IRRADIATION-INDUCED EXPANSION OF ALKALI HALIDE CRYSTALS AT ROOM TEMPERATURE

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(Received July 16, 1962)

Considerable effort has been directed in recent years toward determining the nature of defects and mechanisms by which they are introduced into ionic crystals by ionizing irradiation. Direct displacement processes are not energetically possible in this case. Measurements of mass density, macroscopic linear expansion, and F-center density indicate that Schottky disorder may be generated at room temperature.[1-3] Alternatively, the complement to the negative ion vacancy could be the halogen interstitial. It may be necessary to determine the nature of the complementary defects to the F center before the mechanisms of defect production can be definitely established. The purpose of this paper is to report a substantial increase in the lattice parameter of alkali halide single crystals following x irradiation at room temperature. An increase in lattice parameter suggests that interstitials are generated and/or that there is considerable relaxation in the vicinity of vacancies. It has been argued and assumed, in the past, that neither of these is the case.[1-4]

In Fig. 1 the reflected x-ray intensities in the vicinity of a Bragg maximum are given for unirradiated and irradiated NaCl. Similar data were obtained for several samples of NaCl, LiF and KCl, and fractional increases in the lattice parameter $\Delta d/d$ between approximately 10^{-5} and 10^{-4} were observed. The method of determining the line position from data such as that of Fig. 1 and, in addition, small changes in line shape will be discussed elsewhere in a more complete publication.[5] In Fig. 2, $\frac{1}{3}\Delta V/V$ as calculated from photoelastic data[6,7] is plotted vs $\Delta d/d$ for several LiF samples. Because of assumptions made in calculating $\Delta V/V$ from the photoelastic data, it is expected that this $\Delta V/V$ would be smaller than the true value.[7,8] The important result here, however, is that $\Delta d/d$ as determined by x-ray reflection is proportational to and of the same order of magnitude as the $\frac{1}{3}\Delta V/V$ determined by an optical transmission technique. A similar ratio of $\frac{1}{3}\Delta V/V$ to $\Delta d/d$ was found for one sample of NaCl. This $\Delta V/V$ for NaCl was reported previously to be close to $\Delta\rho/\rho$, the fractional change in mass density.[7] In Fig. 2 the fractional F-center density n_F/N is also given vs $\Delta d/d$.[9] A similar relationship between n_F/N and $\Delta d/d$ was found for two NaCl samples.[9] It is concluded that an important component of the macroscopic expansion is due to an increase in the lattice parameter and further that this $\Delta d/d$ is related to relaxation in the vicinity of interstitials and/or vacancies.[10] The strain causing the $\Delta d/d$ may be an important component of the interaction between

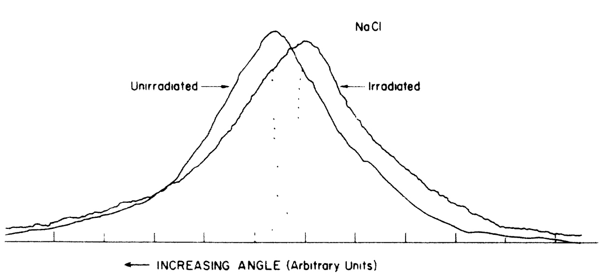

FIG. 1. Reflected x-ray intensity vs crystal angle (arbitrary units) in the vicinity of the (800) Cu $K\beta$ NaCl reflection. From these data $\Delta d/d \approx 1.4 \times 10^{-4}$. The dots indicate the mean angle at each intensity.

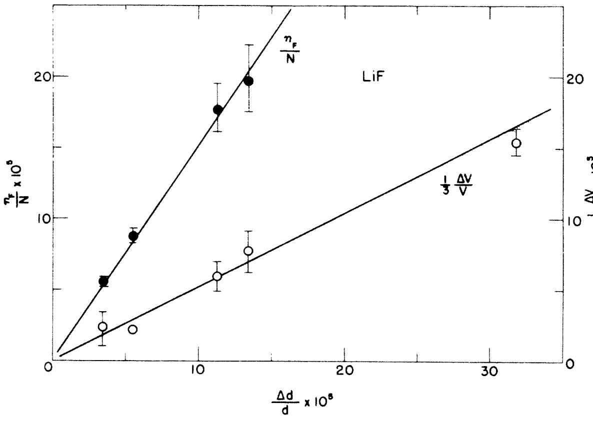

FIG. 2. The fractional F-center density n_F/N (f_F 0.8) and one-third the fractional volume expansion as determined from photoelastic data (see text) vs the fractional increase in lattice parameter $\Delta d/d$ for several samples of LiF. (The F-center densities were estimated by a curve-fitting process since it was not possible to observe directly the large absorption constants at the band maximum.)

these point defects and dislocations, and may also be an important consideration for nuclear magnetic resonance line broadening,[11] and changes in the low-temperature thermal conductivity[12] due to irradiation.

If only vacancies are produced during irradiation we have

$$-\Delta\rho/\rho \approx 3\Delta l/l \approx (\Delta V/V)_{\mathrm{Vac.}} + 3\Delta d/d$$

or

$$-\frac{\Delta\rho}{\rho}\Big/\left(\frac{\Delta V}{V}\right)_{\mathrm{Vac.}} \approx 1 + \frac{3\Delta d}{d}\Big/\left(\frac{\Delta V}{V}\right)_{\mathrm{Vac.}}, \qquad (1)$$

where $\Delta l/l$ is the fractional increase in length, $(\Delta V/V)_{\mathrm{Vac.}}$ is the unrelaxed fractional volume of the vacancies and the $\Delta d/d$ term represents possible relaxation due to the vacancies.[13] In contrast, if only vacancy-interstitial pairs are produced, we have

$$-\Delta\rho/\rho \approx [(3\Delta d/d) = (3\Delta l/l)] - \Delta M/M, \qquad (2)$$

where $\Delta M/M$ represents a possible fractional loss of mass by the escape of interstitials, and $\Delta d/d$ is now the relaxation due to vacancies and the remaining interstitials. In the following, $(\Delta V/V)_{\mathrm{Vac.}}$ is approximated by $(\Delta V/V)_F$, the fractional volume of unrelaxed vacancy pairs calculated on the basis of one pair per observed F center. $(\Delta V/V)_F$ is then a lower limit to $(\Delta V/V)_{\mathrm{Vac.}}$. By taking $(\Delta V/V)_F$ as a reference it is possible to compare the data of various investigators.[3]

Lin[2] and Rabin[3] have found at low and intermediate F-center densities (10^{-6} to 10^{-5}) that $(3\Delta l/l)/(\Delta V/V)_F \approx 1$ for NaCl and KCl. Hence either $3\Delta d/d \approx 0$ [Eq. (1)] or Eq. (1) cannot be satisfied. At intermediate and higher F-center densities (1×10^{-5} to 4×10^{-5}), $-(\Delta\rho/\rho)/(\Delta V/V)_F$ has been found to be in the range of 1.3 to 2.2 for KCl[1] and 1.2 ± 0.3 for one sample of NaCl.[7,14] The wide spread of values for KCl may be due to nonuniform coloration and/or varying perfection of samples. In the present work $(3\Delta d/d)/(\Delta V/V)_F$ was found to be about 2.1 ± 0.4 for LiF and 0.9 ± 0.5 for NaCl[14] ($10^{-5} \leq n_F/N \leq 10^{-4}$).

Although the limitations, precision, and spread of the available data at higher n_F/N are such that it is not possible to clearly distinguish between Eqs. (1) and (2), a consideration of the linear expansion data at smaller n_F/N strongly suggests that Eq. (1) cannot be satisfied.[15] Thus the data to date suggest the production of interstitials at room temperature. The opposite conclusion of Berry[4] may be related to the fact that $(\Delta V/V)_F$ was not measured and $\Delta d/d$ was compared to the $\Delta l/l$ and $\Delta\rho/\rho$ data observed by others. But more recent results have demonstrated that while the expansion is sensitive to sample perfection,[3] the ratio of expansion to F-center density is not so sensitive if allowance is made for vacancies in the lattice before irradiation.[3]

The author wishes to thank the Fulbright Commission in the Federal Republic of Germany for financial support during most of this work. He is also indebted to Professor H. Witte for the hospitality of the Eduard Zintl Institute and to Professor Witte and Professor E. Wöffel for making x-ray equipment available. The author is especially indebted to Dr. A. Weiss for assistance in the discussions about almost every phase of this work. Helpful discussions were also had with Professor W. H. Robinson. Messrs. Paschalis, Zory, and Mumaw assisted with irradiations and measurements.

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*Work was partially supported by the U. S. Atomic Energy Commission.

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[9] The ratio of F- to M-center densities is roughly constant for all of the samples for which $\Delta d/d$ was measured. These samples were irradiated under varying conditions of intensity and energy of x rays and there most certainly were small differences in crystal temperature.

[10] There is considerable experimental evidence that expansion due to relaxations in the vicinity of negative ion vacancies is independent of the presence of the F-center electrons for these materials. See references 2, 4, 7, 8, and S. Mascarenhas, D. A. Wiegand, and R. Smoluchowski, Bull. Am. Phys. Soc. 5, 422 (1960). However, calculations indicate that the sign of the relaxation of nearest-neighbor ions to the negative-ion vacancy may be dependent on the presence of the electron. See M. P. Tosi and F. G. Fumi, Nuovo cimento 7, 95 (1958); T. Kojima, J. Phys. Soc. Japan 12, 918 (1957); B. S. Gourary and F. J. Adrian, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, New York, 1960), Vol. 10, p. 127; and

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[13] It is assumed here that the defects are so distributed that a fractional change in lattice parameter results in an equal fractional change in macroscopic dimensions. For a discussion of this point see J. D. Eshelby, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, New York, 1956), Vol. 3, p. 79.

[14] $f_F = 0.7$ was used for comparison with earlier work.

[15] Consideration of the *M* and *R* bands decreases the possibility of satisfying Eq. (1). See B. J. Faraday, H. Rabin, and W. D. Compton, Phys. Rev. Letters 7, 57 (1961).

FARADAY ROTATION NEAR THE BAND EDGE OF SILICON

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(Received May 10, 1962)

It has been only recently that a renewed interest in the Faraday effect occurring with infrared radiation at wavelengths corresponding to the energy gap has become evident,[1] and as a consequence a meager amount of empirical data exists. Hartmann and Kleman[2] reported on measurements of the room-temperature Verdet coefficients for an intrinsic germanium sample near the edge. The results indicated that both indirect and direct transitions contributed to the dispersion. Intrinsic silicon is an excellent material for studying the effects of indirect transitions on the Faraday rotation, because the direct transitions require such a high photon energy that they should have little or no effect on the dispersion at wavelengths beyond the edge. Hence one should see Faraday rotation phenomena associated only with the indirect transitions when the sample is irradiated with polarized radiation of wavelengths approaching those corresponding to the intrinsic edge.

We have observed Faraday rotation in intrinsic silicon at infrared wavelengths from 1.05 microns to 5 microns at 297°K and at 77°K. The experimental technique is a conventional one and is a modification of that used by Austin in studying Bi_2Te_3.[3] The Verdet coefficients of an *n*-type silicon sample (30-Ω cm) at a magnetic-field strength of 19.1 kilogauss is shown in Fig. 1. We propose that the dispersion effects responsible for these curves are associated only with the mechanism corresponding to indirect transitions.

Lax and Nishina[4] have developed an expression for the Faraday rotation corresponding to indirect transitions based upon a quantum mechanical

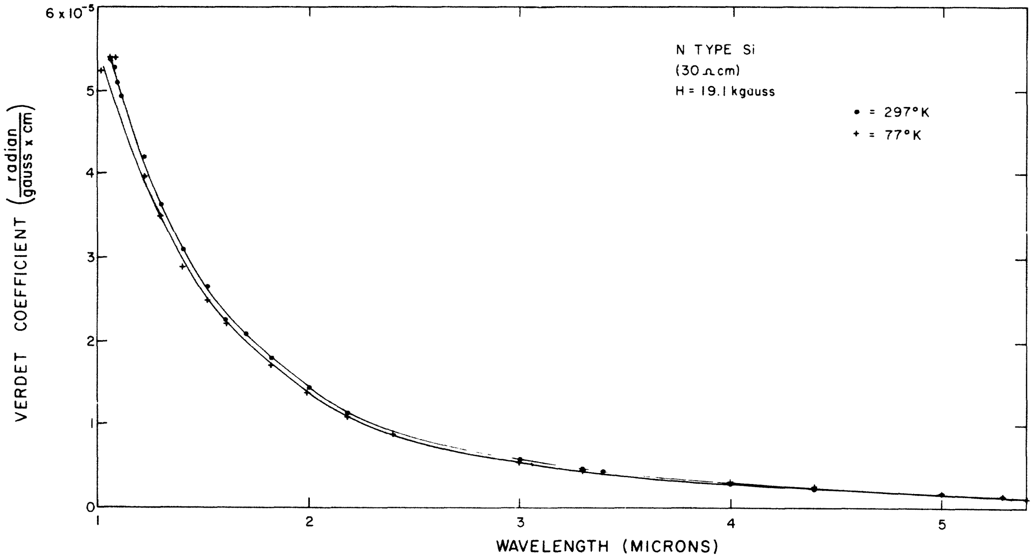

FIG. 1. Verdet coefficients for *n*-type silicon at 77°K and 297°K. Magnetic-field strength 19.1 kG.