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Many-Body Contribution to Self-Diffusion in Rare-Gas Solids*

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The formation and self-diffusion activation energies for single vacancies and divacancies in solid argon are calculated including contributions due to triple-dipole interactions. The triple-dipole interactions lower both the formation and activation energies relative to the values calculated with a pair potential only. The calculated activation energies, 3307 cal/mole for single vacancies and 4192 cal/mole for divacancies, are in equally good agreement with the recent experimental results, 3600–3900 cal/mole. The calculated energy of formation of a vacancy, 1790 cal/mole, is in poor agreement with the value of 1270 cal/mole estimated by corresponding states from krypton experimental data. Consideration of Jansen superexchange forces and four-dipole interactions lowers the vacancy formation energy to ~1430 cal/mole and the divacancy self-diffusion activation energy to ~3510 cal/mole. The agreement between calculated and experimental values of the vacancy formation energy and activation energy (for divacancy diffusion) suggests that self-diffusion in rare-gas solids may occur via divacancies at high temperatures.

I. INTRODUCTION

SEVERAL studies have been done on the experimental properties of defects in solid rare gases. Losee and Simmons[1,2] measured the vacancy formation energy in krypton. It is significantly less than the heat of sublimation from 0°K. The self-diffusion coefficient has been determined in argon,[3–5] krypton,[6] and xenon.[7] The activation energies for self-diffusion are roughly twice the heat of sublimation.

Several investigators[8–13] have attempted to calculate vacancy formation energies and self-diffusion coefficients in solid rare gases. These investigators have employed pair potentials and have obtained the self-diffusion activation energies using absolute-rate theory. These calculations have met with limited success. The calculated vacancy formation energies[9,10,13] are roughly equal to the sublimation energy and are significantly larger than experiment. The self-diffusion activation energies,[11–13] assuming diffusion via a monovacancy mechanism, are twice the sublimation energy and in good agreement with experiment. We would expect to be able to calculate the energy of vacancy formation—an equilibrium process—more accurately than the energy of motion—a dynamical process. The activation energy for monovacancy diffusion is the sum of the vacancy formation and motion energies. Disagreement between calculation and experiment on the vacancy formation energy diminishes the significance of the agreement of the diffusion activation energies.

Losee and Simmons[1,2] (based on experiments on krypton) and Foreman and Lidiard[14] (based on calculations and experiments on argon) have suggested that many-body effects play an important role in vacancy formation for rare-gas solids. Studies of third-virial coefficients[15] have also indicated the importance of many-body forces. It has also been argued that the observed stability of the fcc phase of rare gases indicated the presence of many-body effects. Alder[16] has shown that this argument is fallacious and that the stability of the fcc phase can be obtained with a pair potential. It is of considerable interest to investigate whether many-body effects can account for the observed vacancy formation energies and diffusion activation energies.

Two different types of many-body forces in rare gases have been dealt with theoretically. Axilrod and Teller[17,18] showed that the total energy of interaction between three well-separated polarizable atoms is not just the sum of pair interactions. Considering only induced dipole interactions, Axilrod and Teller obtained an expression for the additional triple-dipole potential energy. The effects of triple-dipole interactions on the stability of the fcc phase,[19,20] binding energies,[21,22] zero-point energies,[21,23,24] elastic constants,[25] and third-

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virial coefficients[15] have been investigated. Consideration of the triple-dipole potential yielded improved agreement with experiment. In addition, Bade[26–28] and Lucas[29,30] have considered multiple-dipole interactions for more than three dipoles. Bade obtained an expression for the general n-dipole potential[26] and calculated the quadruple-dipole contribution of the binding energy for several rare gases.[27,28] The four-dipole term is opposite in sign to the three-dipole and roughly one-third in magnitude. Lucas solved completely the problem of interacting dipoles[29] and also obtained an expansion of the result in a series in the number of interacting dipoles.[30] His results for three and four dipoles are in good agreement with Bade. Lucas showed that the terms in the series expansion alternate in sign in their contribution to the binding energy.

Jansen[31] pointed out that there is a serious problem in the direct application of the Axilrod-Teller–type multiple-dipole forces to the solid. Axilrod and Teller assumed well-separated atoms with no electron exchange. In the solid, the atoms are no longer well separated and the effect of electron exchange must be considered. Jansen[32] has investigated extensively the effect of exchange on the interaction of three close atoms having Gaussian wave functions and has shown that a larger superexchange energy can occur for three close atoms. Jansen has found that the three- and four-atom superexchange potentials lead to stability of the fcc phase in a number of materials.[32] He has also considered the three-atom exchange-potential contribution to vacancy formation energies in rare gases.[33] There are also some problems with Jansen's superexchange potential energies. Swenburg[34] has found that the wave functions used by Jansen give nearest-neighbor overlap more like a metal than an insulator, and Margenau,[35] has not obtained agreement with Jansen[36] on the magnitude of the four-atom superexchange energy.

It is clear at this time that many-body potential-energy effects do exist, and they may be of some importance in the properties of the solids. Accordingly, in this paper, we investigate the contribution of many-body potentials in vacancy formation and in self-diffusion. To do this, we compare computed vacancy formation and motion energies for a model with two-body potentials with those for a model with a three-body potential. Absolute-rate theory is used to calculate the motion energy of the vacancy. Absolute-rate theory is only one possible approach to calculating the motion energy. Flynn[37] has had great success calculating diffusion coefficients from the Debye approximation to the phonon spectrum. The advantage to absolute-rate theory is that it lends itself to simple examination of the dependence of the results on the details of the model.

In Sec. II it is proved that the contribution of an additive n-body potential to the vacancy formation energy is $n-1$ times as large as its contribution to the heat of sublimation.

In Sec. III exact calculations are made of the vacancy formation energies in solid argon for models based on pair potentials (Lennard-Jones) only and pair potentials plus three-body potentials (Axilrod-Teller). Inclusion of the three-body potential lowers the vacancy formation and motion energies and hence the diffusion activation energy. The vacancy formation energy obtained is still much larger than experiment. We also examine the binding and motion energies of divacancies. Inclusion of the three-body potential in the model does not greatly affect either of these.

In Sec. IV the effects of many-body potentials other than the Axilrod-Teller triple-dipole potential are considered. Inclusion of the higher-order multiple-dipole terms worsens the agreement between experimental and calculated vacancy formation energies. However, the Jansen three-atom exchange potential leads to improved agreement between experiment and calculation for the vacancy formation energy. The Jansen potential also gives agreement between calculations and experiment for the diffusion activation energy for a divacancy self-diffusion mechanism.

II. THEORY OF MANY-BODY CONTRIBUTIONS TO VACANCY ENERGIES

A. Additive Potentials

In this section we examine the additive many-body potential contribution to the energy of formation of a vacancy. The effect of the additive n-body potential on the vacancy formation energy will be shown to be $n-1$ times larger than its contribution to the sublimation energy.

Let us define an additive n-body potential as a potential energy of interaction of n atoms $V_n(r_1\cdots r_n)$, where $r_1\cdots r_n$ are the coordinates of the n atoms; $V_n(r_1\cdots r_n)$ cannot be separated into lower-order terms; and the total n-body contribution to a large system can be obtained by summing over all n-sided polygons;

$$E_n=\frac{1}{n!}\sum_{r_1,r_2\cdots r_n} V_n(r_1,\cdots,r_n).$$

The factor $1/n!$ enters in as each n-sided polygon is counted $n!$ times in the sum. With this definition, Van der Waal and Axilrod-Teller potentials are additive

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n-body potentials (two- and three-body potentials, respectively).

The heat of sublimation H_0 of a crystal of N atoms with n-body interactions can be written

$$-H_0=\frac{1}{N}\left\{\frac{1}{2!}\sum_{r_1r_2}V_2(r_1,r_2)+\frac{1}{3!}\sum_{r_1,r_2,r_3}V_3(r_1,r_2,r_3)+\cdots\right\}$$

or

$$-H_0=\sum_{n\geq 2}E_n.$$

Now we consider the formation of a vacancy in the bulk of the crystal. Physically a vacancy is formed by removing an atom from the bulk to the surface. This process is mathematically inconvenient, and so we form a vacancy by an equivalent two-step process:

Step 1. Given a crystal with N atoms and N sites, we add one atom from infinity to give $N+1$ atoms on $N+1$ sites.

Step 2. We now remove one atom from the bulk of the crystal to infinity to give N atoms on $N+1$ sites.

To compute the energy of this two-step process, we focus our attention on one n-body interaction. For step 1, ΔE_n is clearly just the contribution of this n-body potential to the sublimation energy

$$\Delta E_{1,n}=E_n.$$

In step 2, we must break all n-sided polygons to which the atom belongs, taking care to count each polygon exactly once;

$$\Delta E_{2,n}=-nE_n.$$

Hence,

$$\Delta E_n=\Delta E_{1,n}+\Delta E_{2,n}=-(n-1)E_n.$$

The energy of formation of a vacancy is

$$E_v=\sum_n \Delta E_n=\sum_{n\geq 2}-(n-1)E_n,$$

which can be expressed in terms of the heat of sublimation as

$$E_v=H_0+\sum_{n\geq 3}-(n-2)E_n.$$

If only two-body interactions occur, then E_v is identical with H_0 (provided there are no relaxation effects). In general, the additive n-body potential contributes an extra $n-2$ times to the vacancy formation energy. Many-body potentials depend on the configuration of the interacting atoms. Their contribution to complicated defects may be even larger than to the vacancy.

B. Zero-Point Energy

The zero-point energy of a crystal is a many-body effect in that it depends on the interactions of all the atoms. However, zero-point energy is not an additive n-body effect.

When zero-point energy is included, the heat of sublimation is

$$-H_0=\sum E_n+E_z,$$

where E_z is the (positive) zero-point energy.

We now consider the formation of a vacancy in a crystal by the same two steps as above and focus our attention on the zero-point energy. In step 1,

$$\Delta E_{1,z}=E_z.$$

In step 2,

$$\Delta E_{2,z}=-E_z+\delta E_z.$$

Here ΔE_z is the decrease in the zero-point energy due to the change in the forces on the atoms near the just created vacancy. The value of δE_z is dependent on the forces in the lattice. Combining steps 1 and 2,

$$\Delta E_z=\Delta E_{1,z}+\Delta E_{2,z}=\delta E_z.$$

Now, we again consider the energy of formation of a vacancy, this time including n-body energies and the zero-point energy;

$$E_v=\sum_n \Delta E_n+\Delta E_z=\sum_{n\geq 2}-(n-1)E_n+\Delta E_z$$

$$=H_0+\sum_{n\geq 3}-(n-2)E_n-E_z+\delta E_z.$$

The last two terms in E_v are the zero-point contribution. Unless δE_z, the change in zero-point energy due the change in the forces on the atoms near the vacancy, is greater than E_z, the zero-point energy per atom, inclusion of zero-point energy increases the energy of formation of a vacancy.

III. CALCULATIONS

A. Model

Three different models of solid fcc argon are used for this work.

In the first model, hereafter referred to as model 2B (two-body), pairs of argon atoms interact by an additive Lennard-Jones two-body potential of the form

$$V(r)=4\epsilon\{(\sigma/r)^{12}-(\sigma/r)^6\}$$

and all kinetic and quantum effects are neglected.

The second model, model 2BZ (zero-point), is identical with 2B except that quantum effects are treated by the zero-point energy obtained from the Einstein approximation.

The third model, model 3BZ (three-body), is like model 2BZ except that interactions within triples of atoms are described by an additive triple-dipole potential of the form[17,18]

$$V_3(r_1,r_2,r_3)=\frac{\nu(3\cos\theta_1\cos\theta_2\cos\theta_3+1)}{R_{12}{}^3R_{23}{}^3R_{13}{}^3},$$

where R_{ij} is the distance between atoms i and j, θ_k is

TABLE I. Potential parameters ϵ and σ for three models of argon. E_2, E_z, and E_3 are the two-body, zero-point energy, and three-body contributions to the heat of sublimation.

Model	ϵ (cal/mole)	σ (Å)	E_2 (cal/mole)	E_z (cal/mole)	E_3 (cal/mole)
2B	213.5	3.444	−1846		
2BZ	236.3	3.400	−2028	182	
3BZ	254.2	3.367	−2157	174	137

the angle between R_{ki} and R_{kj}, and ν is a constant evaluated from atomic properties.

These models of argon are subject to several objections. In particular, the use of the Einstein approximation for the zero-point energy is not even a correct treatment of the model. There are three-body interactions other than the triple-dipole. There are also other proposed forms of the pair potential. The purpose of this paper is to test the effects of variations in the model on the calculated defect properties of argon and to examine the diffusion mechanism, not to find a new best potential. Accordingly, standard models are used.

For each model, it is possible to write down an expression for the sublimation energy H_0 at $T=0°\mathrm{K}$. The sublimation energy must be a maximum at the experimentally observed value of the nearest-neighbor distance R_0. In model 3BZ, we use the multiplicative constant ν calculated by Bell and Kingston[38] from first principles,

$$\nu = 74.48\times10^{12}\ \mathrm{erg}\ \text{Å}^9.$$

Knowing the experimental parameters[39] $H_0=1846$ cal/mole and $R_0=3.7549$, it is simple to solve for ϵ and σ in the Lennard-Jones potential. These parameters are contained in Table I for argon and are essentially the same as obtained by Chell and Zucker.[23] Table I also contains the two- and three-body contributions to $-H_0$, designated E_2 and E_3 in Sec. II, and the zero-point energy E_z.

As can be seen from Table I, the effect of inclusion of three-body potentials and zero-point energy, both of which contribute a soft repulsion, is to deepen and narrow the two-body well (increase ϵ and decrease σ).

B. Computations

All calculations were performed on an IBM 360 computer. For each model, the energy of formation of a vacancy was calculated for an infinite lattice. Then the relaxations around the vacancy were obtained using a Newton-Rapson procedure to find the configuration of minimum energy. In this step, the energy was summed over approximately 400 atoms. Sufficiently many shells around the vacancy were allowed to relax to assure determination of the vacancy formation energy $E_v{}^f$ to better than 2 cal/mole.

For monovacancy motion, coordinate space was searched to find the saddle-point position. The 23 atoms nearest to the saddle point were allowed to relax and the vacancy motion energy $E_v{}^m$ was obtained.

In determining the divacancy formation energy $E_{v_2}{}^f$, the 23 atoms nearest the divacancy were allowed to relax. For motion of divacancies, the 22 atoms nearest the saddle point (found by searching coordinate space) were allowed to relax to find the saddle-point configuration and divacancy motion energy $E_{v_2}{}^m$.

For each model, determination of the two- and three-body energies of defect formation and motion involved simple lattice summing. However, it was necessary to fall back to the Einstein approximation and absolute-rate theory to get the zero-point energy contributions. The Einstein zero-point energy, with and without a vacancy, is obtained from the Einstein frequencies in a perfect lattice and in a lattice with a vacancy. For the jump process, with N atoms, one considers only $3N-1$ vibrations, neglecting one mode in the direction of the jump which is assumed to be the jump process itself. Then the change in zero-point energy is calculated as though dealing with an equilibrium system.

C. Results

Using all three models of solid argon, the energies of formation $E_v{}^f$ and motion $E_v{}^m$ of single vacancies were calculated. These are contained in Table II. The activation energy for vacancy self-diffusion Q_v is the sum of the vacancy formation and motion energies. The computed values of Q_v are also included in Table II.

The results in Table II are in good agreement with the earlier results of the author using model 2B.[11] The differences with the earlier results are attributable to the choice of potential parameter and the greater number of atoms allowed to relax around the saddle point in this calculation. The agreement with Glyde[12,13] is not good. This discrepancy reflects the differences in the models used and Glyde's attempt to allow for the thermal expansion of the lattice (or our failure to do so).

Certain qualitative variations from model to model are apparent. The inclusion of zero-point energy increases $E_v{}^f$, $E_v{}^m$, and Q_v as ϵ is increased in the Lennard-Jones potential. The energy of formation of a vacancy in model 2BZ exceeds the heat of sublimation. This occurs because the decrease in zero-point energy of the atoms near a vacancy is less than the zero-point energy of a single atom in the infinite lattice. This possibility

TABLE II. Some calculated parameters for diffusion via monovacancies for three models of argon.

Model	$E_v{}^f$ (cal/mole)	$E_v{}^m$ (cal/mole)	Q_v (cal/mole)
2B	1805	1598	3403
2BZ	1905	1619	3524
3BZ	1790	1518	3307

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was pointed out in Sec. II. Inclusion of three-body forces lowers everything. As shown in Sec. II, the contribution of three-body forces to the energy of a vacancy should be equal to E_3, the three-body contribution to the sublimation energy, 137 cal/mole. In the exact calculation, the three-body interaction lowers E_v^f by 117 cal/mole. E_v^m is reduced by 101 cal/mole by the significant narrowing of the pair potential (decrease in σ) when the three-body potential is considered (see Table I).

Table III gives $E_{v_2}^f$, $E_{v_2}^m$, and Q_{v_2}, the parameters for divacancy diffusion; the binding energy of a divacancy relative to two vacancies, E_B, is also tabulated. The principal contribution of the triple-dipole potential to Q_{v_2} is the lowering of the divacancy formation energy.

IV. DISCUSSION

Activation energies Q for self-diffusion have been measured for argon,[3–5] krypton,[6] and xenon.[7] These are in Table IV along with the experimental errors stated by the investigators. Losee and Simmons[1,2] obtained a value for the formation energy of a vacancy E_v^f in krypton by comparing bulk and lattice thermal expansion. Their result is also in Table IV, as are estimates[2] for E_v^f for argon and xenon obtained by corresponding states arguments from the krypton result.

The determination of self-diffusion coefficients and vacancy formation energies in rare-gas solids is very difficult. The problems in this work are perhaps indicated by the spread in the results for the activation energy for argon.[3–5] The Losee-Simmons[1,2] experiment does not give entirely unambiguous results because of the complications of defects other than single vacancies. In addition, estimation[2] of values for argon and xenon by matching corresponding states from krypton data may introduce some errors. Hence, it is not yet possible to attach great significance to the experimental numbers, and the tabulated-error estimates may be a bit optimistic.

The vacancy formation energy in argon is estimated[2] to be 1270±150 cal/mole from experimental data on krypton. This is significantly less than the calculated values of E_v^f for all three models, indicating that none of the models is satisfactory (see Table II). However, inclusion of triple-dipole interactions, model 3BZ, appears to give the best agreement with experiment.

TABLE III. Some calculated parameters for diffusion via divacancies for three models of argon. E_B is the binding energy of a divacancy relative to two monovacancies.

Model	$E_{v_2}^f$ (cal/mole)	$E_{v_2}^m$ (cal/mole)	Q_{v_2} (cal/mole)	E_B (cal/mole)
2B	3423	774	4197	187
2BZ	3610	804	4414	200
3BZ	3381	811	4192	199

TABLE IV. Experimental properties of rare-gas crystals. Q is the activation energy for self-diffusion. E_v is the vacancy formation energy; estimated values are in parentheses.

Rare gas	Q (cal/mole)	E_v (cal/mole)
Argon	3600±150[a] 3865±200[c] 4120[d]	(1270)[b]
Krypton	4800±200[e]	1770±200[b,f]
Xenon	7350±50[g]	(2470)[b]

[a] Reference 5.
[b] Reference 2.
[c] Reference 4.
[d] Reference 3.
[e] Reference 6.
[f] Reference 1.
[g] Reference 7.

All three activation energies for single-vacancy diffusion in argon, Q_v, in Table II are in reasonable agreement with the more recent experimental data,[3–5] 3600–3900 cal/mole. The calculated activation energies for divacancy diffusion on Table III appear to be in disagreement with experiment. However, we note that Q_{v_2} for model 3BZ—which includes triple-dipole interactions and gave the best E_v—is 4192 cal/mole and agrees as well with experiment as does the single-vacancy activation energy for the same model, 3307 cal/mole.

Examining the triple-dipole contribution to vacancy formation and motion energies, we have found that calculated self-diffusion energies for a single-vacancy and a divacancy mechanism are in equally good agreement with experiment when triple-dipole interactions are considered. However, the calculated vacancy formation energy in argon is in disagreement with the value estimated by Losee and Simmons by comparison with krypton. We shall now consider briefly other many-body interactions: four-dipole interactions[26–30] and Jansen three-atom superexchange forces.[31–33] We shall find that consideration of these forces greatly improves the agreement between the experimental and calculated vacancy formation energy and between the experimental self-diffusion activation energy and that calculated for a divacancy mechanism; these many-body interactions worsen the agreement between the experimental activation energy and that calculated for single vacancies. Jansen[33] has previously pointed out that superexchange forces lower the vacancy formation energy to give reasonable agreement with experiment.

Bade[26–28] and Lucas[29,30] have both investigated four-dipole interactions. The major contribution to the four-dipole interaction comes from terms involving three atoms.[28] We may crudely estimate the effect of the four-dipole interaction on vacancy formation and motion by comparison with three-dipole interaction. The four-dipole interaction[28] is about one-third as large as the three-dipole in argon and it is attractive rather than repulsive. Inclusion of the four-dipole interaction would raise $E_v{}^f$ by about 40 cal/mole and Q_v and Q_{v_2} by about 70 cal/mole.

Jansen[31] has pointed out that it is necessary to consider electron exchange at the small separations characteristic of solids. He has shown that electron exchange appreciably affects the total interaction in solid rare gases. Three-atom electron-exchange interactions may reduce the binding energy by as much as 25% in solid argon.[33] The exact numerical contribution of the three-atom electron-exchange interactions is not certain and may be smaller than this.[34] We may again estimate the effect of these interactions on vacancy formation and motion by comparison with triple-dipole interactions. This estimation may be even less justified here than it was with four-dipole interactions; here the basic origin of the effect is different from that of the triple-dipole interaction and the magnitude is much larger. Like triple-dipole interactions, Jansen exchange interactions make a repulsive contribution to the binding energy. Comparison with triple-dipole effects indicates that the vacancy formation energy is greatly reduced, by as much as 400 cal/mole, if we use the numbers given by Jansen[33] for argon. The divacancy formation energy may then be reduced by about 800 cal/mole. The Jansen exchange interactions may reduce $E_v{}^m$ by about 350 cal/mole and probably have only a small effect on $E_{v_2}{}^m$.

We may combine our calculated results and the estimated effects of four-dipole and Jansen exchange interactions to get rough values of vacancy formation and motion energies. These work out to be

$$E_v{}^f \approx 1430 \text{ cal/mole},$$
$$Q_v \approx 2620 \text{ cal/mole},$$
$$Q_{v_2} \approx 3510 \text{ cal/mole}.$$

These estimates are, of course, very uncertain. However, we see that qualitative consideration of the various many-atom interactions reduces the vacancy formation energy to a value comparable with the result 1270±150 estimated by Losee and Simmons.[2] We also see that these interactions reduce the diffusion activation energy for single vacancies to a value well below the experimental results (see Table IV). However, the estimated activation energy for divacancy diffusion is in surprisingly good agreement with the most recent experimental result for argon obtained by Parker *et al.*,[5] 3600±200 cal/mole.

These results suggest that diffusion in rare-gas solids at high temperature may in fact be primarily via divacancies and not by single vacancies, as is usually assumed. This possibility was previously pointed out by the author.[11]

The concentration of divacancies is usually thought to be too small to contribute appreciably to self-diffusion, even at temperatures near the melting temperature. Losee and Simmons[1,2] found that the concentration of vacant sites in solid krypton is 3×10^{-3} near the triple point. This is much larger than found by Simmons and Balluffi[40] for a number of metals. The divacancy concentration may be obtained from

$$[v_2]=[v]^2 e^{\Delta S_B/R} e^{-\Delta E_B/RT},$$

using reasonable estimates of ΔS_B and ΔE_B, the binding entropy and energy of divacancies. ΔS_B has been calculated by Schottky *et al.*[41] for several fcc metals to be about 1 entropy unit. In this work we have calculated ΔE_B to be about 200 cal/mole for argon. Hence, near the triple point, we estimate the divacancy concentration to be $\sim 6\times10^{-5}$. Losee and Simmons[2] suggested the divacancy concentration may be even larger. In order for divacancy diffusion to dominate at high temperatures, the divacancies must move more than 50 times faster than single vacancies, as there are 50 times more single vacancies than divacancies. Comparing only our estimated motion energies, divacancies move about 10 times faster than single vacancies at the melting temperature of argon. If the motion entropy is more than 2 entropy units larger for divacancies than for single vacancies, the divacancies may be the major self-diffusion mechanism at higher temperatures. It is quite possible that the motion entropy for divacancies is significantly larger than that for single vacancies as the divacancy saddle-point configuration is much less constrained than the single-vacancy saddle point.

The argument given above certainly does not prove that divacancies are responsible for self-diffusion in solid rare gases at high temperatures. It merely demonstrates that this is plausible, based on current knowledge and making some reasonable assumptions. If divacancies do account for self-diffusion in rare-gas solids at high temperatures, it is because the relatively scarce divacancies move very rapidly. At lower temperatures, the activation energy must be the determinant of the diffusion mechanism and hence single-vacancy diffusion would dominate. If diffusion at temperatures near the melting temperature is primarily via divacancies, the apparent activation energy for self-diffusion should show some temperature dependence. Experimental data are not yet available over a sufficient temperature range and are not yet sufficiently accurate to test for a temperature dependence in the activation energy.

V. CONCLUSIONS

In this paper, we have calculated the Axilrod-Teller[17–19] triple-dipole interaction contribution to the formation and motion energies of vacancies in solid argon. The triple-dipole interactions lower the formation energies of single vacancies and divacancies and the activation energies for self-diffusion by either of these. Calculated activation energies for both mechanisms are in reasonable agreement with experiment but

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[40] R. O. Simmons and R. W. Balluffi, Phys. Rev. **129**, 1533 (1963).

[41] G. Schottky, A. Seeger, and G. Schmidt, Phys. Status Solidi **4**, 439 (1964).

the calculated vacancy formation energy is much too high.

Consideration of Jansen exchange forces[31–33] and four-dipole interactions[26–30] lowers both the energy of formation of a vacancy and the activation energy for divacancy self-diffusion to give good agreement with experiment. The agreement between experiment and calculation suggests that diffusion in rare-gas solids may be primarily via divacancies at high temperatures.

It was shown that it is not implausible that the relatively scarce divacancies move sufficiently rapidly compared to single vacancies to be responsible for the observed self-diffusion in solid rare gases.

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Quantum Dielectric Theory of Electronegativity in Covalent Systems.
I. Electronic Dielectric Constant*

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Electronegativity difference is redefined as a scaling parameter, generalizing the concept of valence difference. A procedure for its evaluation is developed in terms of the dielectric constants of diatomic crystals. A simple alternative to the Clausius-Mossotti theory of the electronic dielectric constant is developed in terms of this concept. The effect of *d*-electron states and of hydrostatic pressure are discussed, and procedures for their approximate evaluation are developed. The treatment is extended to 68 crystals of the diamond, zincblende, wurtzite, and rock-salt types; values of the electronegativity parameter are tabulated for these crystals.

I. INTRODUCTION

THE concept of the relative electronegativity of the elements is an old one which arose in connection with oxidation-reduction potentials in the eighteenth century. Thomson appears to have been first to discuss a microscopic dielectric model.[1] With the advent of quantum mechanics, interest in dielectric models of electronegativity seems to have waned, apparently because of difficulties with extensive numerical solutions to Schrödinger's equation, which a theory of dielectric functions seemed to require.

Attempts have frequently been made to place the concept on firm ground either semiempirically or through one-electron quantum theory formulated in terms of atomic orbitals.[2] Pauling[3] defined electronegativity as "the power of an atom in a molecule to attract electrons to itself." But his, and all other, efforts to render this definition more precise have met with only partial success. It may be correct to say that many currently regard the concept as qualitatively useful but not refinable quantitatively.

Here we reexamine the concept of electronegativity in the light of modern theory of the dielectric properties of crystals. We use a phase-space model that is consistent with the results of many of those extensive numerical calculations that were unmanageable before the widespread availability of computers.

Previous discussions of electronegativity have centered primarily on the binding or cohesive energies of atoms or molecules. Thus, Mulliken[4] defined atomic electronegativity as the average of the ionization potential and the electron affinity, $X_{m,\alpha}=\frac{1}{2}(I_\alpha+E_\alpha)$, and defined the relative electronegativity difference of two atoms α and β as

$$X_{\alpha\beta}=X_\alpha-X_\beta. \tag{1.1}$$

The relation (1.1) is necessary if $X_{\alpha\beta}$ is to be transitive,

$$X_{\alpha\beta}+X_{\beta\gamma}=X_{\alpha\gamma}. \tag{1.2}$$

Pauling observed that the energy $D_{\alpha\beta}$ binding the atoms α and β in the system α-β is generally larger than the mean of the energies $D_{\alpha\alpha}$ and $D_{\beta\beta}$ binding the systems α-α and β-β. Thus he defined the "extraionic energy" Δ:

$$\Delta=D_{\alpha\beta}-\tfrac{1}{2}(D_{\alpha\alpha}+D_{\beta\beta}), \tag{1.3}$$

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