zincblende structure, and this variation of effective mass was used to determine the energy gap at $\mathbf{k}=0$ and the curvature of the conduction band in HgSe.

ACKNOWLEDGMENTS

Ralph D. Thomas prepared the crystals for this investigation and performed much of the data collection and reduction. His assistance was invaluable and is gratefully acknowledged. Thanks are given to David E. Soule, who was the first to observe magnetoresistance oscillations in HgSe, for the use of his magnet and cryogenic facilities for this work. Discussions with Joel W. McClure and Glen C. Wagoner during the course of this work were very helpful. Thanks also are given to Robert P. Ulman, who assisted in obtaining some of the data, and to Carl Lowell who did the x-ray diffraction work necessary for crystallographically orienting the crystals.

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Optical Probing of the Environment of F Centers in Deformed Alkali Halides*

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The formation of F centers upon Co^{60} irradiation of KCl deformed at room temperature and at 77°K and the environment of F centers formed upon Co^{60} irradiation of deformed KBr were studied by means of optical-absorption measurements with a Cary-14 spectrophotometer. Anomalies of the beta absorption band (exciton band localized at the F centers) and shift of the F-center peak toward blue were observed in deformed KBr at 10 and 80°K. The observed anomalies can be removed by a short annealing near 525°K. Both the dichroic behavior of the beta band and the energy shift of the F band are consistent with the hypothesis that the source of vacancies is the edge-dislocation dipoles from plastic deformation. The F centers formed upon Co^{60} irradiation of deformed KBr are most probably located a few Burgers vectors away from the core of one member of the edge-dislocation dipole in the compression region, a fraction of an interatomic spacing above the slip plane where the edge dislocation is situated.

I. INTRODUCTION

A QUALITATIVE interpretation of the various effects of mechanical deformation on coloration phenomena has been proposed by Seitz,[1] who suggested that mechanical deformation results in an increase in the vacancy concentration. The increased darkenability of deformed crystals and the bleaching effect of plastic deformation of a crystal previously colored by irradiation are understandable in a general sense according to this hypothesis. On the other hand, Nowick[2] ascribes the enhancement of the colorability of the annealed crystals upon plastic deformation to the dispersing action of the plastic deformation, which causes the precipitated impurities to be redissolved on an atomic scale. Smoluchowski and co-workers[3,4] have made extensive studies of the growth of the F band in undeformed, deformed, and heat-treated KCl crystals between liquid-hydrogen temperature and room temperature. The similarity in forms and temperature dependence of the initial coloration in a freshly cleaved crystal and the coloration after plastic deformation suggests that both these stages obtain vacancies from the same source, and they concluded that the source of vacancies is the debris resulting from dislocation interaction and not from the dislocation lines themselves. Further experimental evidence of enhanced coloration in deformed KCl due to the presence of dislocation dipoles is seen in the work of Davidge and Pratt,[5] who remarked,

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[1] F. Seitz, Phys. Rev. **80**, 239 (1950).

[2] A. S. Nowick, Phys. Rev. **111**, 16 (1958).

[3] P. V. Mitchell, D. A. Wiegand, and R. Smoluchowski, Phys. Rev. **121**, 484 (1961).

[4] B. S. H. Royce and R. Smoluchowski, Discussions Faraday Soc. (to be published).

[5] R. W. Davidge and P. L. Pratt, Phys. Stat. Solidi **3**, 665 (1963).

however, that the effect is observable only with hard but not soft x rays.

The purpose of the present study is to re-examine the enhancement of coloration in deformed KCl and to probe the environment of F centers in deformed KBr crystals by means of optical-absorption measurements. If the vacancy source is the dislocation dipoles, the F centers so formed should not be far away from the dipoles. The author[6] has shown recently that the beta-absorption band[7] (exciton band localized near the F centers) exhibits anomalous behavior in deformed alkali halides. The probing of the beta band and the F band in deformed KBr has yielded interesting information on the possible location of these F centers generated in deformed alkali halides.

II. DESCRIPTION OF EXPERIMENTS

The experimental study consists of two parts. Part one concerns the enhancement of F-center formation in undeformed and deformed KCl; part two reports studies of the characteristics of the beta and F-absorption bands in deformed KBr. Optical absorption was made with a Cary-14 spectrophotometer at 10, 80, and 300°K. Deformation of the specimens, both at room and liquid-nitrogen temperatures, was done with a table-model Instron. Deformation by both compression and bending was used. Both the KCl and KBr crystals were obtained from the Harshaw Scientific Company. Coloration was done in a Co^{60} source (about 10^6 R/h) at an ambient temperature of 315°K. Cleaved specimens were polished, etched, deformed, then polished and etched again before they were colored and mounted immediately in darkness in a model CLF cryoflask (Texas Instruments) for optical absorption measurements. The pressure inside the cryoflask was maintained at about 2 to 4×10^{-6} mm of mercury at all times. The thicknesses of the specimens varied between 1 to 2 mm, but were maintained nearly the same in any set of optical-absorption experiments for comparison purposes.

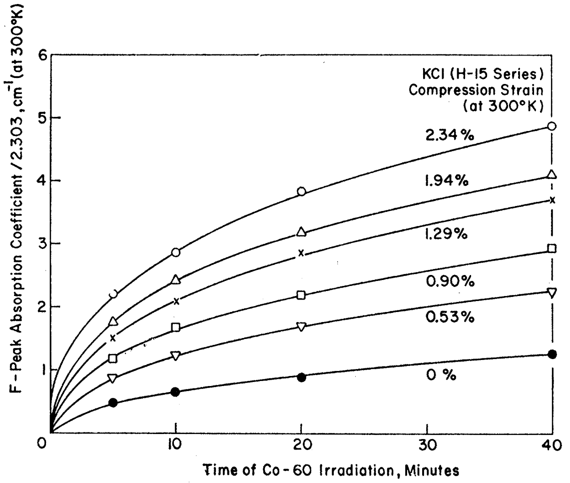

FIG. 1. F-peak absorption (300°K) versus compression strain and Co^{60} irradiation time, KCl (H-15 series) deformed at 300°K.

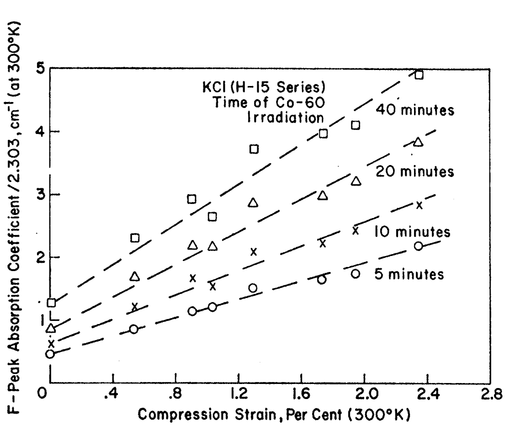

FIG. 2. Same as Fig. 1, a slightly different plot.

III. ENHANCEMENT OF F-CENTER FORMATION IN DEFORMED KCl

A. Compression at 300°K, Coloring at 315°K, Optical Absorption at 300°K

The change of the F-center absorption peak versus compression strain and time of Co^{60} irradiation is typically shown in Figs. 1 and 2. The change of V-center absorption peak (primarily from V_3 centers at 2120 Å and some V_2 centers at 2300 Å) is shown in Fig. 3. A comparison of Fig. 2 with Fig. 3 shows that the F-center peak increases almost linearly with compression strain while the V-center peak is almost independent of compression strain for a given Co^{60} dosage. This observation suggests that the enhancement of F-center formation due to plastic deformation is not the result of the dispersing action which redissolves the precipitated impurities.[2]

At low Co^{60} dosages, the rate curves shown in Fig. 1 can be normalized according to

$$A=A^0(1-e^{-bt}), \tag{1}$$

where A is the absorption at time t, A_0 is the normalized absorption coefficient, and b is a constant characteristic of the material. Separate determinations with our material yield a value of $b=0.10$ per minute, which is within the range of values reported by Mitchell, Wiegand, and Smoluchowski.[3] The curves of Fig. 1 are replotted according to Eq. (1) in Fig. 4. The normalized absorption peak of the F center versus compression strain is shown in the lower plot of Fig. 6.

B. Compression at 77°K, Coloring at 315°K, Optical Absorption at 300°K

The variation of the F-center peak absorption versus compression strain (specimens strained at 77°K) and

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[6] R. Chang, Bull. Am. Phys. Soc. **9**, 630 (1964).

[7] C. Delbecq, P. Pringsheim, and P. Yuster, J. Chem. Phys. **19**, 574 (1951).

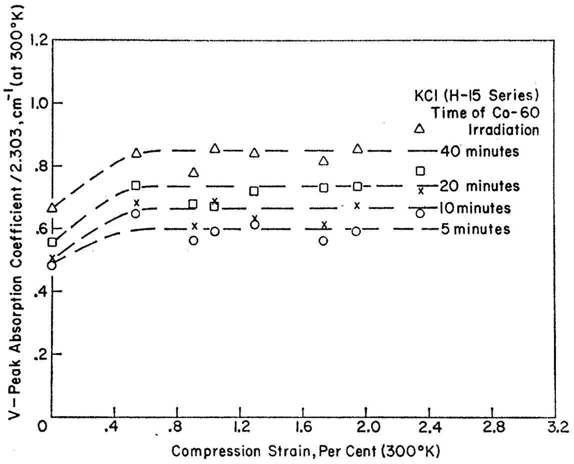

FIG. 3. V-center absorption (300°K) versus compression strain and time of Co^{60} irradiation, KCl (H-15 series) deformed at 300°K.

time of Co^{60} irradiation for the same batch of KCl crystal from Harshaw is shown in Fig. 5. The normalized absorption peak according to Eq. (1) versus compression strain is shown by the upper plot of Fig. 6.

Two points are to be noted from Fig. 6. First, the initial F-center concentration without plastic strain is higher for the specimens used in the 77°K deformation than those used in the 300°K deformation, although both sets of specimens were cleaved from the same block of a Harshaw crystal about the size of a one-inch cube. Second, the rate of F-center formation for each percent strain deformed at 77°K is more than a factor of 2 larger than that deformed at 300°K (3.1 cm^{-1} compared with 1.4 cm^{-1} for each percent strain). The critical shear stress at 77°K for our specimens (5.2 to 5.5×10^7 dynes/cm^2) is also more than a factor of 2 larger than that at 300°K (2.1 to 2.2×10^7 dynes/cm^2). This is consistent with the hypothesis that the source of vacancies in deformed material at low Co^{60} dosages is the dislocation dipoles. The current theories of dislocation-dipole formation[8] suggest that the average dipole width is nearly inversely proportional to the applied resolved shear stress in the slip plane where jogged screw dislocations are moving. Doubling the applied resolved shear stress would half the average dipole width and consequently double the number of dislocation dipoles for a given plastic strain.

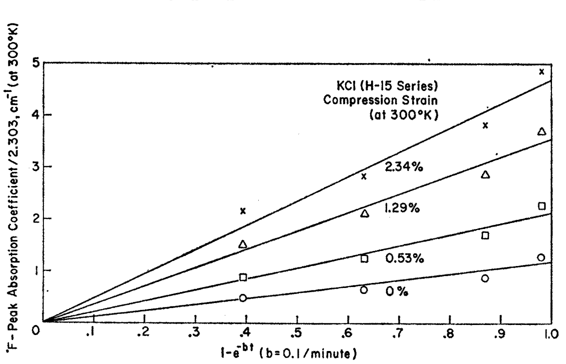

FIG. 4. Normalization of data of Fig. 1.

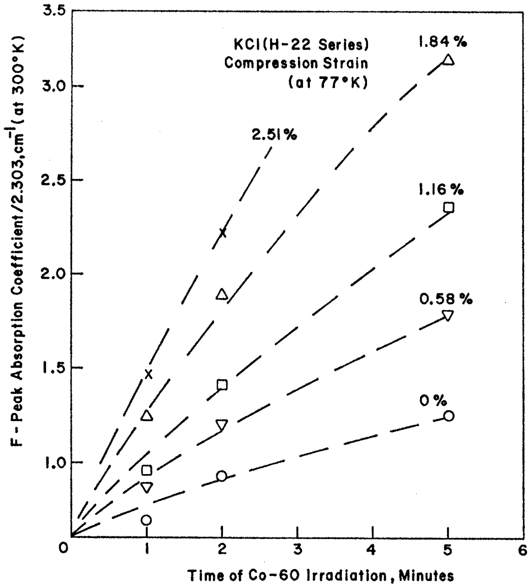

FIG. 5. F-peak absorption (300°K) versus compression strain and time of Co^{60} irradiation, KCl (H-22 series) deformed at 77°K.

C. Annealing Experiments

The microstructural investigations of Davidge and Pratt[5] suggest that dislocation dipoles, but not dislocations, can be removed from deformed KCl crystals

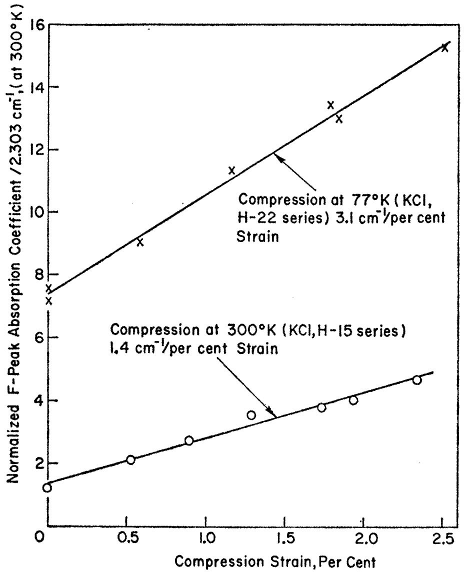

FIG. 6. Normalized F-peak absorption (300°K) versus compression strain, KCl deformed at 77°K (upper curve) and at 300°K (lower curve). Computed from data shown in Figs. 5 and 1.

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[8] W. G. Johnston and J. J. Gilman, J. Appl. Phys. **31**, 632 (1960).

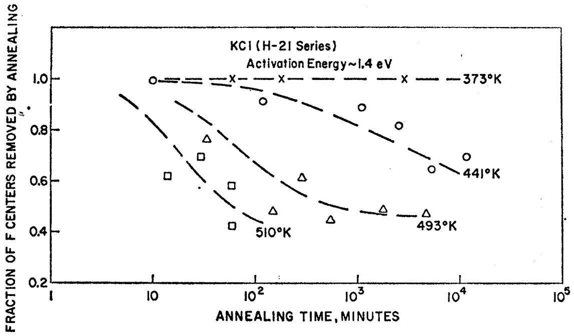

FIG. 7. Annealing of vacancies from plastic deformation and Co^{60} irradiation, KCl (*H*-21 series).

by annealing near 500°K. A series of experiments were conducted to see whether there is a correlation between coloration and annealing near this temperature. Harshaw KCl specimens were deformed, annealed for various lengths of time at indicated temperatures, then colored 5 min in Co^{60} and readied for absorption measurements. The fraction of *F* centers removed by annealing, given by the difference in *F*-center concentration between deformed and undeformed samples after an annealing time *t* divided by the same difference before any annealing treatment, is plotted versus the time at different temperatures in Fig. 7. The data shown in Fig. 7 yield an apparent activation energy of about 1.4 eV, which is not far from that for the motion of anion vacancies in KCl. Annealing studies by Mitchell *et al.* at lower temperatures in a slightly different set of experiments yield an activation energy of about 1.1 eV.[3]

IV. EXPERIMENTS WITH THE BETA-ABSORPTION BANDS IN DEFORMED KBr

A. Typical Spectra

The type of crystals that will yield useful information on the beta-absorption band[7] with a Cary-14 spectrophotometer is rather limited. KBr crystals supplied by Harshaw were used in the following experiments.

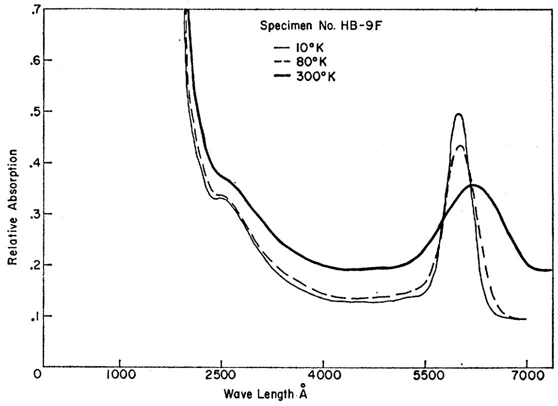

FIG. 8. Typical absorption spectra, deformed KBr, at 10, 80, and 300°K.

Typical absorption spectra of KBr, deformed at room temperature and colored 5 min in Co^{60} at 315°K are shown in Figs. 8 and 9. The beta band, peaked at about 1910 Å, is not observable at room temperature due to interference of the main absorption band. Figure 9 shows that there is a slight difference in the shape of the beta band between 10 and 80°K. The beta band is characterized by a broad peak (later seen to be composed of two peaks) near 1910 Å and two satellite peaks on the high-energy side at about 1880 and 1890 Å measured at 10°K. It is interesting to note that the beta absorption band in undeformed KBr does not show any details as seen in Fig. 9 except a smoothly varying broad band much like the *F* band.

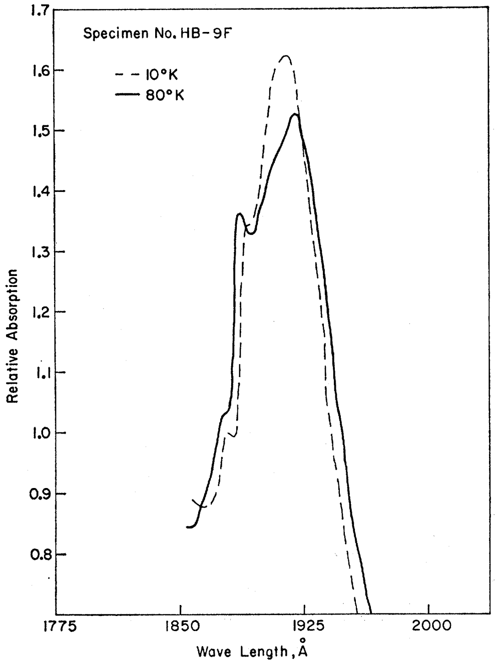

FIG. 9. Typical absorption spectra, deformed KBr, at 10, 80, and 300°K.

B. Dichroism of the Beta Band

The broad peak near 1910 Å is under certain circumstances resolved into two peaks separated by about 20 Å (or 70 wave numbers), depending on the direction of the optical beam with respect to that of the Burgers vector. Cleaved plates from a bent specimen (three-point bending) perpendicular and parallel to the direction of bending yield different band shapes as illustrated in Fig. 10. Specifically, the band is well resolved into two peaks if the optical beam is parallel to the direction of bending (45° to the Burgers vector) while the higher energy peak is lost in favor of the lower energy one if the optical beam is perpendicular to the direction of bending (perpendicular to the Burgers

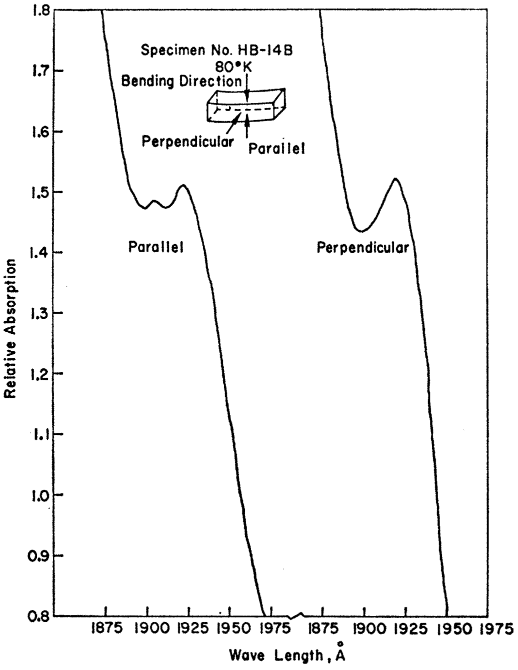

FIG. 10. Plot showing the dichroism of the beta band, deformed KBr, 80°K.

vector) as shown in Fig. 10. It is interesting to note that the dichroic behavior disappears when the deformed sample is annealed at 525°K for a few minutes then colored in Co^{60}. The shape of the beta band after the short annealing resembles that of undeformed samples.

V. DISCUSSION

There are at present two proposed models for the exciton states in ionic crystals. The "excitation" model,[9–11] where the unit excitation of the excition wave is assumed to be sufficiently localized in a unit cell that is somewhat characteristic of an excited state of a free atom, and the "transfer" model,[12–15] where the unit excitation involves the transfer of an electron from a halogen ion to the nearest-neighboring positive ion. They are two slightly different aspects of the same general group-theoretical problem and predictions of these models concerning multiplicity of absorption peaks are shown to be essentially identical.[16] The oscillator strength for the beta band in alkali halides has been estimated by Dexter,[17,18] assuming the "excitation" model in which the halogen ion electrons ($3p$ for Cl^-, $4p$ for Br^-, etc.) make transitions to bound levels in the field of an *F* center. Experimental observations of the beta band have been reported by Delbecq, Pringsheim, and Yuster[7] and others.[19,20]

Prismatic dislocation dipoles in alkali halides are essentially vacancy sheets on {011} type plane (perpendicular to the Burgers vector) which is comparatively long in the $[01\bar{1}]$ direction and short in the [100] direction. This is illustrated schematically in Fig. 11. Both the *F* center and the halogen ions as nearest neighbors to the *F* center feel essentially a tetragonal strain due to the presence of a nearby vacancy sheet or dislocation dipole. Three predictions can be made according to this model about the beta absorption band: (1) splitting of the p states, (2) mixing of the s and d states with the p states giving rise to weakly allowed transitions at slightly higher energies,[21] and (3) dichroism associated with the p states depending on the angle between optical beam and the Burgers vector. These predictions are essentially confirmed by the experiments reported in the previous section.

Although no spectacular changes are expected of the *F*-absorption band when dislocation dipoles are present, one might expect a slight peak shift of the *F*-absorption peak. Indeed such peak shift was repeatedly observed in the deformed KBr specimens. The results are shown in Fig. 12. It is interesting to note that the *F* peak shifted to higher energy in the deformed specimens and returned to values typical of undeformed specimens after brief annealing at 525°K. This is consistent with the hypothesis that the *F* centers are perturbed by the stress fields of the dislocation dipoles. If the coordinates are chosen such that the *Y* axis is parallel to the short dimension of the dipole, *X* axis perpendicualr to the dipole sheet and passing through one member of the two long edge-dislocation lines forming the dipole, and *Z* axis parallel to the same edge-dislocation line, the

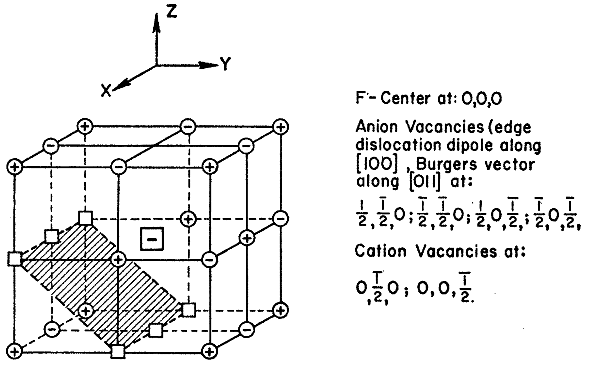

FIG. 11. Schematic diagram showing a unit cell of KBr containing an *F* center and an edge-dislocation dipole.

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[9] D. L. Dexter, Phys. Rev. **83**, 435 (1951).

[10] D. L. Dexter, Phys. Rev. **108**, 707 (1957).

[11] T. Muto, S. Oyaman, and H. Okuno, Progr. Theoret. Phys. (Kyoto) **20**, 804 (1958).

[12] A. von Hippel, Z. Physik **101**, 680 (1936).

[13] A. W. Overhauser, Phys. Rev. **101**, 1702 (1956).

[14] F. Bassani and N. Inchauspé, Phys. Rev. **105**, 819 (1957).

[15] B. Goodman and O. S. Oen, J. Phys. Chem. Solids **8**, 291 (1959).

[16] R. S. Knox and N. Inchauspé, Phys. Rev. **116**, 1093 (1959).

[17] D. L. Dexter, Phys. Rev. **83**, 435 (1951).

[18] D. L. Dexter, Phys. Rev. **83**, 1044 (1951).

[19] E. Berstein and J. J. Oberly, Phys. Rev. **79**, 903 (1950).

[20] H. Dorendorf, Z. Physik **129**, 317 (1951).

[21] H. Haken, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and the Physical Society, London, 1962), p. 462.

dilatational stress field at any point (X,Y) is given by[22]

$$(\sigma_{XX}+\sigma_{YY})=-\frac{bI}{2\pi}\left\{\frac{Y[(2+H)X^2+Y^2]}{(X^2+Y^2)^2+HX^2Y^2}-\frac{(Y+h)[(2+H)X^2+(Y+h)^2]}{[X^2+(Y+h)^2]^2+HX^2(Y+h)^2}\right\}, \quad (2)$$

where h= width of the dislocation dipole,

$$I=(c_{11}+c_{12})\left[\frac{c_{44}(c_{11}-c_{12})}{c_{11}(2c_{44}+c_{11}+c_{12})}\right]^{1/2},$$

and

$$H=\frac{(c_{11}+c_{12})(c_{11}-c_{12}-2c_{44})}{c_{11}c_{44}}.$$

The experimental shift of the F-absorption peak for KBr with hydrostatic pressure according to Eppler and Drickamer[23] is 0.1 wave number per atmosphere up to pressures of a few thousand atmospheres. The experimental shift shown in Fig. 12 thus corresponds to a hydrostatic pressure of about 350 atm. Equating this value with $\frac{1}{2}(\sigma_{XX}+\sigma_{YY})$ and substituting the appropriate elastic constants[22] into Eq. (2), one finds that the F center should be located on a set of curves shown in in Fig. 13 for various values of the dipole width (here three dipole widths are assumed, $5b$, $10b$, and $20b$) with respect to the core structure of an edge dislocation in NaCl according to Huntington and co-workers.[24] Neglecting the difference in core structure of an edge dislocation between NaCl and KBr, the results shown in Fig. 13 suggest that the most likely position of the F center is a few Burgers vectors away from the dislocation core slightly above the slip plane in the compression region of one of the edge-dislocation pairs that constitutes the dipole.

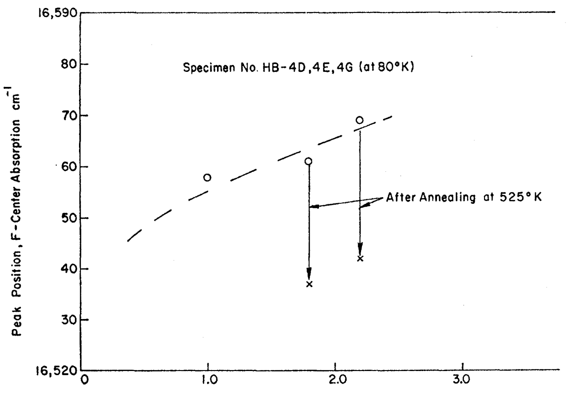

FIG. 12. Shift of F-center peak (at 80°K) with compression strain, deformed KBr.

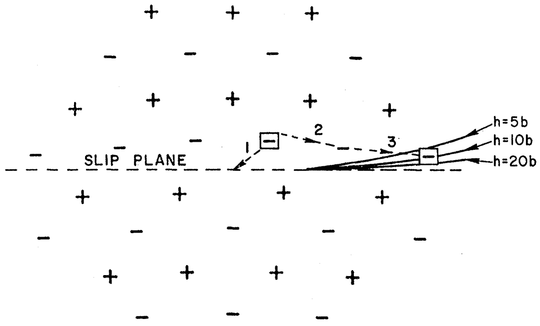

FIG. 13. Schematic diagram showing the core structure of an edge dislocation and possible sites of an F center formed during Co^{60} irradiation at 315°K.

Since Hookian elasticity theory was used to derive Eq. (2), which is not expected to yield valid results very near the core region of an edge dislocation, the location of the F centers described above can only be considered as a rough estimate. One must admit, however, that the estimation cannot be too far off since one is dealing with stress fields a few Burgers vectors away from the dislocation core.

It is to be noted that, in addition to the F centers originating from the dislocation dipoles, there are F centers formed from vacancies already present in the material as indicated by the intercepts at zero strain in Fig. 6. Since the F-absorption band is very broad, the shift of the F peak shown in Fig. 12 is at best an indication that those centers originating from the dislocation dipoles are located near the dipoles. It is difficult to pinpoint the exact location of these centers, although the peak-shift experiments suggest that they are at least two to three Burgers vectors away from the dislocation core, possibly more.

The multipeaks and dichroism associated with the beta-absorption band are interesting. It is not clear at present why the peaks are quite sharp under certain circumstances. Since the deformation was meant to form dislocation dipoles of principally one orientation, it is possible that the F centers originating from these dipoles line up more or less parallel to the dislocation line and give rise to essentially one-dimensional line defects.[6] Further studies are necessary to elucidate this point.

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[22] R. Chang, Acta Met. **10**, 951 (1962).

[23] R. A. Eppler and H. G. Drickamer, J. Chem. Phys. **32**, 1418 (1960).

[24] H. B. Huntington, J. E. Dickey, and R. Thomson, Phys. Rev. **100**, 1117 (1955).