Equivalence of X-Ray Lattice Parameter and Density Changes in Neutron-Irradiated LiF

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The lattice expansion in neutron-irradiated LiF was investigated in order to establish either Frenkel or Schottky defects as the cause of the expansion. For uniformly irradiated crystals, it was shown that x-ray lattice parameter and density changes are equivalent to within 6 percent. It follows that Schottky defects cannot account for more than 6 percent of the expansion and that Frenkel defects are predominant. The annealing of a nonuniformly irradiated crystal indicates a recovery process of order higher than one.

INTRODUCTION

THE lattice expansion of LiF single crystals irradiated with pile neutrons was observed by x-ray lattice parameter and density changes. It is reasonable to assume that the expansion was caused by irradiation induced atomic displacements. If these displacements lead to Frenkel defects, or equal numbers of vacancies and interstitial atoms, then recent theoretical work[1,2] has shown that the x-ray and density changes would be equivalent. On the other hand, if the displacements lead to Schottky defects, or pure vacancies with the extra atoms going to the surface, the density change would be larger. The LiF measurements were used to decide between Frenkel and Schottky defects for an irradiation-induced lattice expansion. The choice of LiF is a convenient one; large lattice expansions may be observed for short irradiations because of the large $Li^6(n,\alpha)H^3$ cross section. This reaction converts the slow-neutron flux of the pile into energetic alphas and tritons, which are the major cause of displacements in the lattice.

X-RAY AND DENSITY MEASUREMENTS

X-ray lattice parameter measurements of the crystals (obtained from the Harshaw Chemical Company) were made with a North American Phillips Company x-ray spectrometer, using the 200 and 400 reflections of the Cu $K\alpha$ doublet. The zero for the Bragg angles was established in each measurement by making the two reflections consistent with Bragg's law, or the ratio of the sines of the 200 and 400 Bragg angles equal to one-half. For 10 unirradiated crystals used in these measurements, the 400 Bragg angles thus corrected agreed to within ±0.3′ of arc (±0.007 percent in lattice parameter). The lattice parameter change induced by irradiation was obtained from the change in the corrected 400 angles of each crystal. (For the relative measurements used here, refractive index effects cancel out.) Some line broadening was observed in the irradiated crystals, but this did not contribute appreciably to the error in the x-ray measurement.

Density measurements were effected by weighing

each crystal in air and CCl_4 at a known temperature. The density of unirradiated crystals between 20 and 26°C was found to be

$$\rho = (2.64639 - 2.916 \times 10^{-4}t) \pm 0.00022, \qquad (1)$$

where t is the temperature in °C. This agrees within experimental error with the value of 2.63905 ± 0.0001 at 25°C[3] and 2.64030 ± 0.00014 at 20°C[4] given by independent measurements. A density *versus* temperature curve was plotted for one irradiated crystal, and the slope was in good agreement with Eq. (1). Further measurements on irradiated crystals were made at one temperature, and the density change was obtained using Eq. (1).

EQUIVALENCE OF X-RAY AND DENSITY CHANGES

a. Pile Neutron Experiment

Since the x-ray measurement, involving a relatively small penetration, will detect changes at the surface of a crystal, and the density measurement changes throughout the volume, care must be taken to irradiate the crystal uniformly. The $Li^6(n,\alpha)H^3$ reaction absorbs the thermal neutrons, and their "e thickness" in LiF is 0.3 cm. In order to use thermal neutrons, a crystal was chosen whose thickness was small compared to 0.3 cm and which was large enough for accurate density measurements.

The crystal was 0.075 cm thick by 2.6 cm square and was given an irradiation of 6×10^{16} neutrons per cm² in the ORNL graphite reactor. This resulted in a lattice expansion as shown by the uppermost point in Fig. 1, where the change in lattice parameter derived from x-ray measurements, $(\Delta a/a)_x$, is plotted against that derived from density measurements, $(\Delta a/a)_\rho$. The lower points represent the results of thermal anneals at successively higher temperatures from 315°C to 550°C, gradually bringing the lattice back to its original state. The points lie along a straight line of slope 1.05 ± 0.02. The straightness of the line indicates that the slope is a valid parameter for comparing x-ray and density changes.

[1] P. H. Miller, Jr., and B. R. Russell, J. Appl. Phys. **24**, 1248 (1953).
[2] J. D. Eshelby, J. Appl. Phys. **24**, 1249 (1953); **25**, 255 (1954).
[3] C. A. Hutchison and H. L. Johnston, J. Am. Chem. Soc. **62**, 3167 (1940).
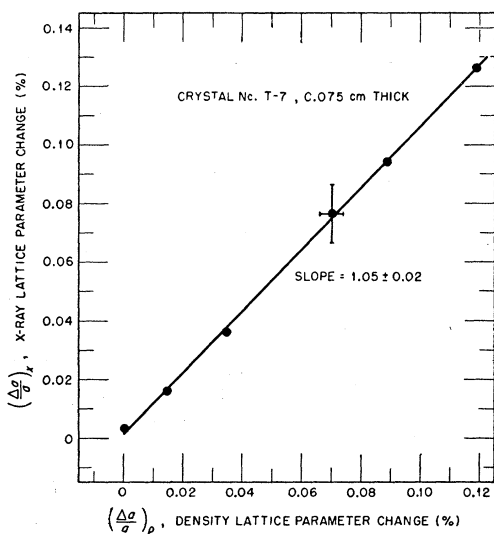[4] D. A. Hutchison, J. Chem. Phys. **13**, 383 (1945).

Fig. 1. Lattice expansion for a thin crystal as derived from x-ray and density measurements.

The crystal thickness was not entirely negligible compared with the e thickness for thermal neutrons, and the small deviation from unity in the slope is caused by neutron attenuation, resulting in a non-uniformity in atomic displacements throughout the crystal. The expansion cannot be explained by helium and tritium impurities since 6×10^{16} neutrons per cm^2 produce a concentration of 3×10^{-6} for each impurity, which would account for less than 0.2 percent of the lattice expansion.

To calculate the slope including neutron attenuation, we note that, disregarding saturation and elastic effects, $(\Delta a/a)_x$ is proportional to the surface yield of the $Li^6(n,\alpha)H^3$ reaction and $(\Delta a/a)_\rho$ is proportional to the volume yield. Since the plot of $(\Delta a/a)_x$ versus $(\Delta a/a)_\rho$ is a straight line with slope near unity, saturation affects both these quantities in the same way. Thus we can ignore saturation, and the slope of the line is related to the ratio of the aforementioned surface-to-volume yields. It is not equal to this ratio because there is an anisotropic expansion of the crystal which will be taken into consideration as a final step in the calculation.

The crystal's dimensions are such that it approximates an infinite slab for which the yields may be calculated analytically. Consider an isotropic flux of uniform energy, nv per unit solid angle, incident upon an infinite slab of thickness x_0. The number of neutrons per cm^2 per sec incident on both surfaces, n_0, is $nv/2$, and the number absorbed is

$$n_a = \int_0^{\pi/2} nv \cos\theta [1 - \exp(-N\sigma_a x_0/\cos\theta)] \sin\theta d\theta, \quad (2)$$

where θ is the incident angle, N the number of Li atoms per cm^3, and σ_a is the $Li(n,\alpha)H^3$ reaction cross

section for thermal neutrons. Assuming, for the moment, a Maxwellian distribution of neutrons and noting that we have a "$1/v$" reaction,

$$\sigma_a = 1.128\sigma_0(T/293)^{\frac{1}{2}},$$

where σ_0 is the absorption cross section for mono-energetic neutrons at 0.025 ev, and T is the neutron temperature in °K.[5] The neutron cross-section tables[6] give 70 barns for σ_0, and T may be estimated by adding 140°C[7] to the moderator temperature of about 140°C. This gives 57.4 barns for σ_a. An error of 5 percent in σ_a will result in an error of less than 1 percent in slope. Integrating Eq. (2) and dividing by $n_0 x_0$, we obtain the fraction of neutrons absorbed per unit thickness,

$$\frac{n_a}{n_0 x_0} = \frac{1}{x_0}\left\{1 + (\alpha_a x_0 - 1)e^{-\alpha_a x_0} - \alpha_a^2 x_0^2 \int_{\alpha_a x_0}^{\infty} \frac{e^{-y}}{y} dy\right\}, \quad (3)$$

where $\alpha_a = N\sigma_a$ and the integral is tabulated.[8] This result has been obtained by many investigators.[9]

The rate of neutron absorption per cm^3 in a surface layer, normalized to unit thickness, is

$$n_{as} = \frac{1}{2}\int_0^{\pi/2} (nv \cos\theta)\left(\frac{\alpha_a}{\cos\theta}\right)\left[1 + \exp\left(-\frac{\alpha_t x_0}{\cos\theta}\right)\right] \sin\theta d\theta$$

$$= \frac{nv}{2}\alpha_a\left(1 + e^{-\alpha_t x_0} - \alpha_t x_0 \int_{\alpha_t x_0}^{\infty} \frac{e^{-y}}{y} dy\right), \quad (4)$$

where $\alpha_t = N(\sigma_a + \sigma_s)$, and σ_s is the sum of the scattering cross sections for Li and F (5.5 barns).

The ratio of the surface-to-volume yields for thermal neutrons is

$$R = \frac{n_{as}/n_0}{n_a/n_0 x_0}$$

$$= \alpha_a x_0 \frac{1 + e^{-\alpha_t x_0} - \alpha_t x_0 \int_{\alpha_t x_0}^{\infty} \frac{e^{-y}}{y} dy}{1 + (\alpha_a x_0 - 1)e^{-\alpha_a x_0} - \alpha_a^2 x_0^2 \int_{\alpha_a x_0}^{\infty} \frac{e^{-y}}{y} dy}. \quad (5)$$

Substituting the values for the crystal in Fig. 1, 3.52 cm^{-1} for α_a, 3.86 cm^{-1} for α_t, and 0.075 cm for x_0, we obtain 1.07 for R.

To correct for epithermal neutrons assume a "cadmium ratio" of 20, or that 5 percent of the yield is due

[5] D. J. Hughes, Pile Neutron Research (Addison-Wesley Press, Inc., Cambridge, 1953), p. 90.
[6] Neutron Cross Sections, Atomic Energy Commission Report AECU 2040 (Office of Technical Services, Department of Commerce, Washington 25, D. C., 1952).
[7] G. M. Branch, Manhattan District Declassified Document MDDC-747, 1946 (unpublished).
[8] E. Jahnke and F. Emde, Tables of Functions with Formulae and Curves (Dover, New York, 1945).
[9] See the references in R. Keyes, Atomic Energy Commission Report AECD-3000, 1950 (unpublished).

to epithermals, neglecting attenuation. The epithermal yield is comparatively uniform throughout the crystal and is introduced by adding $0.1\alpha_a$ to n_{as}/n_0 and n_a/n_0x_0 in the first part of Eq. (5). The result is a corrected ratio of 1.06.

Since there is a nonuniform distribution of defects, the calculation of the experimental slope becomes a problem of a self-strained system with cubic anisotropy. In order to evaluate the lattice expansion in the direction of the crystal thickness (z axis), we assume Hooke's law, net zero tensile stresses in the x and y directions, and zero stress at the surface. The resultant strain on the surface in the z direction will be given by

$$e_z = \frac{\beta}{1-\nu}\left\{\frac{n_{as}}{n_0}(1+\nu) - 2\nu\frac{n_a}{n_0x_0}\right\},$$

where β is the constant of proportionality in a non-constrained system between e_z and the fraction of neutrons absorbed, and ν is Poisson's ratio. The average strain in the z direction is $\beta n_a/n_0x_0$, and the experimental slope S is the ratio of the two, or

$$S = \frac{1+\nu}{1-\nu}R - \frac{2\nu}{1-\nu}.$$

Taking 0.278 as a value of ν, for Harshaw crystals,[10] we obtain 1.11 ± 0.05 for S. Comparing with the experimental slope of 1.05 ± 0.02, the deviation from unity not caused by neutron attenuation is 6 ± 5 percent. Thus we have established the equivalence of x-ray and density changes caused by lattice defects within 11 percent.

b. Epithermal Neutron Experiment

Neutron attenuation may be reduced by shielding the crystal with cadmium, leaving only the epicadmium flux effective for the (n,α) reaction and for any direct atomic displacements. The appropriate cross sections for these processes are much smaller, and an irradiation 17 times as long was required for comparable results. Two crystals, one twice as thick as the other, were shielded with 0.030'' of cadmium, and the results of the irradiation and successive anneals from 315°C to 550°C are shown in Fig. 2. Since the data scatter about the same straight line, within error, there is no detectable effect caused by thickness or attenuation, and $(\Delta a/a)_x$ may be compared with $(\Delta a/a)_\rho$ directly, yielding the fact that x-ray and density changes are equivalent within 6 percent. The fact that these data require no correction for neutron attenuation makes the result more reliable, and we conclude that x-ray and density changes in neutron-irradiated LiF are equivalent to within 6 percent.
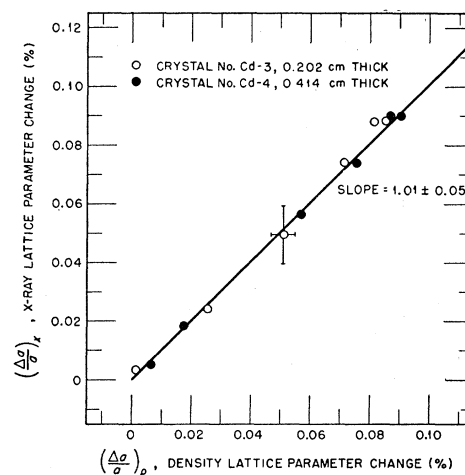
[10] S. Rao, Curr. Sci. 18, 336 (1949).

FIG. 2. Lattice expansion for cadmium shielded crystals as derived from x-ray and density measurements.

FRENKEL *VERSUS* SCHOTTKY DEFECTS

The displaced atoms causing the expansion may lead to either Schottky or Frenkel defects. A Schottky defect is produced when an atom at a normal lattice site comes to the surface leaving a vacancy behind. The additional atomic volume on the surface is seen by the density, but not the x-ray, measurement. This was pointed out by Seitz[11] in connection with experiments determining Avogadro's number. For Schottky defects, Seitz showed in effect that[12]

$$n_s = -\Delta(\rho v_c)/\rho v_c, \qquad (6)$$

where ρ is the density, v_c is the volume of a unit cell, as seen by x-rays, and n_s is the concentration of Schottky defects. In our notation,

$$n_s = 3[(\Delta a/a)_\rho - (\Delta a/a)_x]. \qquad (7)$$

From the previous section, the quantity in square brackets is zero to within 6 percent of the lattice expansion, or n_s is at most equal to 6 percent of the volume expansion. Since Schottky defects cause a volume expansion about equal to their concentration, this mechanism cannot account for more than 6 percent of the observed expansion.

The above restriction does not apply to Frenkel defects, or vacancy interstitial pairs. Recent theoretical work[1,2] has shown that these defects are characterized by an exact equivalence of $(\Delta a/a)_x$ and $(\Delta a/a)_\rho$. We therefore conclude that the lattice expansion in neutron-irradiated LiF is predominantly due to Frenkel defects.

THE ANNEALING PROCESS

In order to study the annealing process, several non-uniform irradiations were made on thick crystals.

[11] F. Seitz, Revs. Modern Phys. 18, 384 (1946).
[12] See reference 11. Equation (6) shows a minus sign not shown in Seitz's article, where he was concerned only with absolute magnitudes.

FIG. 3. Lattice expansion for thick crystals as derived
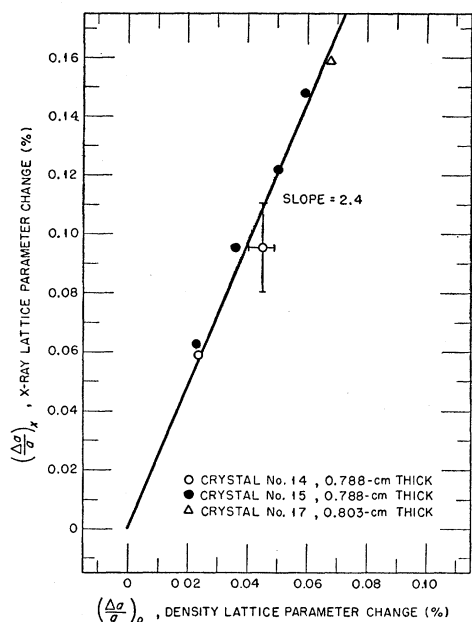from x-ray and density measurements.

FIG. 4. Annealing data for a thick crystal as derived
from x-ray and density measurements.

Three crystals 2.6 cm square by 0.8 cm thick were sub-
jected to single or successive irradiations that totaled
up to 6×10^{16} neutrons per cm^2, and the results are
shown in Fig. 3. X-ray measurements were taken on
the 2.6-cm square surfaces. Crystal No. 17 was then
annealed at successively higher temperatures from
275°C to 560°C, with the results shown in Fig. 4. The
original slope of 2.4 in Fig. 3 indicates a nonuniform
distribution of defects, as expected, while the annealing
points in Fig. 4 approach a line of smaller slope, in-
indicating a change toward a more uniform defect
distribution.

To explain the annealing process, we need a rough
approximation to the original defect distribution. Tak-
ing the e thickness for thermal neutrons as 0.3 cm and
the average path for a neutron as twice the perpendicu-
lar distance from the largest surface, the neutrons from
one large face of the crystal are attenuated to about
$e^{-8/3}$ on reaching the center and $e^{-16/3}$ on reaching the
opposite face. Adding the contributions from both
sides, the ratio of neutrons reaching the surface to
those reaching the center is about 1.00 to 0.14. Since
the x-ray measurement will detect changes at the sur-
face and the density measurement changes throughout
the volume, any change in defect distribution will show
up easily starting with the above ratio.

There are two processes which might change the
distribution, diffusion and recombination of vacancies
and interstitials. The two compete since, if recombina-
tion occurs over a short diffusion path, diffusion will
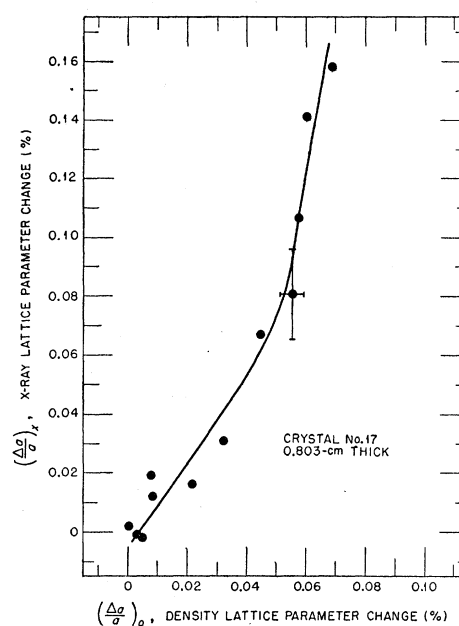not change the defect distribution. In fact, an order

of magnitude argument shows that this is the case.
In the least favorable region for recombination, the
center of the crystal, there was originally a lattice ex-
pansion of 14 percent that on the surface, or a $(\Delta a/a)_x$
of 2.2×10^{-4}. If we assume that a vacancy interstitial
pair is equivalent at most to an extra average atomic
volume, the minimum concentrations of pairs in the
interior is 6.6×10^{-4}. Then a vacancy or interstitial
will have to take only 1.5×10^8 interatomic steps before
recombination. Assuming a random-walk process, the
average distance travelled in any one direction is a
factor of 10^6 smaller than the crystal thickness, too
small to change the macroscopic defect distribution.
The argument is even stronger in the higher defect
concentration near the surface.

Having eliminated diffusion, consider the recombina-
tion processes. In a process of order one, such as the
recombination of neighboring vacancies and inter-
stitials, there would be no change in the defect dis-
tribution. In a process of order higher than one, the
high concentration of defects near the surface decreases
proportionately faster than the low concentration in the
interior, tending toward a more uniform defect dis-
tribution. This explains the curvature of the line in
Fig. 4 and establishes the annealing process as of order
higher than one.