Nonadditive forces and vacancies in rare-gas crystals

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Many-body forces in the short-range part of the potential of rare-gas crystals are investigated in the Hartree-Fock approximation within the extended Hückel theory. These are seen to be small since overlap between adjacent atoms is small. A molecular model of the vacancy problem is set up. It is then seen that short-range three-body forces contribute a negligible fraction of the vacancy formation energy within this model.

I. INTRODUCTION

A continuing puzzle in rare-gas-crystal (RGC) studies is the large concentration $c(T) = e^{-(h-sT)/kT}$ of vacancies observed in the heavier RGC near their triple points. In Kr, Lossee and Simmons[1] observe a formation enthalpy $h = 1780 \pm 200$ cal/mole vacancies and a formation entropy $s/k = 2.0^{+1.0}_{-0.5}$, and Korpiun and Coufal[2] find $h = 1985 \pm 200$ cal/mole vacancies and $s/k = 2.8^{+0.8}_{-0.9}$. However, if the Kr atoms are assumed to interact via pair-wise forces, an enthalpy $h \simeq 2620$ cal/mole or h nearly equal to the sublimation energy $L_0 = 2666$ cal/mole is predicted.[3] This result is essentially independent of the functional form chosen to describe the pair potential. When the long-range many-body dipole-dipole interactions are included, Druger[4] finds h is reduced by $0.06L_0$ giving $h \simeq 2460$ cal/mole. In Ne the predicted $h \simeq 490$ cal/mole[3] including these effects agrees quite well with the value $h = 475 \pm 60$ cal/mole observed by Schoknecht and Simmons.[5]

Since the predicted h in Kr lies $\simeq 25\%$ above the observed value, a possible reduction of h due (a) to a many-body component in the short-range potential or (b) to distortion of electron wave functions around the vacancy has been proposed. Jansen[6] has examined (a) in the form of exchange forces between triplets of atoms. Employing Gaussian atomic orbitals with empirical parameters he finds the exchange forces reduce h by $\sim 25\%$. The forces also permit substantial relaxation around the vacancy.[6,7] The magnitude of the exchange forces, which depends critically upon the size of the overlap between adjacent atoms, is, however, in some dispute.[8,9]

Doniach and Huggins[10] have examined (b) within the shell model in which the outer atomic electrons are represented by a separate shell of charge q harmonically bound to the core of the atom. When a vacancy is introduced, they find that this shell can relax away from the atom core reducing h by $\sim 10\% L_0$. In this model, however, it is difficult to determine the shell to core and intershell force

constants with confidence. This question is intimately related to lattice dynamics since similar distortions are expected when the atoms are displaced during thermal vibrations and such shell displacements are included in models of both dynamics and defects in the alkali halides.[11,12]

To investigate the role of many-body short-range forces here, we simulate fcc solid argon by a molecule containing a central Ar atom plus its 12 nearest neighbors. The electronic binding energy of this molecule is then computed using an approximate Hartree-Fock (HF) theory to describe the outer eight electrons on each atom. Since the restricted Hartree-Fock method does not include correlation, a semiempirical attractive van der Waals potential is added and the molecular energy is computed with and without the central atom to simulate vacancy formation.

In Sec. II the approximate HF theory is discussed. The validity of the approximation is investigated in Sec. III by computing the inter-atomic overlap and by comparing the computed repulsive pair potential with potentials extracted from experiment and computed by other methods. Three-body forces in a simple model are discussed in Sec. IV and the vacancy is considered in Sec. V.

II. EXTENDED HÜCKEL THEORY

To obtain the approximate energy of a large molecule of argon atoms containing many electrons we use the simple noniterative extended Hückel (EH) approximation[13] to the HF theory. Gilbert[14] has shown that the EH theory can be derived from the full HF equations

$$F\Phi_l = \epsilon_l \Phi_l \tag{1}$$

by expanding the matrix elements of the Fock operator F in powers of the interatomic overlap S and retaining terms of lowest order in S only. The EH theory should then be appropriate for interatomic separations found in condensed argon (where S is small as we shall see).

Briefly, if the exact self-consistent solutions of (1) for the molecular orbitals Φ_l are expressed, by

a *linear transformation*, in terms of a sum of distorted atomic orbitals[15] ϕ_{ai} centered about each nucleus a,

$$\Phi_l = \sum_{ai} T_{l,ai} \phi_{ai}, \tag{2}$$

then (1) reduces to

$$\sum_{ai} (F_{ai,bj} - \epsilon_l S_{ai,bj}) T_{l,ai} = 0. \tag{3}$$

Here $F_{ai,bj} = \langle \phi_{ai} | F | \phi_{bj} \rangle$ and $S_{ai,bj} = \langle \phi_{ai} | \phi_{bj} \rangle$ are the exact Fock and overlap matrix elements, respectively. Gilbert then expands $F_{ai,bj}$ in powers of S and to first order finds for closed-shell ions:

$$F_{ai,aj} = \delta_{ij} \epsilon_{ai} + \langle \phi_{ai} | v_a | \phi_{aj} \rangle \tag{4a}$$

and

$$F_{ai,bj} = S_{ai,bj} (\epsilon_{ai} + 1/|\vec{R}_a - \vec{R}_b|$$
$$+ \langle \phi_{ai} | v_{ab} | \phi_{bj} \rangle - \langle \phi_{ai} | -\tfrac{1}{2} \nabla^2 | \phi_{bj} \rangle \tag{4b}$$

for the one- and two-center matrix elements, respectively. The ϵ_{ai} are the distorted atomic orbital energies and v_a and v_{ab} are the monopolar Coulomb potentials due to the atoms subtracting, respectively, the contribution from atom a and then from both atoms a and b. In an infinite neutral RGC, the net charge on each atom should be zero resulting in null v_a and v_{ab}. (Higher multipole contributions to the Coulomb field and exchange all give second- or higher-order matrix elements.) In this limit the EH theory approximates (4) by

$$F_{ai,bj} = S_{ai,bj} (\epsilon_{ai} + \epsilon_{bj}) \tfrac{1}{2} K_{ai,bj}, \tag{5}$$

where $K_{ai,bj} = 1$ if $ai = bj$ and $K_{ai,bj} = 1.75$ for $ai \neq bj$ has been found to best simulate the kinetic-energy term of (4b).[16]

To apply the EH theory to an argon molecule, we make two further approximations. Firstly, the distorted orbitals ϕ_{ai} are replaced by undistorted atomic orbitals ϕ_{ai}^0 of the Slater[17] type for isolated atoms [$S_{ai,bj} \to S_{ai,bj}^0$ in (3)]. An extended $3s^2 3p^6 3d^{10}$ basis (one $3s$, three $3p$, and five $3d$ Slater orbitals) for each atom is used. Other choices of Slater exponents, such as that proposed by Clementi and Raimondi[18] and exponents chosen to fit the average electronic distribution radius[19] given by the true HF atomic orbitals,[23] were also considered. However, these variations did not improve the Ar-Ar pair potential discussed in Sec. III. The atomic orbital energies ϵ_{ai} were set at the observed ionization potentials.[20] With these choices, (3) can then be diagonalized to obtain the molecular orbital energies ϵ_l and the orbitals Φ_l from (2). Secondly, the diatomic potential was calculated from

$$V_{EH}(R_{ab}) = 2 \sum_{ai} \epsilon_{ai} - 2 \sum_l \epsilon_l (R_{ab}). \tag{6}$$

This approximation has been found to give good estimates of the dissociation energy when there is little charge transfer and when it is used in the context of the above-defined Hückel theory.[16] (This is not the complete HF energy.)

The above approximations, while severe, should provide a good order-of-magnitude estimate of $V_{EH}(R_{ab})$ if $S^2 \ll S$ and if the atomic orbitals are not greatly distorted when the molecule is formed.[21] These two conditions are clearly related and we go on to consider them for argon densities found in condensed matter in Sec. III.

III. OVERLAP AND PAIR POTENTIAL

A typical overlap matrix element for a pair of argon atom orbitals is shown in Table I at three spacings. The values obtained for the Slater[22] and true Hartree-Fock atomic orbitals differ by $\simeq 25\%$ and both show that $S^2 \ll S$ for spacing found in condensed argon [the inter-atomic spacing in solid argon is $R = 7.08$ bohr (3.75 Å) at $T = 0\ ^\circ K$].[24] Kunz[25] calculated the distorted atomic orbitals ϕ_{ai} for crystalline argon and found that these orbitals differed little from the ϕ_{ai}^0 and thus that the $S_{ai,bj}$ also remained very small. Gordon and Kim[26] found that they could predict the Ar-Ar pair potential well using a theory that assumed that the electron density around each atom remained undistorted when the pair was brought together.

To test (6) and the assumption that $\phi_{ai} \simeq \phi_{ai}^0$, the repulsive part of the Ar-Ar potential calculated using the EH theory [$V_{EH}(R_{ab})$] is shown in Fig. 1. The $V_{EH}(R)$ compares well with more accurate calculations for $R \lesssim 5$ bohr. Particularly, for $R \gtrsim 5.5$ bohr the $V_{EH}(R)$ compares well with the repulsive part of the Barker-Fisher-Watts (BFW) potential and particularly with the exponential-spline-BFW (ESBFW) potential which includes the improvements to the short-range repulsive region proposed by Aziz.[27] At $R \lesssim 5.5$ bohr, $V_{EH}(R)$ lies above the ESBFW suggesting that there may be distortion of the atomic orbitals at R values less than 5.5 bohr not adequately predicted by the EH theory. At $R = 5.5$ bohr (3.0 Å), $S_{3s,3s} \approx 10^{-2}$ and we take this as the limit of the validity of the EH theory.

IV. THREE-BODY FORCES

We first set up a simple analytical model that will reveal the dependence of many-body forces on

TABLE I. Overlap between $3s$ orbitals centered on two first-neighbor Ar atoms.

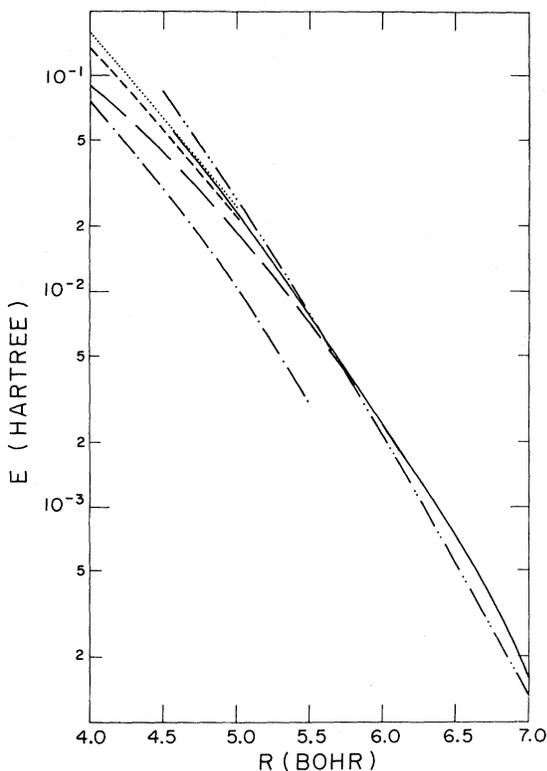| R (Å) \ S	Slater orb.	Hartree-Fock orb.
3.493	0.004 22	0.005 31
3.598	0.003 16	0.004 24
3.704	0.002 35	0.003 38

FIG. 1. Repulsive parts of various Ar-Ar potentials: Solid line, exponential-spline Barker-Fisher-Watts (ESBFW); Aziz (Ref. 27); long-dashed line, Barker-Fisher-Watts (Ref. 30); dotted line, linear combination of atomic orbitals and short-dashed line, augmented asymptotic self-consistent field, Gilbert and Wahl (Ref. 30), dot-dashed line, Gordon and Kim (Ref. 26); dot-dot-dashed line, EH this work with Slater orbitals and $\epsilon_{a,3s}$ = 1.075, $\epsilon_{a,3p}$ = 0.5788, $\epsilon_{a,3d}$ = 0.0665 in hartrees. The ESBFW is regarded as the best representation of the repulsive region.

tne parameters of the calculation. The electronic distribution around each argon atom is simulated by only one doubly occupied orbital and the secular equation (3) is solved using EH theory. The potential obtained for a pair of atoms and for three atoms in equilateral configuration is, respectively,

$$V_2(R) = 4\epsilon(K-1)S^2/(1-S^2), \qquad (7a)$$

$$V_3(R) = 12\epsilon(K-1)S^2/(1+S-2S^2), \qquad (7b)$$

where ϵ is the orbital energy.

When we expand each of the above potentials in powers of the overlap, we find

$$3V_2(R) - V_3(R) = 12\epsilon(K-1)S^3 + O(S^4). \qquad (7c)$$

This shows that, in the limit of small overlap, three-body forces are proportional to S^3 and are attractive. Rosen and Magnasco et al.[28] also find that n-body forces are proportional to S^n in He using completely different and more precise tech-

niques.

We can verify that this result is consistently carried by our simple theory by solving the secular equation for bigger clusters of atoms and neglecting the interaction between non-nearest-neighbors. We then find that the two-body plus three-body potentials correctly add up to the same energy we find by diagonalization, up to fourth order in S.[29] We also find that the potential obtained numerically with the full $3s^2 3p^6 3d^{10}$ basis has the gross behavior described by (7) if the parameters are correctly reinterpreted in terms of mean values.

Before going to the vacancy problem, we note that the three-body potential in a three-atom molecule at the inter-atomic spacing found in condensed argon is predicted to be of the order of 0.3% of the total potential by solution of the secular equation with the full basis.

V. VACANCY

The fcc solid is represented by a molecule of 13 atoms (a central atom and its 12 nearest neighbors). The repulsive energy of the molecule is computed using (6) and solving the secular equation (3). To this an attractive pair-wise interaction between each pair of the form

$$V_A(R) = - (C_6/R^6 + C_8/R^8 + C_{10}/R^{10})$$

is added, where the coefficients C_6, C_8, and C_{10} taken from the Barker-Pompe potential.[30] The molecule is then bound with energy

$$E_n = V_{EH}(R_1, R_2, \ldots, R_{13}) + \sum_{a<b} V_A(R_{ab}) \qquad (8)$$

having a minimum at the interatom spacing $R = 6.86$ bohr (3.63 Å).

A total pair potential can be constructed as a sum of the pair EH repulsive potential $V_{EH}(R_{ab})$ of Sec. III and the attractive potential $V_A(R_{ab})$. This pair potential has a well depth of 131 °K at a separation $R = 3.66$ Å, which agrees reasonably well with model potentials used to describe solid argon.[30] The pair energy of the molecule

$$E_p = \sum_{a<b} [V_{EH}(R_{ab}) + V_A(R_{ab})] \qquad (9)$$

at $R = 6.86$ bohr was 0.36% greater than that given by (8) suggesting that the three-body forces lower the molecular energy by this percentage.

The vacancy formation energy is the energy difference between N atoms on $N+1$ sites and N atoms on N sites. We calculate this difference ϵ here by removing the central Ar atom and computing a properly normalized energy difference per atom. This difference was computed, firstly, using (8) to obtain a formation energy ϵ_n including many-body short-range forces and, secondly, using (9) to obtain a formation energy ϵ_p including pair forces only. The first neighbors were found to relax in-

ward around the vacancy by 0.2 and 0.3% of the original inter-atom spacing using (8) and (9), respectively. Expressed as a precentage change, we find

$$(\epsilon_n - \epsilon_p)/\epsilon_p = (1.2 \pm 0.3)\%,$$

which is small and positive since three-body forces increase the binding. If short-range interactions are assumed negligible beyond first neighbors then the difference between ϵ_n and ϵ_p due to many-body effects should be similar in the solid and the molecule.

VI. DISCUSSION AND CONCLUSION

Within the EH theory, we find that the many-body short-range potential contribution increases the vacancy formation energy by ~ 1% of the pair-potential value. In addition there is little change in the relaxation around the vacancy when many-body forces are included. The validity of the EH theory here was tested by showing that it is a perturbation theory in the overlap S between adjacent atoms and that at the density of solid Ar, $S \approx 10^{-3}$. Also the EH theory predicted a pair potential in good agreement with empirical potentials for $R \gtrsim 5.5$ bohr (3.0 Å). However, it is still a very approximate theory and the above result is therefore probably accurate to within a factor of 2 or 3 only. The result does suggest that many-body short-range effects are most unlikely to reduce the pair-potential result by the 25% needed to find agreement with the observed result in Kr where the overlap is about twice that in Ar.

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