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Quantum Crystal Effects in Solid Hydrogen at Zero Temperature

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Using our theory of correlation effects in quantum crystals, which was originally developed to calculate the properties of solid helium, we obtain the ground-state energy and pressure of solid hydrogen for molar volumes in the range 24–10 cm^3. The results are applied to a determination of the effect of zero-point motion on the intermolecular interaction and on the λ-transition temperature. The crystal field is also discussed.

I. INTRODUCTION

Correlation effects in crystals of small atomic or molecular mass have been extensively studied[1-8] in recent years. The large zero-point motions of the atoms in a "quantum crystal," such as helium, lead to instability of the calculated phonon spectrum[2] if not treated properly. This difficulty was overcome by Nosanow, who took the short-range correlations into account,[3] and a self-consistent scheme for computing the phonon spectrum has been given.[4] It appears that a good understanding of quantum crystals has been achieved.

Despite the fact that solid hydrogen H_2 has a smaller molecular mass than solid He, short-range correlations are not expected to be more important in the former material; the reason is the deeper attractive well in the intermolecular potential which causes a H_2 molecule to be more effectively localized than a He atom.[9] Thus, one does not expect any particularly novel behavior of solid hydrogen. The present study is motivated in part by the interest in solid H_2 at extremely high pressures, $\sim 10^6$ atm, where it is thought that molecular hydrogen should undergo a transition to a metallic phase[10,11] and may even become superconducting.[12] The astrophysical implications, needless to say, are very interesting.[11] A reasonable conclusion concerning these speculations requires, however, accurate equations of state which have also been calculated by Krumhansl and Wu[13] and Trubitsyn.[14]

Also, solid hydrogen has been subjected to intensive experimental investigation recently. Certain types of experiments, for example, Raman scattering[15] and magnetic resonance,[16] are conducted with great precision. It was pointed out by Harris[17] and by Noolandi and Van Kranendonk[18] that in order to achieve meaningful comparison of theory with these experiments, the effect of the zero-point motion on the various intermolecular interactions must be included. Because of the generally satisfactory agreement with experiment we have obtained in calculating the static properties of crystalline helium,[8] we believe it is worthwhile to use the same formalism to calculate various properties of solid molecular hydrogen.

As pointed out in Ref. 8, our numerical results depend quite strongly on the intermolecular potentials used in the numerical calculations. For both He and H_2, there are a number of different but equally acceptable potentials available for use. These are generally determined at least in part phenomenologically by fitting experimental data in the gaseous phase and cannot be taken too seriously in calculations at high pressure in the solid phase.[13] We believe that our formalism should work even better in H_2 than in He and that comparison of our calculated ground-state energy and pressure with existing data[19] may have a bearing on the reliability of the various potentials, especially the hard cores thereof.

In Sec. II, the formalism is briefly reviewed. Numerical results for the ground-state energy and pressure as functions of molar volume are presented in Sec. III, and in Sec. IV these results are used to investigate how the quadrupole-quadrupole, dispersive, valence, and dipole-dipole interactions are modulated by the zero-point motion. The effects on the λ-transition temperature and the crystal field are also considered.

II. FORMALISM

We briefly review the theory of Ref. 8 in the $T=0$ limit. The single-particle Green's function for H_2 localized at position $\vec{R}_i$ is given by[20]

$$g_i(1,1';\nu)=\sum_p \phi_{ip}(1)\phi_{ip}(1')/(\omega_\nu-\epsilon_p) \tag{1}$$

in the frequency representation. The single-particle wave function $\phi_{ip}(1)$ obeys the equation

$$[-\nabla_1{}^2/2m+u_i(1)]\phi_{ip}(1)=\epsilon_p\phi_{ip}(1), \tag{2}$$

where

$$u_i(1)=u_0+(\alpha^4/2m)(\vec{r}_1-\vec{R}_i)^2\equiv u_0+V_i(1) \tag{3}$$

in the harmonic approximation; m is the molecular mass and $\omega_\nu=i\pi(2\nu+1)T+\mu$ for fermions and $i\pi 2\nu T+\mu$ for bosons. Here, ν is an integer; T, the temperature; and μ, the chemical potential. The force constant α is determined from a self-consistency condition [Eq. (7) below] which relates the single-particle self-energy and the two-particle Green's function $G_{ij}(12;1'2)$. The particles are approximated as moving in a static self-consistent field in which case all multiple-particle Green's functions have the same pole as g_i in Eq. (1) when viewed as functions of ω_ν. Consequently, the two-particle Green's function for particles localized around sites i and j has the form

$$G_{ij}(12,12;\nu)=\phi_{i0}^2(1)\phi_{j0}^2(2)\chi_{ij}(1,2)/(\omega_\nu-\epsilon_0),$$

where the summation over p in Eq. (1) is omitted because we are interested only in the $T=0$ limit. This means that $p=0$ in what follows so we drop this subscript.

The correlation function $\chi_{ij}(1,2)$ is found in Ref. 8 to obey the equation

$$\{-\nabla_1{}^2/2m-\nabla_2{}^2/2m+V(1,2)+{\sum_k}'\int\phi_k^2(3)[V(1,3)\chi_{ik}(1,3) + V(2,3)\chi_{jk}(2,3)]d^3r_3+\Delta_{ij}(1,2)\}\phi_i(1)\phi_j(2)\chi_{ij}(1,2)=\lambda_0\phi_i(1)\phi_j(2)\chi_{ij}(1,2), \tag{4}$$

where the summation is over positions $k\neq i,j$ and V is the interatomic potential, $V(1,3)=v(\vec{r}_1,\vec{r}_3)$. The choice of λ_0 in Eq. (4) determines the asymptotic behavior of $\chi_{ij}(1,2)$ for large separation of $\vec{r}_1$ and $\vec{r}_2$. The function $\Delta_{ij}(1,2)$ is given by

$$\Delta_{ij}(1,2)={\sum_k}'\int\phi_k^2(3)\{V(1,3)[\chi_{jk}(2,3)-1]\chi_{ik}(1,3) + V(2,3)[\chi_{ik}(1,3)-1]\chi_{jk}(2,3)\}d^3r_3. \tag{5}$$

Equations (4) and (5) are derived by writing down the equation of motion for the two-particle Green's function and approximating the three-particle Green's function as

$$\phi_i^2(1)\phi_j^2(2)\phi_k^2(3)\chi_{ij}(1,2)\chi_{jk}(2,3)\chi_{ik}(1,3)(\omega_\nu-\epsilon_0)^{-1}.$$

The normalization condition on $\chi_{ij}(1,2)$ is

$$\int\chi_{ij}(1,2)\phi_i^2(1)\phi_j^2(2)d^3r_1d^3r_2=1. \tag{6}$$

The self-consistency condition for $u_i(1)$ is

$$u_i(1)\phi_i^2(1)={\sum_j}'\int V(1,2)\phi_i^2(1)\phi_j^2(2)\chi_{ij}(1,2)d^3r_2, \tag{7}$$

where the sum on j excludes the term $j=i$; this relation may be substituted into Eq. (4) with the result

$$\{-\nabla_1{}^2/2m-\nabla_2{}^2/2m+u_i(1)+u_j(2)+V(1,2)-[\int\phi_j^2(\bar{2})V(1,\bar{2})\chi_{ij}(1,\bar{2})d^2\bar{r}_2 +\int\phi_i^2(\bar{1})V(\bar{1},2)\chi_{ij}(\bar{1},2)d^3\bar{r}_1]+\Delta_{ij}(1,2)\}\phi_i(1)\phi_j(2)\chi_{ij}(1,2)=\lambda_0\phi_i(1)\phi_j(2)\chi_{ij}(1,2). \tag{8}$$

Equations (2), (5), (7), and (8) form the basis of the theory used in Ref. 8 to calculate the static properties of solid helium. Given any choice of u_0 and α, Eq. (8) can be solved for χ_{ij} which is then used in Eq. (7) to find new u_0 and α. The procedure is repeated until α and u_0 are determined self-consistently. The ground-state energy per particle is finally given by

$$E_0=\tfrac{1}{2}u_0+9\alpha^2/8m. \tag{9}$$

Because of the complexity of Eq. (5), we use the simple approximation

$$\Delta_{ij}(1,2)=\Delta_0+p(r_{12}-R_{ij}), \tag{10}$$

where $R_{ij}=|\vec{R}_i-\vec{R}_j|$ and the constant Δ_0 may be absorbed into λ_0. The parameter p is chosen such that the physically reasonable condition

$$\int(\vec{r}_{12}-\vec{R}_{ij})\cdot\vec{R}_{ij}\,\chi_{ij}(1,2)\,\phi_i^2(1)\,\phi_j^2(2)\,d^3r_1\,d^3r_2=0 \tag{11}$$

is satisfied. The value of p determined in this way is compatible[8] with that which is obtained by expanding Eq. (5), given the final result for $\chi_{ij}(1,2)$. We want to emphasize that this simple approximate procedure is used for $\Delta_{ij}(1,2)$ only because of the large expenditure of computer time that would be required to treat it more exactly.

III. NUMERICAL PROCEDURES AND RESULTS

Equation (8) with $\Delta_{ij}(1,2)$ given in Eq. (10) is solved using the same numerical program as in Ref. 8; in particular, the correlation function χ_{ij} which is in principle a function of $\vec{r}_1$ and $\vec{r}_2$ is approximated as depending only on $r_{12}=|\vec{r}_1-\vec{r}_2|$, the distance between the molecules. Insofar as the self-consistency condition Eq. (7) is concerned, two different procedures were investigated. This equation gives $u_i(1)$ unambiguously only if we do not make the harmonic approximation, Eq. (3). This approximation introduces a certain arbitrariness into the choice of u_0 and α^2 because the right-hand side of Eq. (7) is not of precisely the same form as the left-hand side in this case. Several different schemes for choosing u_0 and α have been proposed. The two that we have used are as follows:

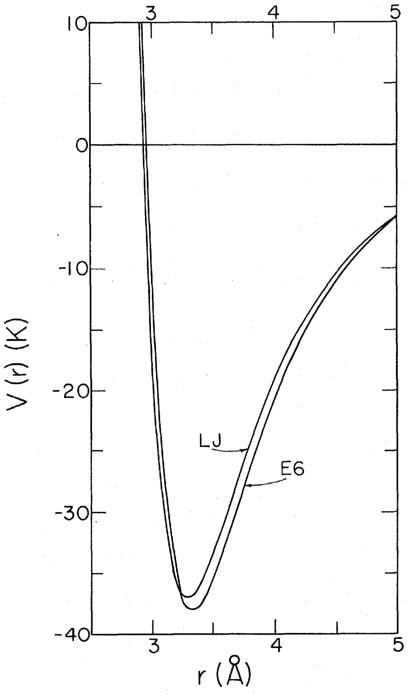

FIG. 1. Intermolecular potentials LJ and $E6$ in units of °K as functions of distance (Å).

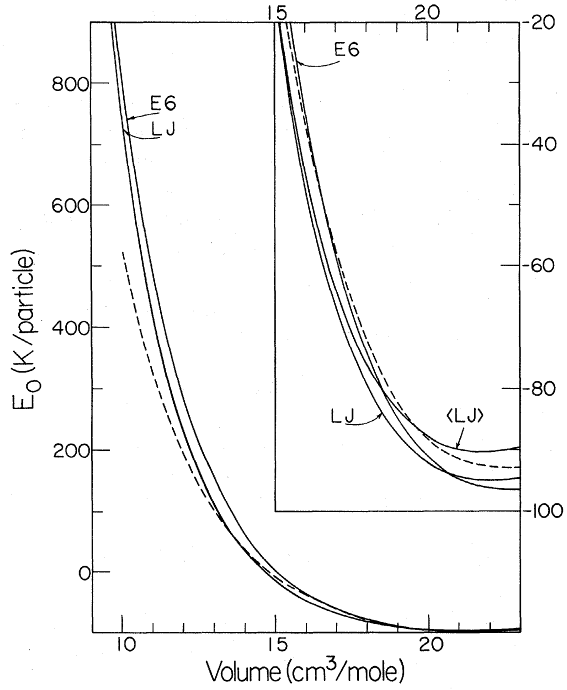

FIG. 2. Ground-state energy (°K/particle) vs molar volume (cm³/mole). Curves are labeled according to the potential used. The dashed curve is obtained from experiment. The inset shows the lower portion of the curves with an expanded energy scale.

Method I. The most straightforward procedure, although not necessarily the best in the sense of obtaining a good approximate self-energy, is that of Iwamoto and Namaizawa[21] and consists of expanding the right-hand side, averaging over directions to get isotropy, and identifying u_0 and α^2 as coefficients of the zero-order and quadratic terms in the expansion. This method is suspect because the expansion does not necessarily converge very rapidly; higher-order terms could be important even when $|\vec{r}_1-\vec{R}_i|$ is quite small.

Method II. To avoid the difficulty of method I, one may use some sort of averaging procedure as proposed by Guyer.[22] Specifically, we find u_0 according to method I and then find α^2 by integrating Eq. (7) over all $\vec{r}_1$ and demanding that the two sides be identical. This procedure takes into account approximately the higher-order terms on the right-hand side which are ignored in method I.

Two different intermolecular potentials are treated. The first (LJ) is the usual Lennard-Jones 6-12 potential,[23]

TABLE I. Calculated values of $\alpha^2 a^2$ vs molar volume (cm^3/mole).

$V(\mathrm{cm}^3/\mathrm{mole})$	$\alpha^2 a^2$
23	45.8
21.5	51.2
20.1	57.3
18.8	64.3
17.5	72.2
16.3	81.1
15.1	91.3
14.0	103.2
13.0	116.7
12.0	132.8
11.0	150.7
10.15	171.0

$$v(r) = 4\epsilon\left[(\sigma/r)^{12} - (\sigma/r)^6\right],$$

$\epsilon = 37.0$ °K, and $\sigma = 2.928$ Å. The second ($E6$) is a modified Buckingham (exp-6) potential with a hard core,[24]

$$v(r) = \begin{cases} \dfrac{\epsilon_0}{1-6/\alpha}\left[(6/\alpha)\,e^{\alpha(1-r/r_m)} - (r_m/r)^6\right], & r > r_{\max} \\ \infty, & r < r_{\max} \end{cases}$$

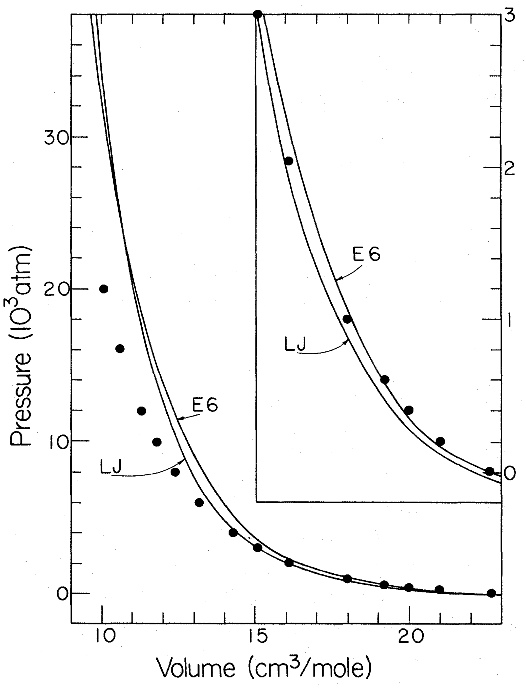

FIG. 3. Pressure (10^3 atm) vs molar volume (cm^3/mole). The points are experimental data from Ref. 19. Theoretical curves are labeled according to the potential used. The inset shows the lower portion of the curves with an expanded pressure scale.

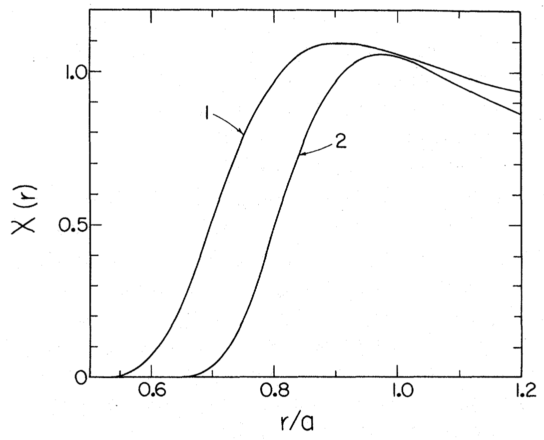

FIG. 4. Correlation functions $\chi(r)$ vs r/a for nearest-neighbor molecules. Curve 1 is for $V = 23$ cm^3/mole and curve 2 for $V = 10$ cm^3/mole.

where $\epsilon = 38.02$ °K, $r_m = 3.339$ Å, $\alpha = 14.0$, and $r_{\max}/r_m = 0.20319$. Potential $E6$ was also used in Ref. 13.

The two potentials are compared in Fig. 1 while in Fig. 2 we plot the ground-state energy of hcp hydrogen as a function of molar volume. The curve designated $\langle \mathrm{LJ} \rangle$ was found using method II for treating Eq. (7) while the curves marked LJ and $E6$ were found via method I. The labels on the curves indicate which potential is used. The dashed curve is experimental and was found[14] by integrating Stewart's pressure data, using the heat of sublimation to determine the constant of integration.

The calculated curves LJ and $E6$ reflected closely the difference between the potentials, crossing at a molar volume of 20.6 cm^3 and again at about 9 cm^3. These two volumes correspond to nearest-neighbor distances $a = 3.64$ and 2.76 Å. The potentials, on the other hand, cross at $r = 3.25$ Å and again at $r = 2.55$ Å. Even for a classical crystal, one would not find that the theoretical curves cross precisely when the nearest-neighbor distance a is equal to that value of r for which the potentials are equal because of the contribution of shells beyond the first to the binding energy. The point we wish to make is that the behavior we find here is very like what one would expect classically.

A similar conclusion may be drawn from a comparison of the theoretical curves LJ and $\langle \mathrm{LJ} \rangle$ in Fig. 2. At large molar volumes, the former is lower by about 4 °K, and as V decreases the two curves approach one another (1 °K separation at $V = 15\,\mathrm{cm}^3$). This occurs because $\alpha^2 a^2$, for which we give representative values in Table I, increases steadily as V decreases; the particles become better localized. Consequently, terms beyond the quadratic one in the expansion of Eq. (7) become less important; the crystal approached classical behavior.

Finally, we note that the equilibrium ($P=0$) molar volume depends on the choice of potential. The experimental volume[19] is 22.65 cm^3 which is quite close to the minimum of curve $E6$.

In Fig. 3 we show the calculated pressure vs molar volume. The labels are as in Fig. 2 and the points are Stewart's data. The fit of theory and experiment is quite good down to $V \approx 14$ cm^3/mole, but a systematic deviation appears at smaller volumes. It is not clear whether this is due to inaccuracies in the hard-core part of the potential or not but this must be considered a possibility, especially if one is interested in continuing the calculation down to volumes such that P approaches 10^6 atm. It does not seem useful to continue the present calculations down to this point since they already show considerable deviation from experiment at 2×10^4 atm.

The nearest-neighbor correlation function $\chi(r)$ is plotted in Fig. 4 for molar volumes of 10 and 23 cm^3. The peaks in these functions are considerably less pronounced than in the corresponding ones for helium[8] and the correlation functions $\chi(r)$ for shells beyond the first are very nearly constant for r larger than the repulsive core of the intermolecular interaction.

IV. APPLICATIONS

The nonlocality and short-range correlations of the molecules in solid hydrogen affect the properties of this material in certain ways. We discuss here three applications of the results of Sec. III. (i) We consider how the various interactions[25] between molecules are modulated by the quantum crystal effects as functions of molar volume. (ii) The effect on the molar volume dependence of the λ-transition temperature T_λ is calculated. (iii) The effect on the crystal field is considered.

TABLE II. Various modulating factors f for several molar volumes (cm^3/mole) for nearest neighbors.

f \ V	22.6	20.0	18.75	17.5	15.02
f_{0v}	2.98	2.61	2.08	1.89	1.59
f_{2v}	2.75	2.43	1.97	1.80	1.53
f_{4v}	2.27	2.02	1.74	1.60	1.41
f_{0d}	1.30	1.27	1.22	1.19	1.15
f_{2d}	1.21	1.19	1.15	1.14	1.11
f_{4d}	1.02	1.02	1.02	1.02	1.02
f_{0QQ}	1.19	1.17	1.14	1.12	1.09
f_{2QQ}	1.10	1.09	1.08	1.07	1.06
f_{4QQ}	0.93	0.94	0.96	0.97	0.97
f_{0dd}	1.05	1.04	1.03	1.03	1.02
f_{2dd}	0.98	0.98	0.98	0.99	0.99
f_{4dd}	0.83	0.85	0.88	0.89	0.91

TABLE III. Modulating factors f for several molar volumes (cm^3/mole) for third nearest neighbors.

f \ V	22.6	20.0	18.75	17.5	15.02
f_{2v}	5.15	3.31	2.76	2.36	1.84
f_{4v}	4.80	3.14	2.64	2.27	1.79
f_{2QQ}	1.06	1.04	1.04	1.04	1.02
f_{4QQ}	1.00	1.00	1.00	1.00	1.00
f_{2dd}	1.00	1.00	1.00	1.00	1.00
f_{4dd}	0.94	0.95	0.96	0.96	0.97

A. Intermolecular Interactions

There are a number of interactions between molecules in solid H_2. These include (a) the valence interaction $V_v \sim e^{-r/\rho}$, where $\rho \ll a$, $\rho \cong a/13$ at the $P=0$ equilibrium molar volume; (b) the dispersive interaction $V_d \sim 1/r^6$; (c) the quadrupole-quadrupole interaction $V_{QQ} \sim 1/r^5$; and (d) the dipole-dipole interaction $V_{dd} \sim 1/r^3$. Here only the radial dependence of each interaction is given explicitly. We wish to find averages over the zero-point motion of these interactions including the angular parts. These can always be broken down into averages of the radial functions listed above multiplied by Legendre polynomials[17] $P_n(\cos\theta)$, where

$$\cos\theta = (\vec{r}_{12} \cdot \vec{R}_{ij})/(|\vec{r}_{12}||\vec{R}_{ij}|),$$

$\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$, and $\vec{R}_{ij} = \vec{R}_i - \vec{R}_j$. In our formalism these averages are given by

$$\int \phi_i^2(1)\phi_j^2(2)\chi_{ij}(1,2)V_k(|\vec{r}_{12}|)P_n(\cos\theta)d^3r_1d^3r_2 \equiv [V_{n,k}(r_{ij})]_{\text{av}}; \qquad (12)$$

the subscript k refers to the individual interaction (radial part). We next define the modulating functions $f_{n,k}$:

$$f_{n,k} \equiv [V_{n,k}(R_{ij})]_{\text{av}}/V_k(R_{ij}), \qquad (13)$$

which are equal to unity in the classical limit; deviations from unity provide a measure of the importance of quantum crystal effects.

Table II lists all of the modulating factors which appear in the averages of the four interactions when sites i and j are nearest neighbors. These are given at several molar volumes. Because the interactions are short ranged, nearest neighbors are usually all that will be important. Also, $\chi_{ij} \approx 1$ is a good approximation for more widely separated molecules. In Table III we give all important $f_{n,k}$ for the third shell ($R_{ij} = 1.633a$). Note that for decreasing volume, all $f \to 1$, reflecting the increased localization of the particles.

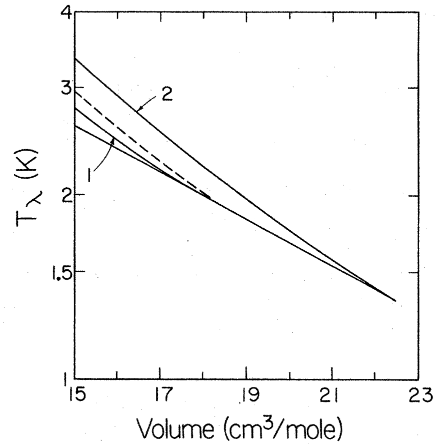

FIG. 5. Relative value of T_λ vs molar volume (cm^3/mole). The straight line is a $V^{-5/3}$ power law; the dashed line is experimental, taken from Ref. 27. Curve 1 is calculated using only the QQ interaction; curve 2 is found using all of the interactions in Eq. (14).

B. Temperature of λ Transition

We are interested in the volume dependence of T_λ as a test of the effect of zero-point motion on the interaction of two orthohydrogen (o-H_2) molecules. Insofar as the dependence of T_λ on p-H_2 concentration and related subjects is concerned, we refer the reader to existing literature.[26–28]

The interaction between two o-H_2 molecules[25] is proportional to $H_a(r)P_4(\cos\Theta_{ij})$,

$$H_a(r)=\frac{8}{25}\frac{3e^2\mu^2}{4r^5}+4\lambda_2^2 Ve^{-r/\rho}-\frac{2R}{25r^6}, \qquad (14)$$

where r is the intermolecular distance. The first term in $H_a(r)$ is the quadrupole-quadrupole interaction (QQ), equal to $\frac{8}{25}2.8\times10^{-16}$ erg when $r=r_0=3.75$ Å. The second term is the valence interaction which is $\approx 0.14\times10^{-16}$ erg at $r=r_0$. The last term is the dispersive interaction $\approx 0.07\times10^{-16}$ erg at $r=r_0$. It should be mentioned that the valence and dispersive forces are not accurately known.

Because we are interested only in the volume dependence of the various interactions, no attempt is made to compute T_λ from $H_a(r)$. It is obvious, however, that no matter what theory one uses,[26] $T_\lambda=cH_a(a)$, where c is volume independent but is different for different theories. If one includes zero-point motion, $T_\lambda=[cH_a(a)]_{\text{av}}$.

In order to achieve a meaningful comparison with experimental data and to detect the quantum crystal effects, we have matched the theory to the experimental value at the largest molar volume. The results are illustrated in Fig. 5. The experimental data (dashed curve) deviate from a $V^{-5/3}$ power by about 10% at $V=15$ cm^3 relative to 22.5 cm^3, according to the empirical formula of Ref. 27. In the figure, curve 1 is obtained by using the QQ interaction only, whereas curve 2 is obtained by taking all terms in $H_a(r)$. The straight line is the $V^{-5/3}$ law. Although our calculation of quantum crystal effects may be subject to corrections because of numerical approximations,[8] it does not seem likely that these will be substantial. Thus $T_\lambda(V)$ is a good test of the magnitude of the valence interaction in Eq. (14) since $e^{-\alpha/\rho}$ is extremely sensitive to the molar volume. As a matter of fact, if the magnitude of this interaction is reduced by a factor of 2, then curve 2 very nearly coincides with the experimental curve. In view of the uncertainty in the experimental data, we have made no attempt to obtain a fit by adjusting the parameters of the interaction.

C. Crystal Field

It is often suggested in the literature[28] that the crystal field observed in experiments[29] may be caused by zero-point motion which destroys the symmetry of the hcp structure; consequently, when $P_2(\cos\theta_{ij})$, which appears in the interaction Hamiltonian

$$H_c=[-1.4e^{-(r-r_0)/\rho}+0.9(r_0/r)^6]$$

$$\times P_2(\cos\theta_{ij})(3J_z{}^2-1)\times10^{-16}\,\text{erg} \qquad (15)$$

is averaged over the nearest and next-nearest neighbors, the result may not be zero. Harris[17] has pointed out that a correlation function which depends only on intermolecular separation $\chi_{ij}(1,2)\to\chi_{ij}(r_{12})$ can be used to average an interaction over the zero-point motion without altering the angular dependence of the interaction. As a result quantum crystal effects do not give rise to a crystal field from the first two shells in the approximation we use here. The modulating function for the valence force in the distant ($n\geq3$) shell is large, but the short range makes its contribution negligible. The dispersive part is practically unaffected by the zero-point motion. The sum of H_c over all shells is[29]

$$H_c=2.7\times10^{-3}\,{}^\circ\text{K}\times(3J_z^2-2).$$

This gives a crystal splitting of $\sim 8m\,{}^\circ$K in agreement with experimental measurement,[30] but the sign is in disagreement with the latest data.[31] We should mention that many factors including a very small crystal distortion may contribute to the crystal field.

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