

not observed, presumably because either the strength is lower or the resonance width is appreciably greater (i.e., the pole at $\omega = \omega_F$ is further from the real axis). The angular positions at which these peaks would occur are shown by arrows A and B in Fig. 5.

V. SUMMARY

A quantum approach to phonon-assisted (or acoustically induced) optical-harmonic generation based on perturbation theory has been developed. The results obtained in second order suggest that resonant behavior may be observed if the acoustic beam is almost normal to the optical beam. This possibility is studied experimentally in LiNbO_3 with a $1.06\text{-}\mu$ optical fundamental and 300-MHz longitudinal

acoustic wave. A double resonance peak is observed, with a separation of 1.2° in the rotational position of the crystal. This separation agrees closely with the expected separation of $\frac{1}{2}\mu$ between resonances due to the pole at $2\omega_F$ for the two processes of absorption and stimulated emission of phonons. Two more resonances which could occur (due to the pole at ω_F) have not been observed.

ACKNOWLEDGMENTS

The authors are indebted to Dr. G. H. Azarbayejani for providing excellent lithium-niobate crystals, R. F. Steinberg for the transducer work, and to D. M. Shupe and Dr. R. K. Mueller for useful discussions.

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¹P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich, *Phys. Rev. Letters* **7**, 118 (1961).

²S. E. Harris, R. W. Wallace, and G. F. Quate, *IEEE J. Quantum Electron.* **QE-4**, 354 (1968).

³G. D. Boyd, F. R. Nash, and D. F. Nelson, *Phys. Rev. Letters* **24**, 1298 (1970).

⁴D. F. Nelson and M. Lax (unpublished).

⁵C. Y. She, *Phys. Rev.* **176**, 461 (1968).

⁶See, for example, A. Yariv, *Quantum Electronics* (Wiley, New York, 1967), Chap. 21; N. Bloembergen, *Nonlinear Optics* (Benjamin, New York, 1965), Chap. 4 and references therein.

⁷See, for example, P. Roman, *Introduction to Quantum Field Theory* (Wiley, New York, 1969), Chap. 4.

⁸It should be noted that $2\omega_F + \Omega_q$ is essentially the true second harmonic since $\Omega_q \sim 10^{-6}\omega_F$ for $\sim 300\text{-MHz}$ phonons. Similarly, $\omega_F + \Omega_q \approx \omega_F$ to a high degree of accuracy.

⁹It should be noted that the converse does not necessarily apply, because Eq. (14) is invalid when αL is not small. In fact, the first term in Eq. (14) decreases as $(\alpha L)^{-3}$

when αL is large.

¹⁰For the same reason, it is not possible to satisfy both $\tilde{\kappa}_1 = 0$ and $\omega_{F2} = 2\omega_F$ (i.e., for the second term), although $\omega_{F2} = 2\omega_F$ and $\tilde{\kappa}_2 = 0$ can be satisfied simultaneously.

¹¹J. A. Giordmaine, *Phys. Rev. Letters* **8**, 19 (1962); C. Deutsch, D. M. Shupe, and P. N. Keating, *Bendix Tech. J.* **2**, 101 (1969).

¹²It is worth noting here that experimental data for conventional SHG and Brillouin scattering indicates that in practice the F requirement is usually less stringent than the f requirement. This is probably due to the importance of refractive-index inhomogeneities in the SHG process.

¹³These results are approximate because the usual SHG index-matching conditions are not satisfied (i.e., the points A and B in Fig. 2 are not coincident). However, the approximation is usually a very good one.

¹⁴J. F. Geusic, H. J. Levinstein, S. Singh, R. G. Smith, and L. G. Van Uitert, *Appl. Phys. Letters* **12**, 306 (1968).

¹⁵E. G. Spencer, P. V. Lenzo, and K. Nassau, *Appl. Phys. Letters* **7**, 67 (1965).

Free Energies of Vacancies and Rare-Gas Crystal Mixtures

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(Received 21 December 1970)

The Gibbs-Bogolyubov variational principle is used to calculate the free energy of vacancy formation $g_v(T)$ in solid Kr, Ne, and Cu and the interchange parameter w for dilute Ar-Kr mixtures. These calculations include vibrational properties and, since any temperature can be considered, all other thermal properties can be obtained. For the vacancy, the formation energy obtained in this way as $h_v = g_v - (dg_v/dT)_P T$ is essentially the same as expected from equivalent static-lattice calculations at $T = 0^\circ\text{K}$. Thus, the vibrational motion does not encourage further relaxation and there remains a large discrepancy between computed and observed h_v in solid Kr, although the entropies s_v compare well. The computed w 's agree very well with the observed values of Fender and Halsey.

I. INTRODUCTION

Most calculations of point-defect properties such

as the formation energy¹⁻⁴ or substitutional energy are done for $T = 0^\circ\text{K}$ only. This is because (a) a static vibration-free lattice is considered and (b)

only at $T = 0^\circ\text{K}$ can an energy variational principle be used to find the relaxation about the defect. Here, we extend this sort of calculation to $T \geq 0^\circ\text{K}$ using the Gibbs-Bogolyubov free-energy variational principle to replace the usual energy principle. It is then possible to include the vibrational motion, to calculate the free energy from which all other thermodynamic properties can be obtained and to investigate temperature dependences.

In Sec. II the free-energy principle is expressed in a form useful for thermodynamic properties of defects. The method is then applied specifically to vacancies in solid Kr and Ne in Sec. III. The chief purpose is to test whether including the atomic vibrational amplitudes, which are $\sim 10\text{--}13\%$ near the melting temperature in Kr, can improve agreement between theory³⁻⁵ and experiment^{6,7} by allowing greater atomic relaxation around the vacancies. Cu is also briefly considered. In Sec. IV the expression for the interchange parameter w in the theory of mixtures⁸ is generalized to include vibrational effects for dilute mixtures. The w is then calculated for Ar-Kr dilute mixtures and compared with experiment. The applicability of regular solution theory for solid Ar-Kr mixtures is also discussed.

II. GIBBS-BOGOLYUBOV PRINCIPLE FOR THERMAL PROPERTIES OF DEFECTS

The Gibbs-Bogolyubov theorem^{9,10} states that if the exact density function $\rho \equiv e^{-\beta H} / \text{Tr}\{e^{-\beta H}\}$ for a system with Hamiltonian H is approximated by a convenient trial density ρ_T , then the free energy $F_T \equiv \text{Tr}(\rho_T H) + \beta^{-1} \text{Tr}(\rho_T \ln \rho_T)$ is an upper bound to the exact free energy $F = E - TS = -\beta^{-1} \ln \text{Tr}(e^{-\beta H})$. Here $\beta \equiv (kT)^{-1}$ where k is Boltzmann's constant. This may be proved using the general inequality⁹⁻¹¹

$$\text{Tr}(\rho_T \ln \rho) \leq \text{Tr}(\rho_T \ln \rho_T), \quad (1)$$

which holds for any two arbitrary unit trace matrices ρ_T and ρ . On substituting the density ρ , the left-hand side of (1) becomes

$$\text{Tr}[\rho_T(-\beta H - \ln \text{Tr} e^{-\beta H})] = -\beta \text{Tr}(\rho_T H) + \beta F. \quad (2)$$

Combining (1) and (2) gives

$$F \leq \text{Tr}(\rho_T H) + \beta^{-1} \text{Tr}(\rho_T \ln \rho_T) \equiv F_T. \quad (3)$$

The great usefulness of (3) lies in the direct relation between the convenient approximate model described by a model Hamiltonian H_m and

$$\rho_T = e^{-\beta H_m} / \text{Tr}(e^{-\beta H_m}). \quad (4)$$

Then, since $F_T \geq F$, we may parametrize H_m and minimize F_T with respect to these parameters to find the best H_m which describes the real system.

For a solid with two-body forces

$$H = T + \frac{1}{2} \sum_{i \neq j} v(\vec{r}_i - \vec{r}_j). \quad (5)$$

Inequality (3) has been applied to perfect-crystal dynamics¹² with success using a model harmonic picture

$$H_m = H_h = T + \frac{1}{2} \sum_{i,j} \vec{u}_i \cdot \vec{\Phi}_{ij} \cdot \vec{u}_j, \quad (6)$$

where $\vec{u}_i \equiv \vec{r}_i - \vec{R}_i$ are the atomic displacements and $\vec{\Phi}_{ij}$ are variational parameters. On writing

$$H = H_h - \frac{1}{2} \sum_{i,j} \vec{u}_i \cdot \vec{\Phi}_{ij} \cdot \vec{u}_j + \frac{1}{2} \sum_{i \neq j} v(\vec{r}_i - \vec{r}_j) \quad (7)$$

and substituting H in Eq. (3)

$$F_T = F_h - \frac{1}{2} T_h + \frac{1}{2} \sum_{i,j} \langle v(\vec{r}_i - \vec{r}_j) \rangle, \quad (8)$$

where $F_h \equiv \text{Tr} \rho_T (H_h + \ln \rho_T)$ and $T_h \equiv \sum_{i,j} \sum_{\alpha\beta} \Phi_{i\alpha,j\beta} \times \langle u_{i\alpha,j\beta} \rangle$ are the harmonic free and vibration energies, respectively, and $\langle 0 \rangle \equiv \text{Tr}(\rho_T 0)$. In normal coordinates¹²

$$F_T = \beta^{-1} \sum_{\mathbf{k}\lambda} [\ln \langle 2 \sinh(\frac{1}{2} \beta \hbar \omega_{\mathbf{k}\lambda}) \rangle - \frac{1}{4} \beta \hbar \omega_{\mathbf{k}\lambda} \coth(\frac{1}{2} \beta \hbar \omega_{\mathbf{k}\lambda})] + \frac{1}{2} \sum_{i \neq j} \langle v(\vec{r}_i - \vec{r}_j) \rangle, \quad (9)$$

where $\omega_{\mathbf{k}\lambda}$ are the harmonic frequencies.

To describe point defects, we reduce this model to an Einstein approximation. At high temperatures, the region of experimental interest here, this should be a good approximation. Also, since we want only averaged properties over the degrees of freedom (which are nearly $\frac{1}{2} kT$ in energy at high temperature) and the explicit kinetic part of F is small, we do not need a precise description of the vibrational frequency spectrum. Then, on introducing an Einstein frequency ω_E for each atom i , F_T can be written as

$$F_T = \beta^{-1} \sum_{i\alpha} \left\{ \ln \left[2 \sinh \left(\frac{\Theta_E(i\alpha)}{2T} \right) \right] - \frac{1}{4} \frac{\Theta_E(i\alpha)}{T} \coth \left(\frac{\Theta_E(i\alpha)}{2T} \right) \right\} + \frac{1}{2} \sum_{i \neq j} \langle v(\vec{u}_{ij} + \vec{R}_{ij}) \rangle, \quad (10)$$

where $\sum_{i\alpha}$ is over the atoms i and directions α , and $\Theta_E(i\alpha) \equiv \hbar \omega_E(i\alpha)/k$ is the Einstein temperature. For a pure crystal each $\Theta_E(i\alpha)$ is identical. Near defects we expect the atoms to vibrate differently and allow these atoms i to have a private $\Theta_E(i\alpha)$ along axis α .

Following Eq. (16) of Ref. 12, $\langle v(\vec{r}_i - \vec{r}_j) \rangle$ may be expressed as a space average, which in the Einstein model, is

$$\langle v(\vec{r}_i - \vec{r}_j) \rangle = \int d\vec{r}_i d\vec{r}_j v(\vec{r}_i - \vec{r}_j) \times \prod_{i\alpha} (A_{i\alpha}/\pi)^{1/2} e^{-A_{i\alpha}(\vec{r}_i - \vec{R}_i)^2_{\alpha}}, \quad (11)$$

where

$$A_{i\alpha} = \frac{mk\Theta_E(i\alpha)}{\hbar^2} \tanh\left(\frac{\Theta_E(i\alpha)}{2T}\right). \quad (12)$$

The variational parameters are then the interatomic separations and the $\theta_E(i\alpha)$ (or equivalently the rms deviations $\langle u_{i\alpha}^2 \rangle^{1/2}$). In a simple Einstein model $\langle u_{i\alpha}^2 \rangle = (2A_{i\alpha}^2)^{-1}$. For equivalent force constants, the Debye and Einstein frequencies are related by $\omega_D^2 = \frac{5}{3}\omega_E^2$. Then at high temperature for a Debye model

$$\langle u_{i\alpha}^2 \rangle_D = \frac{3}{5} \langle u_{i\alpha}^2 \rangle_E = \frac{3}{5} (2A_{i\alpha}^2)^{-1} \equiv \frac{1}{3} U^2.$$

The atoms were assumed to interact via a pair-wise Morse potential

$$V(r) = \epsilon(e^{-2\gamma(r-r_0)} - 2e^{-\gamma(r-r_0)}). \quad (13)$$

For the rare-gas crystals, the parameters ϵ , r_0 , and γ were obtained¹³ by fitting to three $T = 0^\circ\text{K}$ solid properties plus the mixture rules $\epsilon_m = (\epsilon_1\epsilon_2)^{1/2}$ and $r_{0m} = \frac{1}{2}(r_{01} + r_{02})$. For Cu, the parameters of Girifalco and Weizer¹⁴ were used. The Morse potential is useful since (11) can be integrated analytically for spherically symmetric $A_{i\alpha}$ values.

III. VACANCIES

In a perfect crystal with free energy $F(0)$, the N atoms occupy N lattice sites. To form a single vacancy, we place the N atoms on $N+1$ sites and the free energy of formation f_v is defined¹⁵ as the total resulting free-energy change (other than the configurational part)

$$f_v = F(1v) - F(0). \quad (14)$$

The equilibrium number n of such noninteracting vacancies at temperature T is¹⁵

$$c_v = n/(N+n) = e^{-f_v/kT}. \quad (15)$$

The $F_T(0)$ is calculated for given T here by introducing the observed¹⁶ interatom spacing $R_{ij}(T)$ into Eq. (10) and minimizing $F_T(0)$ with respect to Θ_E . This provides both $F_T(0)$ and the perfect lattice rms vibrational amplitude $U \equiv (27/104)^{1/2}$ from (12). For $F(1v)$, a model for the distortion about the vacancy must be introduced. Here the first three neighbor shells were allowed separate amplitudes $U_1(1)$, $U_{||}(1)$, $U(2)$, and $U(3)$, with each atom in a given shell assumed identical. For the first shell, a different amplitude perpendicular (\perp) and parallel (\parallel) to the vacancy was permitted. All other amplitudes were fixed at U . The first three shells were allowed to relax separately either radially inward or outward. The outer shells could relax as if imbedded in an elastic continuum with radial displacement at point r given by¹⁷

$$\vec{u}(r) = -c/r^2. \quad (16)$$

The c was determined so that the continuum relaxation $\vec{u}(r)$ joined continuously onto the third-shell displacement. The interatomic potential was cut off after five shells and an elastic representation used thereafter. $F_T(1v)$ was then computed via (10) by minimizing it with respect to all these parameters. Since the whole crystal can relax via (16), the only reference to the pure crystal is through the rms amplitude U . In each case a test relaxation calculation was made with an atom placed in the vacant site. This verified that the computed relaxation was, indeed, due to the vacancy and not a result of simple shrinkage of the perfect crystal.

A. Vacancies in Solid Kr and Ne

The computed $f_v(T)$ in Kr for four temperatures are listed in Table I. Since the $pV(1v)$ term in $g_v = f_v + pV(1v)$ is negligible, these values also give g_v which is plotted in Fig. 1. From this plot the entropy and energy of formation can then be obtained from the definitions $s_v \equiv -(dg_v/dT)_p$ and $h_v = g_v + s_v T$.

From Table I, the rms deviation of the first neighbors vibrating toward the vacancy, $\langle u_{||}^2(1) \rangle^{1/2} \equiv U_{||}(1)$, is seen to increase by $\sim 13\%$ while that perpendicular decreases by $\sim -1\%$. These changes are displayed pictorially in Fig. 2. The rms deviations of the second and third shells decreased only slightly ($\sim -0.3\%$) and are not listed. The mean position of the first and third shells (and thus the shells beyond) relax inward while the second relaxes outward.

The vibrational changes and relaxations about a vacancy in Ne were essentially the same as in Kr, so only $g_v(T)$ for Ne is shown in Fig. 1. As a result we do not expect any difference between Ne and Kr defect properties to arise from kinetic effects. Although the (kinetic energy)/(potential energy) is much greater in Ne, the (rms deviation)/(interatom spacing), U/R , is essentially constant near the triple point for all the rare-gas crystals and the U/R ratio appears to be the physically important parameter.

Observations of the vacancy concentration c_v are made at saturated vapor pressure (svp) and usually presented⁶ as $(\ln c_v)_{\text{svp}}$ vs $1/T$. To great accuracy, svp may be taken as constant pressure here, so that $-k$ times the slope of this plot is

$$-k \left(\frac{\partial \ln c_v}{\partial (1/T)} \right)_P = \frac{\partial}{\partial T^{-1}} (g_v/T)_P = -T \left(\frac{\partial g_v}{\partial T} \right)_P + g_v = h_v(T), \quad (17)$$

where the above definitions of s_v and h_v have been used. In principle $h_v(T)$ can depend on temperature. However, if $g_v(T)$ can be fitted by a straight line of form $g_v(T) = g_0 - g'T$ ($-s_v = g'$, a constant), then $h_v(T) = (g_0 - g'T) + g'T$ is a constant g_0 . In Kr the $g_v(T)$ can be fitted well by a straight line (since we attach no physical significance to the wiggle in Fig. 1) and this gives, in the temperature range

80 to 115 °K for Kr

$$\begin{aligned} s_v &= 2.3 R, \\ h_v &= 2850 \text{ cal/mole.} \end{aligned} \quad (18)$$

In Ne the $g_v(T)$ cannot be fitted by a straight line. Taking the tangent at high temperatures gives for Ne

$$\begin{aligned} s_v &= 2.2 R \\ h_v &= 574 \text{ cal/mole.} \end{aligned} \quad (19)$$

At lower temperatures $s_v = 1.3 R$, $h_v = 538 \text{ cal/mole}$. The nonlinear temperature dependence of $g_v(T)$ in Ne arises since, at $T \leq 15^\circ \text{K}$, the zero-point energy makes a significant contribution to the lattice expansion and keeps it from contracting linearly with T .

The remarkable feature of the h_v in (18) and (19) is that they essentially equal the values obtained from a static-lattice calculation at $T = 0^\circ \text{K}$. In this limit and for no relaxation, h_v is just the potential energy per atom E_p in the pure lattice.¹⁸ For Kr and Ne

$$E_p \approx 2810 \text{ and } E_p \approx 590 \text{ cal/mole,}$$

respectively, using the observed values of the sublimation energy and calculations of the zero-point energy.¹³

B. Vacancies in Cu

To test whether a temperature dependent h_v in a metal could be predicted with this model, h_v for Cu at $T = 550, 700, 850, \text{ and } 1000^\circ \text{C}$ was computed. In this temperature range, g_v was well fitted by

$$g_v = 3.28 - (1.82 k)T \text{ eV,} \quad (20)$$

with h_v constant within 0.01 eV. This h_v is somewhat higher, but comparable with $h_v = 3.19 \text{ eV}$ obtained by Doyama and Cotterill¹⁹ in a static-lattice calculation at $T = 0^\circ \text{K}$ [h_v (observed)²⁰ = 1.17 eV]. Although the Morse potential is poor for Cu, (20) suggests that h_v is a constant and that $T = 0^\circ \text{K}$ values of h_v will represent high temperatures well. Since the zero-point energy and the U/R ratio in Cu is

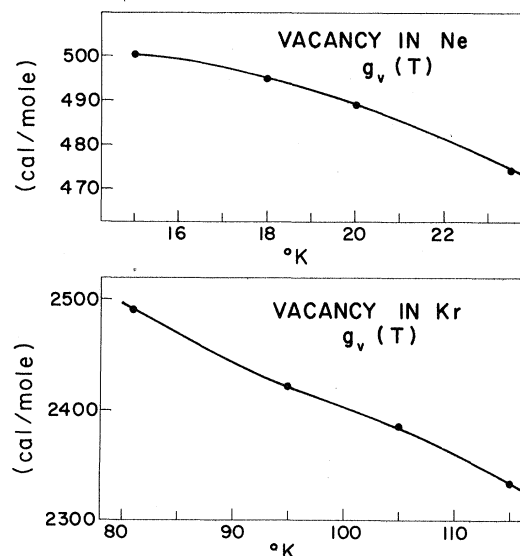


FIG. 1. The Helmholtz free energy of vacancy formation in solid neon and krypton.

much less than in Kr, this could also be inferred from the Kr results.

IV. DILUTE Ar-Kr SOLID MIXTURES

In a dilute solution of atoms A in a host B , the quantity of most direct experimental interest is the partial vapor pressure P_A of A ,^{8,21}

$$P_A/P_{A_0} = e^{\beta(\mu_A - \mu_{A_0})} = x e^{w/kT}. \quad (21)$$

Here P_{A_0} is the vapor pressure above a pure A solution at temperature T , μ_A and μ_{A_0} are the chemical potentials of A in the mixture and pure A solutions, and x is the concentration of A in B . The w is the interchange parameter which we now derive and calculate using the second relation in (21) as its definition. The first relation can be derived by noting the free-energy change on transferring a mole of A from the pure A to the AB solution via their respective vapors.²²

TABLE I. The free energy of vacancy formation in solid krypton. U/R is the ratio of the rms vibrational amplitude to the interatom spacing in perfect Kr. $\delta U_{\perp}(1)/U$ and $\delta U_{\parallel}(1)/U$ are the changes in U for the first-neighbors atoms for vibration toward (\parallel) and perpendicular (\perp) to the vacancy. δR_i is the change in distance from the vacancy of neighbor shell i .

T (°K)	f_v (cal/mole)	$\frac{U}{R}$ (%)	$\frac{\delta U_{\perp}(1)}{U}$ (%)	$\frac{\delta U_{\parallel}(1)}{U}$ (%)	$\frac{\delta R_1}{R}$ (%)	$\frac{\delta R_2}{R_2}$ (%)	$\frac{\delta R_3}{R_3}$ (%)
115	2332	9.95	-1.3	12.5	-0.40	0.07	-0.09
105	2387	9.38	-0.8	13.1	-0.35	0.07	-0.03
95	2420	8.84	-0.4	13.3	-0.30	0.10	0.0
80	2491	8.03	-0.2	13.4	-0.30	0.10	0.0

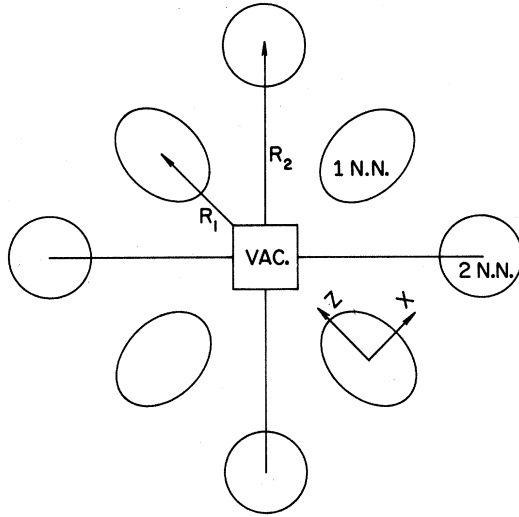


FIG. 2. A schematic representation of the atomic relaxation and vibrational amplitude changes around a vacancy in Kr as listed in Table I.

By dilute we mean the A atoms are so widely separated that they do not interact. Then the solution energy E is independent of the configuration of A 's. Thus, in calculating the mixture free energy, $e^{-\beta E}$ is independent of configuration so that

$$\begin{aligned}
 F_M &= -\beta^{-1} \ln \left(\sum_{\text{all config states}} e^{-\beta E} \right) \\
 &= -\beta^{-1} \ln \left(\sum_{\text{states}} e^{-\beta E} \sum_{\text{all config}} 1 \right) \\
 &= -\beta^{-1} \ln \left[\sum_{\text{states}} e^{-\beta E} \left(\frac{N!}{N_A! N_B!} \right) \right] \\
 &= -\beta^{-1} \ln (\text{Tr} e^{-\beta E}) - \beta^{-1} \ln \left(\frac{N!}{N_A! N_B!} \right). \quad (22)
 \end{aligned}$$

For the first term of (22) we use the trial free energy (10) which we write as a sum over free energies per atom f_i

$$F_T = \sum_i f_i. \quad (23)$$

It is convenient to break this sum up as

$$\begin{aligned}
 F_T &= N_A(f_A + F_{B,a}) + (N - nN_A)f_{B,u} \\
 &= N_A(f_A + F_{B,a} - nf_{B,u}) + Nf_{B,u}. \quad (24)
 \end{aligned}$$

Here f_A and $f_{B,u}$ are the free energies of an A atom and a B atom unaffected by the presence of A . The $F_{B,a}$ is the free energy of the nB atoms near each A which are affected by the presence of the A atom. The free energy of the pure A solution is just $F_0 = N_A f_{A0}$. Thus using (22) and (24)

$$\begin{aligned}
 \mu_A - \mu_{A0} &\equiv \left(\frac{\partial F_M}{\partial N_A} - \frac{\partial F_0}{\partial N_A} \right) \\
 &= (f_A + F_{B,a} - nf_{B,u} - f_{A0}) \\
 &\quad + \beta^{-1} \ln(N_A/N_A + N_B),
 \end{aligned}$$

so that from (21)

$$w \equiv (f_A + F_{B,a} - nf_{B,u} - f_{A0}). \quad (25)$$

Using the Einstein trial free energies (10),

$$f_A = f_{hA} - \frac{1}{2} t_{hA} + \frac{1}{2} \sum_{j \neq A} \langle v_{Aj}(AB) \rangle \quad (26)$$

and

$$\begin{aligned}
 F_{B,a} - nf_{B,u} &= \sum_{i=1}^n \left(\delta f_{hB} - \frac{1}{2} \delta t_{hB} + \sum_{j \neq i, A} \delta \langle v_{ij}(BB) \rangle \right) \\
 &\quad + \left(\frac{1}{2} \sum_{j \neq A} \langle v_{Aj}(AB) \rangle - \frac{1}{2} \sum_{j \neq B} \langle v_{Bj}(BB) \rangle \right). \quad (27)
 \end{aligned}$$

The first term in (27) arises from the vibrational changes and the relaxations of the nB atoms around each A . The second arises since each of the nB atoms has one of its original BB bonds replaced by an AB bond when near an A atom.

If we now take the static-lattice limit and assume pure A and B have identical lattice spacings then w reduces to

$$w = \sum_{j \neq A} v_{jA}(AB) - \frac{1}{2} \sum_{j \neq i} [v_{ij}(AA) + v_{ij}(BB)], \quad (28)$$

which is exactly the definition given for this limit by Guggenheim⁸ (p. 23). His w was defined such that if we start with two pure lattices and inter-

TABLE II. The interchange parameter w for dilute solution of Kr in Ar. U_0 and U_I are the rms vibrational amplitudes of the host Ar and impurity Kr, respectively. δU_{\parallel} and δU_{\perp} are the change in rms amplitudes of the first-neighbor Ar for vibration of parallel (\parallel) and perpendicular to the Kr impurity. δR is the change in the first-shell spacing R .

T (°K)	Pure Ar	Kr impurity		First Ar neighbor to Kr			w (cal/mole)
	$\frac{U_0}{R}$ (%)	$\frac{U_I}{R}$ (%)	$\frac{U_I - U_0}{U_0}$ (%)	$\frac{\delta U_{\parallel}}{U_0}$ (%)	$\frac{\delta U_{\perp}}{U_0}$ (%)	$\frac{\delta R}{R}$ (%)	
80	10.1	8.1	-20	-5.1	+0.6	+0.7	109.22
70	9.3	7.6	-18	-7.1	+1.6	+0.8	123.58
60	8.4	6.9	-18	-8.5	+1.4	+0.8	138.94

TABLE III. The interchange parameter w for dilute solution of Ar in Kr. U_0 , U_I , δU_{II} , δU_I , and δR have the same meaning as in Table II.

T (°K)	Pure Kr $\frac{U_0}{R}$ (%)	Ar impurity $\frac{U_I}{R}$ (%)		First Kr neighbor to Ar			w (cal/mole)
			$\frac{U_I - U_0}{U_0}$ (%)	$\frac{\delta U_{II}}{U_0}$ (%)	$\frac{\delta U_I}{U_0}$ (%)	$\frac{\delta R}{R}$ (%)	
100	9.1	11.5	+26	+5.2	-0.6	-0.4	(149)
90	8.6	10.8	+26	+5.6	-0.8	-0.4	151.6
80	8.0	10.2	+26	+6.1	-0.4	-0.4	157.3
70	7.5	9.5	+26	+6.4	-0.4	-0.4	161.3

change one A with one B the total energy increase is $2w$.

To compute w at a given T , we first calculate f_{A0} and $f_{B0} = f_{B,u}$ by inserting the observed lattice spacing¹⁶ $R(T)$ in (10) and minimizing (10) in each case. f_{A0} can be used directly in (25) and $f_{B,u}$ in (27). Then an A atom is inserted in the B lattice and the free energy of this structure minimized. In this minimization, the A atom was allowed a distinct vibrational amplitude U_I and the surrounding B's were given the same parametrization as in the vacancy case. When the minimum F_M is found, (27) can be calculated.

A. Results

The results for dilute Ar-Kr mixtures are tabulated in Tables II and III. Only the rms amplitude of the host (U_0), of the impurity (U_I), and of the first shell of B's, along with the relaxation of the first shell, are listed since the other parameters changed little.

From Table II we see the rms amplitude of Kr impurity is less than that of the host Ar, as expected from the increased mass, with $(U_I - U_0)/R \sim -1.8\%$. Using the position of the minimum of the Morse potential as a measure of the "core" size of the atom, we see that the Kr core is greater by $[r_m(\text{Kr}) - r_m(\text{Ar})]/r_m(\text{Ar}) \sim +6.7\%$. Thus despite the reduced amplitude, Kr appears larger than Ar by $\sim +4.9\%$. As a result, the first-shell Ar atoms relax outward and their vibrational amplitude toward the Kr (U_{II}) is reduced. For Ar in Kr, a similar estimate finds a net decrease in Ar size relative to Kr of $\sim -4.1\%$. Thus the first-shell Kr atoms relax inward and increase their amplitude toward the Ar—though less in magnitude than the Kr in Ar case. It is interesting to note that the rms amplitudes of Ar and Kr at a given temperature are approximately the same, irrespective of which lattice they are in.

B. Implications of Results for Nondilute Mixtures

From Tables II and III, we see that w is not the same at a given temperature for Ar- and Kr-rich mixtures. Thus we expect w to vary with composi-

tion in a general Ar-Kr mixture. This variation is due to the different lattice constants of Ar and Kr. Since the basic assumption of the strictly regular solution theory is a constant w , this theory cannot be expected to hold exactly for nondilute Ar-Kr mixtures.

The w is also temperature dependent. Provided this is recognized, it does not affect the validity of regular solution theory.⁸ In the temperature range 60–100 °K, the $w(T)$ here can be fitted by

$$\begin{aligned} w(T) &= 226 - 1.46T \text{ for dilute Kr in Ar,} \\ w(T) &= 203 - 0.66T \text{ for dilute Ar in Dr.} \end{aligned} \quad (29)$$

There is no foundation for this dependence—this form just happens to fit. Also, this dependence for the Ar in Kr limit is not well determined for at $T = 90^\circ\text{K}$ and $T = 100^\circ\text{K}$ the points of Table III are unreliable. These are unreliable since pure Ar does not exist above $T = 83.8^\circ\text{K}$, and $f_{\text{Ar},0}$ above this must be obtained by extrapolation. Since w is obtained from a sensitive cancellation of large quantities, any error in this extrapolation is multiplied by about 20 in w . For this reason the temperature dependence is poorly determined.

For temperatures considered here $(w/kT) \leq 1$. Thus, should regular solution theory hold, the zeroth approximation to it should give good results for $T \geq 60^\circ\text{K}$. In this approximation, the partial vapor pressures for concentrations of A, $0 \leq x \leq 1$, are⁸

$$\begin{aligned} P_A/P_{A0} &= x e^{(1-x^2)/kT}, \\ P_B/P_{B0} &= (1-x) e^{x^2 w/kT}. \end{aligned} \quad (30)$$

Fitting (30) to observed pressures would provide w within 4% at the worst limit of $x = \frac{1}{2}$ and low temperature, and within 1% if fitted up to $x = \frac{1}{4}$ or $\frac{3}{4}$ at high temperature, with w being underestimated.

Finally, the heat of mixing, $H_M = Nx(1-x) \times (w - Tdw/dT)$, for $x = \frac{1}{2}$ is $H_M = 55$ and 51 cal/mole using the $w(T)$ in Tables II and III, respectively. The temperature of critical mixing, given by $w(T)/kT_c \sim 2.45$, is $T_c = 36$ and 37°K for these two values of $w(T)$.

C. Comparison with Experiment

The $w(T)$ of Table III may be compared directly with the observed values of Fender and Halsey.²¹ They found w between 169.6 cal/mole at 85°K and 144.3 cal/mole at 100°K, and that their results were well fitted by

$$w = 291 - 1.39T \text{ cal/mole.} \quad (31)$$

Thus the values in Table III agree reasonably well although the temperature dependence does not—which probably results from the extrapolation problem discussed in Sec. IV B. A similar problem arises in experiment since the pure Ar vapor pressure must be extrapolated above $T = 83.8^\circ\text{K}$ to get w .

The measurements were extended to Ar concentrations $x = 0.15$. At this x , w decreased by 6 ± 3 cal/mole. Assuming a linear extrapolation between the results in Tables II and III at $T = 80^\circ\text{K}$, the calculations predict a decrease of 7 cal/mole, which is of the correct sign and magnitude.

From the point of view of testing calculations, experiments on Kr in Ar would be most interesting since no extrapolation problems arise there.

V. DISCUSSION

The basic variational model used here, Eq. (10), is very similar to the variational cell model used by Mansoori and Canfield²³ to describe melting. The Gibbs-Bogolyubov principle has also been used by them to describe pure²⁴ and mixed liquids²⁵ with a hard-core interatomic-potential system used as a model. Critiques and comparisons²⁶ with perturbation theory of this work has also been presented. A most interesting general discussion of variational principles with historical references has been presented by Huber.⁹

On expanding $\langle v(u_{ij} + R_{ij}) \rangle$ in (11) about the lattice points, we see that F_T retains all even anharmonic terms with all odd terms vanishing since the Gaussian is an even function. Thus F_T includes an approximate treatment of anharmonicity and it is for this reason that it has been successful in pure crystals,¹² though corrections to it are not insignificant.²⁷ A defect calculation similar to the present one (but using a method proposed by Mayer) which retains the quartic anharmonic term with no self-consistency has been given by Allnatt and Rowley.²⁸

The novel feature of the present vacancy calculation is a self-consistent evaluation of the vibration-

al motion and an investigation of temperature dependences. The purpose was to test whether additional atomic relaxation and thus a reduced h_v in better agreement with experiment for Kr would be obtained when the large vibrational motion was incorporated. Also, an elastic boundary around the vacancy was included. The basic result is that the relaxation and h_v found are essentially the same as found in static-lattice calculations at $T = 0^\circ\text{K}$.^{3,5} There thus remains a large and unsatisfactory disagreement between the calculated h_v for Kr in Eq. (18) and the observed $h_v = (1780 \pm 200)$ cal/mole.^{6,7} The present results serve largely, then, to eliminate one possible explanation of this disagreement. The entropy computed here is in quite good agreement with the observed values^{6,7} for Kr ($s_v = 2.0^{+1.0}_{-0.5} R$ and $s_v = 3.4^{+0.5}_{-1.1}$) but since h_v is not, this is perhaps fortuitous.

The presence of many-body potential contributions in solid Kr is a much discussed solution to this disagreement.^{4,6,29} However, if the well-documented triple-dipole interaction between triplets of atoms is consistently included, this reduces h_v by only ~ 150 cal/mole.⁴ The four-dipole contribution increases it by ~ 60 cal/mole,⁴ so h_v still remains well above the observed value. It is only when the exchange interaction between electrons on neighboring atoms, suggested by Jansen,³⁰ is included that a much decreased h_v is obtained.^{4,29} To decrease h_v to the observed value these three-atom electron-exchange interactions would also make a 20–25% contribution to the potential in perfect crystals.³⁰ Since there is much disagreement on the theoretical estimates of these forces³¹ and since the properties of perfect crystals are quite well predicted using model pair forces between rigid ions,³² the magnitude of the triple-exchange contribution remains an open question.

The interchange parameter w calculated for Ar-Kr mixtures is discussed in Secs. IV B and IV C, and we note here only that w agrees well with the observed value.

The computed entropy of vacancy formation in Cu, Eq. (20), agrees well with a similar quasi-harmonic calculation³³ and with the observed value.³⁴ The computed formation energy, however, differs markedly from the observed value.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge valuable discussions with Dr. J. A. Barker, T. Bricheno, Dr. J. A. Morrison, and Dr. B. L. Smith.

¹See J. R. Beeler, in *Physics of Many-Particle Systems*, edited by E. Meeron (Gordon and Breach, New York, 1966), Sec. 3, and references cited therein.

²*Lattice Defects and Their Interactions*, edited by R. R. Hasiguti (Gordon and Breach, New York, 1967).

³J. J. Burton and G. Jura, *J. Phys. Chem. Solids* **27**, 961 (1966).

⁴J. J. Burton, *Phys. Rev.* **182**, 885 (1969).

⁵H. R. Glyde and J. A. Venables, *J. Phys. Chem. Solids* **29**, 1093 (1968).

- ⁶D. L. Losee and R. O. Simmons, *Phys. Rev. Letters* **18**, 451 (1967).
- ⁷R. H. Beaumont, H. Chihara, and J. A. Morrison, *Proc. Phys. Soc. (London)* **78**, 1462 (1961).
- ⁸E. A. Guggenheim, *Mixtures* (Oxford U. P., London, 1952).
- ⁹A. Huber, Proceedings of the Eighth Scottish Summer School in Physics, University of St. Andrews, 1967 (unpublished).
- ¹⁰A. Isihara, *J. Phys. A* **1**, 539 (1968).
- ¹¹M. Delbrück and G. Molière, *Abhandl. d. Preuss Akad. d. Wiss. Phys.-Math. Kl. Jahry.* **1**, 1 (1936).
- ¹²N. S. Gillis, N. R. Werthamer, and T. R. Koehler, *Phys. Rev.* **165**, 951 (1968).
- ¹³H. R. Glyde, *J. Phys. C* **3**, 810 (1970).
- ¹⁴L. A. Girifalco and V. G. Weizer, *Phys. Rev.* **114**, 687 (1959).
- ¹⁵R. E. Howard and A. B. Lidiard, *Rept. Progr. Phys.* **28**, 161 (1964).
- ¹⁶For Ne, Ar, and Kr see D. N. Batchelder, D. L. Losee, and R. O. Simmons, *Phys. Rev.* **162**, 767 (1967); O. G. Peterson, D. N. Batchelder, and R. O. Simmons, *ibid.* **150**, 703 (1966); D. L. Losee and R. O. Simmons, *ibid.* **172**, 944 (1968). For Cu see W. Hume-Rothery and K. W. Andrews, *J. Instr. Methods* **68**, 19 (1942).
- ¹⁷J. D. Eshelby, *Solid State Phys.* **3**, 79 (1956).
- ¹⁸H. R. Glyde, *J. Phys. Chem. Solids* **27**, 1659 (1966).
- ¹⁹M. Doyama and R. M. J. Cotterill, in Ref. 2.
- ²⁰J. E. Hilliard, B. L. Averbach, and M. Cohen, *Acta Met.* **2**, 621 (1954).
- ²¹B. E. F. Fender, and G. D. Halsey, *J. Chem. Phys.* **42**, 127 (1965).
- ²²Reference 8, p. 6.
- ²³G. A. Mansoori and F. B. Canfield, *J. Chem. Phys.* **51**, 4967 (1969).
- ²⁴G. A. Mansoori and F. B. Canfield, *J. Chem. Phys.* **51**, 4958 (1969).
- ²⁵G. A. Mansoori and T. W. Leland, Jr., *J. Chem. Phys.* **53**, 1931 (1970).
- ²⁶D. Henderson and J. A. Barker, *J. Chem. Phys.* **52**, 2315 (1970).
- ²⁷V. V. Goldman, G. K. Horton, and M. L. Klein, *Phys. Rev. Letters* **21**, 1527 (1968).
- ²⁸A. R. Allnatt and L. A. Rowley, *J. Phys. Chem. Solids* **30**, 2187 (1969).
- ²⁹L. Jansen, *Phil. Mag.* **8**, 1305 (1963).
- ³⁰L. Jansen, *Phys. Rev.* **135**, A1292 (1964), and references cited therein.
- ³¹C. E. Swenberg, *Phys. Letters* **24A**, 163 (1967).
- ³²G. K. Horton, *Am. J. Phys.* **36**, 93 (1968).
- ³³P. Wynblatt, *J. Phys. Chem. Solids* **30**, 2201 (1969).
- ³⁴R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **129**, 1533 (1963).

Dispersive Contribution to the Cohesive Energy of an Optically Active Crystal

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(Received 1 December 1970)

The second-quantization method of Hopfield and Mahan for the calculation of the van der Waals energies in solids is extended to the case where the molecules of the solid are optically active. The crystal energy of cohesion is computed by taking the difference of the zero-point energies of the crystal with and without the intermolecular interactions and is written in terms of an integral of a response function at imaginary frequencies. A part of the energy is shown to be proportional to the optical rotatory strengths of the molecules. The leading term that discriminates between enantiomeric interactions is the same as that obtained by summation of the two-body potential found by Craig, Power, and Thirunamachandran. Finally, this discriminating energy is expressed as an integral over the optical rotation angles at imaginary frequencies.

I. INTRODUCTION

In a recent paper, Craig, Power, and Thirunamachandran¹ have investigated the interactions between optically active molecules in crystals using the perturbation method. They showed that the interaction between one dextro- and another dextro-molecule is different from a dextro- and a laevo-molecule. This difference arises in part from the fact that transitions from the ground to excited states are both electrically and magnetically allowed. Thus the energy expression includes electric as well as magnetic dipolar coupling terms.

In the present paper, we supplement the earlier work by adopting an alternative viewpoint following Hopfield² and Mahan.³

The low-energy excited states of a molecular crystal are called exciton states and the existence of such states has been demonstrated experimentally for a number of systems. For such crystals the dispersion forces form an important contribution to the binding energy and it was pointed out by Hopfield that the dispersion energy may be interpreted as the decrease in zero-point energy of excitons due to dipolar interactions. This viewpoint was further developed by Mahan, who obtained an ex-