VACANCY CONCENTRATION MEASUREMENTS AND MANY-BODY FORCE EFFECTS IN KRYPTON CRYSTALS*

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Three-body interactions have been considered by Jansen and coworkers to account for the observed stability of the fcc structure of the noble gas solids[1] and for the observed stability of numerous other nonmetallic crystal structures.[2] Other workers have examined the effects of many-body interactions on such noble-gas crystal properties as stacking-fault energy,[3] elastic constants,[4] vacancy-formation energy,[5] and lattice relaxation around the vacancy.[6] The actual magnitudes of the many-body contributions to the cohesive energies of insulating solids have remained controversial, however, because little direct experimental evidence is available.[7]

Measurement of the vacancy formation energy ϵ in a noble-gas crystal should yield particularly well-defined evidence about possible many-body forces. The major contribution to ϵ comes from the potential-energy change of the crystal lattice when a crystal of N atoms occupying N atomic sites goes to a configuration having N atoms on $N+1$ sites. In the static rigid-lattice approximation it is easily shown that

$$\epsilon = -E_P/N - E_3/N + (\text{higher order terms}), \quad (1)$$

where E_P/N is the (negative) potential energy per atom relative to atoms separated at infinity, and E_3 is the (positive) three-body contribution to the potential energy of the crystal. Additional contributions to ϵ in the real crystal come from lattice and electronic relaxation around the vacancy and from changes in the vibrational spectrum of the lattice. Most calculations for vacancies in argon indicate only rather small lattice relaxation energies, of order $+0.02E_P/N$.[6,8] Further, Doniach and Huggins[9] estimate that electronic distortion around an argon vacancy may account for a contribution to ϵ of order $+0.1E_P/N$ at most.

We have measured directly the formation of thermally generated vacancies in three large-grained rods of solid krypton, by means of simultaneous length and lattice-parameter expansion measurements. The specimens were of nominal 99.995% purity and were supported in an unconstrained manner in a carefully thermostated cryostat. The experimental arrangement is indicated in Fig. 1. Visual observation, through filar micrometer microscopes, of tiny (50 μm average diameter) steel spheres embedded with the body of the transparent specimens permitted measurements of the change in length which were relatively independent of the unstable specimen surface (vapor pressure ~0.7 bar near the triple point). Lattice-parameter changes were obtained by an oscillating back-reflection x-ray camera.

The atomic fraction of extra, thermally generated, substitutional atomic sites $\Delta N/N$ is given at temperature T by[10]

$$(\Delta N/N)_T = 3(\Delta l/l_0 - \Delta a/a_0)_T, \quad (2)$$

where Δl and Δa are changes in length and lattice-parameter relative to reference values l_0 and a_0. l_0 and a_0 are measured at a temperature where the equilibrium vacancy concentration is negligible. Relation (2) is indepen-

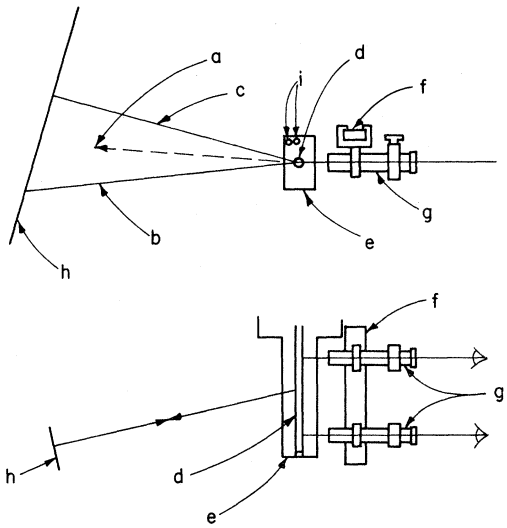

FIG. 1. Schematic diagram of length and lattice-parameter measurement apparatus. *a*: diffracting plane normal. *b*: diffracted x-ray beam. *c*: incident x-ray beam. *d*: specimen. *e*: thermostated specimen chamber. *f*: Invar bar. *g*: filar micrometer microscopes. *h*: x-ray film plane. *i*: resistance thermometers.

dent of lattice relaxation about the vacancies.

Figure 2 shows the results of our measurements. The measurements have been carried out over the temperature range 4.2-100°K for specimen No. 2. The bulk and x-ray expansion data for this specimen are in excellent agreement for $T < 75$°K, while above 75°K the bulk expansion exceeds the lattice-parameter expansion. Difficulties with the gauge length of specimen No. 1 make the data for this specimen somewhat less certain though measurements were carried out up to 114°K. However, data for this specimen are in essential agreement with data for specimen No. 2 and have also been indicated. Furthermore, the expansion measurements obtained for specimen No. 3 firmly substantiate our other results. At 100°K we find $\Delta l/l_0 - \Delta a/a_0 = (3.2 \pm 0.4) \times 10^{-4}$. This leads to the vacancy free energy of formation $g = 1380 \pm 26$ cal/mole vacancy at 100°K.

From the temperature dependence of $\Delta N/N$ we deduce the monovacancy enthalpy of formation $h = 1780 \pm 200$ cal/mole vacancy and entropy of formation $s = (2.0^{+1.0}_{-0.5})k$, where k is Boltzmann's constant. Here we have taken account of multiple-vacancy clustering at the higher temperatures to a first approximation.[10,11]

The experimentally determined vacancy enthalpy is related to ϵ by $h = \epsilon + pv$, where v is the vacancy volume of formation. At the pressures of the experiments, the term pv is negligible. Salter[12] has shown that the potential energy of the static lattice may be determined through analysis of vapor-pressure data. For krypton he finds $-E_P = 2747 \pm 18$ cal/mole using the vapor-pressure data of Beaumont and co-workers.[11] This value of $-E_P$ is in good agreement with the calorimetric determination $-E_P = 2790 \pm 29$ cal/mole.[11] In the following we adopt the approximate mean value $-E_P = 2760 \pm 30$ cal/mole. Thus, using Eq. (1) and the approximate relaxation corrections noted below it, we estimate the many-body contribution to the potential energy of solid krypton to be $+650 \pm 300$ cal/mole. The stated limits of uncertainty include contributions both from possible errors in our measurements and from uncertainties in the corrections.

The value ~650 cal/mole is consistent with recent calculations for the triple-dipole interaction,[4,7] or with calculations of three-body exchange energy,[5] which are similar in magnitude. We therefore cannot discriminate between various possibilities for the origin of the many-body force contributions nor assign their importance relative to one another. Some further indication that three-body effects may be important in krypton comes from the experimentally determined value of the Poisson ratio near $T = 0$, $\sigma = 0.274 \pm 0.006$.[13] For a solid having only central-two-body interactions, one expects $\sigma = \frac{1}{4}$.[14]

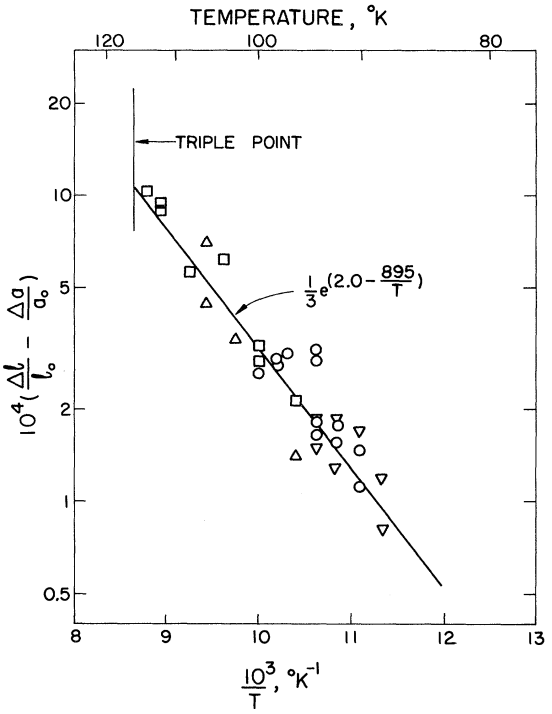

FIG. 2. Measured values of $\Delta l/l_0 - \Delta a/a_0$ versus reciprocal temperature. □, specimen No. 1, heating run; △, specimen No. 1, cooling run; ○, specimen No. 2, heating run; and ▽, specimen No. 3, heating run.

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[9]S. Doniach and R. Huggins, Phil. Mag. 12, 393 (1965).

[10]R. O. Simmons, in Radiation Damage in Solids, Proceedings of the International School of Physics "Enrico Fermi," Course XVIII, edited by D. S. Billington (Academic Press, Inc., New York, 1962), p. 568. See also references cited there.

[11]Our value for h is in good agreement with that estimated in an ad hoc manner from caloric data by Beaumont and coworkers, 1770 ± 200 cal/mole vacancy, but our value for the entropy of formation differs from the value of those workers, $s = (3.4^{+0.5}_{-1.1})k$ [R. H. Beaumont, H. Chihara, and J. A. Morrison, Proc. Phys. Soc. (London) 78, 1462 (1961)].

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[14]We note that the presence of zero-point vibrations in the crystal will contribute slightly to produce σ values different from $\frac{1}{4}$. The 6-12(1N) model of T. H. K. Barron and M. L. Klein [Proc. Phys. Soc. (London) 85, 533 (1965)] includes such zero-point effects and predicts $\sigma = 0.257$. It is this model which makes the best published prediction of Θ_0^C, the equivalent Debye temperature in the limit $T \to 0$.

CHANGE IN THE DIELECTRIC CONSTANT OF SbSI CAUSED BY ILLUMINATION

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We have measured the change in the dielectric constant of SbSI caused by illumination. The change is positive below the Curie temperature and negative above. The result is discussed in connection with the strain caused by illumination reported previously.

In this Letter, we report a change in the dielectric constant ϵ' of SbSI along the c axis caused by illumination. The change is discussed in connection with the strain $\Delta L^i/L$ along the c axis caused by illumination in the presence of a dc electric field along the c axis.[1]

The area of the (001) faces of the specimens used was about 10^{-2} mm^2, and the Curie temperature (T_C) was about 19.5°C. Evaporated gold on both sides [(001)] was used as electrodes. The measurements were made at 1 kc/sec using an inductive arm bridge, which is similar to that described by Cole and Gross.[2] The strength of the applied ac electric field in a specimen was less than 0.1 V/cm. The dc electric field was applied from a stabilized voltage supply to a specimen through a high resistance. The illumination was provided by a normal 150-W incandescent lamp through an interference filter.

Typical experiment results are shown in Fig. 1. Curve A shows the temperature dependence of ϵ' in the dark without the dc electric field. Curves B and C show the temperature dependence of ϵ' in the dark and that of ϵ' affected by the illumination, respectively, in the presence of a dc electric field of 1 kV/cm along the c axis. ϵ' is increased by the illumination below T_C and decreased above. Furthermore, it should be noted that ϵ' decreases when a dc electric field of 1 kV/cm is applied.

If the observed change in ϵ' caused by the illumination were attributed to the change of the applied electric field E which might come

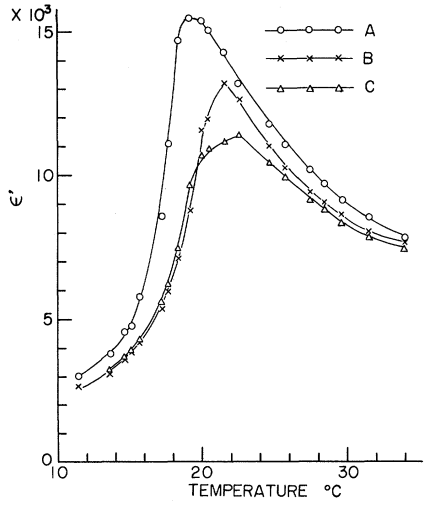

FIG. 1. A: temperature dependence of ϵ' in the dark. B: ϵ' in the dark in the presence of 1.0 kV/cm. C: ϵ' affected by an illumination of 550-mμ wavelength in the presence of 1.0 kV/cm.