the model and the small number of parameters determined from experimental data. Since no information about $\alpha_0(T)$ was used in setting up the model, the ability of our model to predict a value of $\alpha_0(T)$ at 290 °K that is within 3% of the experimental value is quite satisfying. Nevertheless, the larger discrepancies between the predicted and experimental values at lower temperatures (see Fig. 5) indicate that the model still needs considerable refining. Probably the most serious shortcomings of the ADD model, as used here, are its neglect of the coefficient $\phi^{(4)}$ in the expansion of the free energy and its failure to accurately approximate the experimental values of C_{44} and $(\partial C_{44}/\partial P)_T$. If known, the second pressure derivative of the bulk modulus could be used to determine $\phi^{(4)}$, while agreement with the experimental values of C_{44} and $\partial C_{44}/\partial P$ could be obtained by including next-nearest-neighbor overlap forces in the model.

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PHYSICAL REVIEW B VOLUME 7, NUMBER 10 15 MAY 1973

Monte Carlo Calculations for Solid and Liquid Argon[*]

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Monte Carlo methods are used to evaluate pressure, energy, and specific heat for solid and liquid argon for volumes and temperatures at or near melting. The potential energy is assumed to be the sum of pair-wise-additive potentials recently determined by Barker and co-workers plus the Axilrod–Teller three-body interaction. Quantum corrections are included. The agreement with presently available high-pressure data is excellent.

I. INTRODUCTION

The dynamical behavior of solids with large-amplitude motions is an active area of contemporary solid-state physics, and all the powerful and elegant techniques of many-body theory have been applied to this problem,[1] as well as Monte Carlo[2,3] and molecular dynamics techniques[4] that had proved so successful for fluids. At the same time, the problem of the interatomic forces between simple atoms,[5] along with the questions of nonadditivity in the condensed phases,[6] is one of the continuing problems of molecular physics. These research activities are not completely orthogonal but are, as might be expected, intimately connected. One of the simplest examples of this is solid Ar which, for many reasons, has become the testing ground both for models of the dynamics of many-body systems as well as models for the interatomic forces.

This paper is one of a series that has been concerned with these questions and in particular is devoted to a Monte Carlo study of solid and liquid Ar for volumes V and temperatures T, at or near melting. Under these conditions we have at present no adequate dynamical theory of the solid[7] although cell models appear, for reasons not clearly understood, to provide a good approximate method for calculating certain thermodynamic properties.[8] Here, however, we wish to study both the solid and the liquid using realistic pair potentials as well as including three-body forces. The work of Barker, Fisher, and Watts (BFW) has shown that the Monte Carlo methods can be adapted to do this.[6] Thus, our work can be regarded as extending BFW's liquid studies to higher pressures and to the solid phase. Low-pressure solid-state results have been presented by Fisher and Watts.[6a] Unfortunately, it is still costly to simulate melting directly on the computer[7,9,10] so that we choose to fix V and T and then calculate by Monte Carlo methods the pressure p, energy E, and specific heat C_V. The melting line of argon has recently been studied in detail up to about 15 kbar and we will make extensive comparisons with these data.[11–13] Other high-pressure studies on argon include the (p, T) isochores[14] and a direct measurement[15] of C_V. These too will be compared with our calculations. An outline of our method of calculations is given in Sec. II and the results are discussed in Sec. III. We shall see that ther is over-all excellent agreement with all of these experiments.

II. OUTLINE OF THEORY

We assume, following BFW,[6] that the potential energy of solid and liquid Ar can be written as the sum of pair-wise-additive forces plus a correction due to three-body forces:

$$U = U_2 + \nu U_3 ,$$

where

$$U_2 = \sum_{k<l=1}^{N} u(kl) \quad \text{and} \quad \nu U_3 = \sum_{k<l<m=1}^{N} u(klm) .$$

For the pair potential $u(kl)$, we use either the BFW pair potential that gave the best fit to the liquid studies or the earlier potential of Bobetic and Barker (BB) which gave an equally good fit to solid-state properties at low temperatures.[16] As in earlier work,[6] the triplet potential is taken to be the triple-dipole potential. We shall be concerned with solid and liquid Ar at temperatures where the h^2 term in the Wigner–Kirkwood expansion[17] of Helmholtz energy F is adequate. If we assume that νU_3 is small, the Helmholtz energy can be further expanded[6] in powers of ν. From the usual thermodynamic relations and ignoring terms of order ν^2, νh^2, and h^4, we find

$$E_i = \frac{\partial(\beta F)}{\partial\beta} - \tfrac{3}{2}NkT = \langle U_2 \rangle + \nu\epsilon_3 + h^2\epsilon_Q ,$$

$$pV = -V\frac{\partial F}{\partial V} = NkT + \langle P_2 \rangle + \nu P_3 + h^2 P_Q ,$$

$$\frac{C_V}{k} = -\beta^2\frac{\partial E}{\partial\beta} = \tfrac{3}{2}N + \beta^2(\langle U_2U_2\rangle - \langle U_2\rangle^2) + \nu\underline{C}_3 + h^2\underline{C}_Q .$$

Here $\beta = 1/kT$ and the ensemble average is over the classical system with only two-body forces:

$$\langle X \rangle = \frac{\int\cdots\int e^{-\beta U_2} X d\tau_1 \cdots d\tau_N}{\int\cdots\int e^{-\beta U_2} d\tau_1 \cdots d\tau_N} ,$$

and we have used the following definitions:

$$P_2 = -\sum_{i<j}\frac{1}{3}\,\frac{R_{ij}\partial}{\partial R_{ij}}\,u(ij) ,$$

$$U_Q = (\beta/12m)\sum_{i<j}\nabla_i^2 u(ij) .$$

The quantities P_3, P_Q, ϵ_3, ϵ_Q, $\underline{C}_3$, and $\underline{C}_Q$ are defined in the Appendix, together with some other quantities appearing in the thermodynamic Grüneisen parameter.

III. RESULTS

Our method of calculation is identical to that of BFW.[6] Briefly, we use 108 particles arranged in a cubic box with periodic boundary conditions. Potentials are truncated at a distance equal to one-half the box edge and we correct for this using the the continuum approximation as discussed in detail by BFW and McDonald and Singer.[18] Apart from this we make no correction for finite-system effects. For a given V and T, our Monte Carlo program evaluates the pressure p, energy E_i, and specific heat C_V. We carried out calculations using the BFW pair potential[6] that spanned the whole range of precision studies[11–13] of the melting line of the solid and the region from 5 to 15 kbar in the liquid. In these calculations we used as input the experimentally determined V, T. We also carried out a single run in the liquid and solid for volumes 1% smaller than the melting volume. In this way we can assess the sensitivity of the calculations to possible errors in the experimental volumes and also obtain the bulk modulus B_T. Lattice dynamical calculations[19] have shown that in the solid B_T and C_V for the BFW and BB potentials differ by only about 1% over the whole temperature range of the zero-pressure solid. Thus, we would expect the pressures from these potentials to show only small systematic differences. To test this, we have compared the BFW and BB potentials at volumes corresponding to the zero-pressure solid and the solid at 180 °K on the melting line. Finally, we have used the BB potential to derive three points on the isochore for $V = 23.65$ cm^3 mole^{-1}. For these points a sufficient number of configurations were sampled to obtain C_V to better than 2%. All these results are collected in Table I. It should be noted that the values of C_V in Table I do not include the contributions from $\underline{C}_3$ and $\underline{C}_Q$. Statistical errors for the 900 000 configuration run are estimated as ± 6 J mole^{-1} for the energy E_i and ± 10 bar for the pressure p. For other runs the error should go roughly inversely as the square root of the number of configurations.

Before proceeding to a comparison of our calculations with the available experimental data, we shall discuss the evaluation of C_V. As in previous work,[6] the fluctation terms that occur in ϵ_3, ϵ_Q, P_3, P_Q were evaluated on a subset (every 1000th configuration) of the main Monte Carlo chain. This procedure is adequate for these terms as well as for c_3^a, c_Q^a, d_3^a, and d_A^a. However, a detailed study of the term c_3^b revealed very poor statistics using the above procedure (see Table II). In fact, because of the poor statistics it is impossible to distinguish the term $\underline{C}_3$ from zero. There are two reasons for believing $\underline{C}_3$ to be very small. First, the three-body energy terms are known to depend little on configuration but only on the density.[20] Second, from the point of view of quasiharmonic lattice dynamics, the C_V differs from $3Nk$ by a term proportional to the average of the square of the frequencies of vibration. Three-body forces only contribute about +2% to the latter[16] so that $\underline{C}_3 \sim \frac{1}{50}\, \underline{C}_Q$, which is negligible. Of course, there will also be an effect of the three-body terms on the anharmonic terms but these also are likely to be small. For these reasons Table I lists only the two-body C_V. No attempt was made to calculate

TABLE I. Monte Carlo results.

Pair potential	No. of configs. (10^6)	V (cm^3 mole^{-1})	T (°K)	$(C_V/Nk)^*$	$-E_i$ (kJ mole^{-1})	p(Calc) (bar)	p(Expt) (bar)
Solid							
BB	0.3	23.66	60.0	2.89	7.481	27	0[a]
BB	0.6	24.44	50.0	2.80	7.156	57	0.40[a]
BB	0.9	23.65	65.0	2.82	7.438	174.9	•••
BB	1.3	23.65	90.0	2.81	7.201	846.3	•••
BB	1.3	23.65	115.0	2.82	6.941	1536	•••
BB	0.8	22.09	180.15	2.92	6.382	5036	4999[b]
Fluid							
BB	0.6	23.10	201.32	3.03	5.203	6201	6335[b]
Solid							
BFW	0.9	23.75	63.10	2.85	7.471	1	0[a]
BFW	0.9	24.30	77.13	2.75	7.227	28	0.25[a]
BFW	0.6	24.03	108.12	2.76	6.964	1028	1051[b]
BFW	0.6	23.05	140.88	2.74	6.794	2650	2708[b]
BFW	0.7	22.55	160.4	2.89	6.586	3808	3805[b]
BFW	0.6	22.09	180.15	2.80	6.382	4964	4999[b]
BFW	0.9	21.70	201.32	2.86	6.118	6199	6335[b]
BFW	0.4	21.47	197.78	2.94	6.104	6593	6140[c]
BFW	0.4	20.12	273.11	2.86	4.927	11974	11380[c]
BFW	0.4	19.92	273.11	2.96	4.810	12686	•••
BFW	0.4	19.41	323.14	3.12	3.937	15988	15354[c]
Fluid							
BFW	0.6	23.66	180.15	2.89	5.428	4907	4999[b]
BFW	0.4	22.96	197.78	2.80	5.169	6319	6140[c]
BFW	0.6	23.10	201.32	2.96	5.171	6143	6335[b]
BFW	0.4	21.31	273.11	2.90	3.934	11645	11380[c]
BFW	0.4	21.09	273.11	3.08	3.866	12585	•••
BFW	0.4	20.46	323.14	3.21	2.780	15513	15354[c]

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[b] Reference 12.

[c] Reference 13(b).

TABLE II. Specific heat of solid Ar at 23.65 $\text{cm}^3\ \text{mole}^{-1}$.

T (°K)	C_2/Nk	h^2C_Q/Nk	c_3^a/Nk	c_3^b/Nk
65	2.82	−0.18	0.05	−0.08
90	2.81	−0.09	0.05	+0.01
115	2.82	−0.06	0.05	−0.04

c_Q^b which appear to be similar to c_3^b, instead $\underline{C}_Q$ was evaluated by numerical differentiation of values of ϵ_Q using $\underline{C}_Q = -\beta^2(\partial\epsilon_Q/\partial\beta)$. Values of dp/dT for $V = 23.65\ \text{cm}^3\ \text{mole}^{-1}$ can be obtained by direct differentiation of the pressure values in Table I. No attempt was made to program the detailed expression of Sec. II. Similarly, C_V can be obtained from $\partial E/\partial T$.

IV. COMPARISON WITH EXPERIMENT

We shall consider first the solid near zero pressure. The BFW potential yields pressures that are a little high at 77 °K. The statistical error is believed to be around ± 10 bar and the errors incurred by the use of the continuum approximation for the tail connection are believed smaller than this.[6] Thus, there is a small residual disagreement with experiment. The 80 °K results for the BB potential appear to be about 30 bar above those of the BFW potential in agreement with lattice-dynamical calculations.[19]

For the solid and liquid along the melting line, the p, T data from three different laboratories appear[11–13,21] to agree within their claimed uncertainties in regions where they overlap. However, the volumes sometimes appear to differ by rather more than the claimed uncertainties. This is unfortunate because an error in the volume of only $0.02\ \text{cm}^3\ \text{mole}^{-1}$ in the solid at 108 °K on the melting line will give rise to a systematic error of about 20 bar in our Monte Carlo calculations. At higher pressures such errors are even more serious. With this in mind, the agreement of the BFW potential with the data of Crawford and Daniels up to 180 °K is excellent. The latter experimental point lies between the values predicted by the BB and BFW potentials. The data of Stishov and Fedositov[13] for the solid and liquid are systematically lower than the BFW potential values. The differences are about three times larger for the solid than for the liquid. We believe this is in part due to a systematic error in the experimental-melting volumes. This claim appears to be borne out when one considers the results around 200 °K. If one takes the BFW potential as a guide, Crawford and Daniels's solid and liquid volumes at 201 °K appear to be too large while the volumes of Stishov and Fedositov appear to be too small. We do not show a comparison of the values of E_t with those derived by Crawford and Daniels.[12] The agreement up to about 180 °K is excellent, but there appears to be a large disagreement at 200 °K. This may be related to the possible error in melting volume mentioned above. The changes in internal energy ΔE upon melting follow quite closely the results of Stishov and Fedositov[13] and the minimum in ΔE as a function of T that occurs around 200 °K is confirmed. The small differences between the calculated values of ΔE at 273 and 323 °K and experiment[13] can be correlated with differences in the pressure (Table I) due to a possible experimental error in the melting volume of the solid.

Figure 1 shows a comparison of our Monte Carlo specific heats C_V taken from Table II with the experiments of Haenssler, Gamper, and Serin.[15] These values were computed using the BB potential which is slightly less accurate than the BFW potential, but the effect of this on C_V is too small to justify repeating the computation. The excellent agreement between the Monte Carlo calculations and experiment also confirms the failure of C_V based on self-consistent phonon theories at high temperatures.[19] The values of C_V obtained by numerical differentiation of $E_t(T)$ in Table I confirms the value of C_V shown in Fig. 1.

Finally, the isochore for $V = 23.65\ \text{cm}^3\ \text{mole}^{-1}$ can be compared with values interpolated from Benson's thesis.[14] The agreement of p and $(dp/dT)_V$ appears to be good.

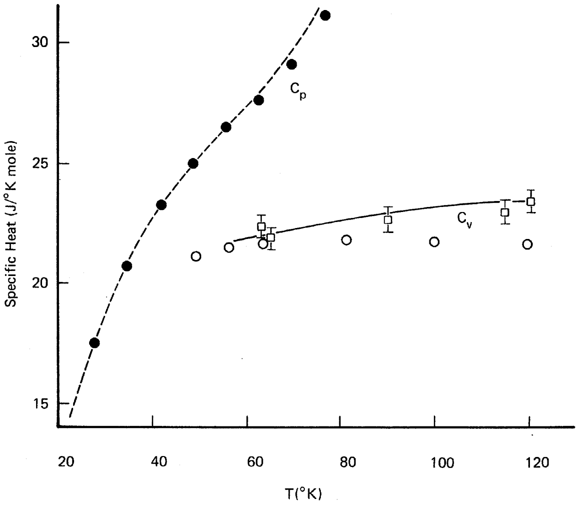

FIG. 1. Specific heat of solid Ar. The full circles are calculated using the BB pair potential and ISC (improved self-consistent) phonon theory. The dashed curve is the experimental C_p. The open circles are C_V calculated for the BFW pair potential using ISC phonon theory. The squares are Monte Carlo C_V values for the BB potential. The solid curve is the experimental C_V from Ref. 15. The C_V values correspond to the constant volume $V = 23.5\ \text{cm}^2\ \text{mole}^{-1}$.

V. CONCLUSION

Monte Carlo calculations using the BFW pair potential and the triple-dipole three-body force are seen to be in excellent over-all agreement with the thermodynamic properties of solid and liquid argon at or near melting over a wide range of pressures. There are no clear indications that nonadditive forces, other than those considered here, are important. However, in this connection we must remember the relatively large uncertainties in the currently available volume determinations at high pressures. Three-body long-range dipole-quadrupole interactions have recently been considered by Doran and Zucker,[22] and Johnson and Spurling.[23] It is apparent from the results of the former authors that there is substantial cancellation between these interactions and the fourth-order triple-dipole interaction. In fact, within the uncertainty of the estimates the net contribution of these terms, to the ground-state energy at zero pressure, could be as low as zero or as high as 90 J mole^{-1}. Even the latter figure is relatively small, being only about 15% of the three-body triple-dipole contribution. The contribution of these terms to the properties considered here should be relatively even smaller. Our results give no evidence for significant effects due to three-body exchange or overlap interactions.

APPENDIX

We list here certain quantities needed for evaluating three-body and quantum corrections used in the text. With the definition

$$P'_Q = -\frac{\beta}{36m} \sum_{i<j} \frac{R_{ij}\partial}{\partial R_{ij}} \nabla_i^2 u(ij) ,$$

we find

$$\epsilon_3 = \langle U_3 \rangle - \beta(\langle U_2 U_3 \rangle - \langle U_2 \rangle \langle U_3 \rangle) ,$$

$$\epsilon_Q = 2 \langle U_Q \rangle - \beta(\langle U_Q U_2 \rangle - \langle U_Q \rangle \langle U_2 \rangle) ,$$

$$P_3 = 3 \langle U_3 \rangle - \beta(\langle U_3 P_2 \rangle - \langle U_3 \rangle \langle P_2 \rangle) ,$$

$$P_Q = \langle P'_Q \rangle - \beta(\langle U_Q P_2 \rangle - \langle U_Q \rangle \langle P_2 \rangle) .$$

The expressions for $\underline{C}_3$ and $\underline{C}_Q$ are more complicated. In particular,

$$\underline{C}_3 = c_3^a + c_3^b ,$$

where

$$c_3^a = 2\beta^2(\langle U_3 U_2 \rangle - \langle U_2 \rangle \langle U_3 \rangle)$$

and

$$c_3^b = -\beta^3(\langle U_2 U_3 U_2 \rangle - 2\langle U_2 \rangle \langle U_3 U_2 \rangle + 2\langle U_2 \rangle^2 \langle U_3 \rangle - \langle U_2 U_2 \rangle \langle U_3 \rangle) .$$

Also,

$$\underline{C}_Q = 2\beta\langle U_Q \rangle + c_Q^a + c_Q^b ,$$

where

$$c_Q^a = 4\beta^2(\langle U_Q U_2 \rangle - \langle U_Q \rangle \langle U_2 \rangle)$$

and

$$c_Q^b = -\beta^3(\langle U_2 U_Q U_2 \rangle - 2\langle U_Q U_2 \rangle \langle U_2 \rangle + 2\langle U_2 \rangle^2 \langle U_Q \rangle - \langle U_2 U_2 \rangle \langle U_Q \rangle) .$$

For completeness, we also derive a quantity that occurs in the thermodynamic Grüneisen parameter, $(V/C_V)(\partial p/\partial T)_V$, namely,

$$\frac{\beta^2}{k} \frac{\partial(pV)}{\partial\beta} = N + \beta^2(\langle P_2 U_2 \rangle - \langle P_2 \rangle \langle U_2 \rangle) + \nu\underline{D}_3 + h^2\underline{D}_Q ,$$

where

$$\underline{D}_3 = d_3^a + d_3^b ,$$

where

$$d_3^a = 2\beta^2(\langle P_3 U_2 \rangle - \langle P_3 \rangle \langle U_2 \rangle) ,$$

$$d_3^b = -\beta^2(\langle U_2 U_3 P_2 \rangle - \langle U_2 \rangle \langle U_3 P_2 \rangle - \langle U_3 \rangle \langle U_2 P_2 \rangle - \langle P_2 \rangle \langle U_2 U_3 \rangle + 2\langle U_3 \rangle \langle U_2 \rangle \langle P_2 \rangle) ,$$

and

$$\underline{D}_Q = d_Q^a + d_Q^b - \beta\langle P_Q \rangle ,$$

where

$$d_Q^a = 2\beta^2(\langle U_Q P_2 \rangle - \langle U_Q \rangle \langle P_2 \rangle) + \beta^2(\langle P_Q U_2 \rangle - \langle P_Q \rangle \langle U_2 \rangle) ,$$

$$d_Q^b = -\beta^3(\langle U_2 U_Q P_2 \rangle - \langle U_2 \rangle \langle U_Q P_2 \rangle - \langle U_Q \rangle \langle U_2 P_2 \rangle - \langle P_2 \rangle \langle U_Q U_2 \rangle + 2\langle U_Q \rangle \langle U_2 \rangle \langle P_2 \rangle) .$$

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Transmittance Spectra and Optical Constants of Alkali-Antimony Compounds K_3Sb, Na_3Sb, and Na_2KSb

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Measurements of the transmittance spectra of alkali-antimony compounds K_3Sb, Na_3Sb, and Na_2KSb, carried out from 0.5 to 6.2 eV at room temperature, are analyzed by the Kramers–Kronig dispersion relations to yield the refractive index and the extinction coefficient. The refractive index at photon energies less than the lowest band gap is about 2.0 for these compounds. The $\epsilon_2(\omega)$ curve shows two pronounced peaks at 2.3 and 3.45 eV for hexagonal K_3Sb and at 2.7 and 3.6 eV for cubic K_3Sb, whereas it shows only one pronounced peak at 2.5 eV for Na_3Sb and at 3.05 eV for Na_2KSb.

I. INTRODUCTION

Because of their high-photoemissive properties, Cs_3Sb and multialkali antimonide $Na_{3-x}K_xSb$ are well-known and widely used photoemissive compounds. In an earlier paper,[1] the refractive index and the extinction coefficient have been reported for Cs_3Sb. For the other alkali-antimony compounds, these two sets of the optical constants have not been reported, despite the many publications concerning photoemission, light absorption, photoconductivity, and crystal structure. These publications were summarized by Sommer.[2] Transmittance properties of K_3Sb have been investigated quite extensively by Spicer,[3] Taft and Philipp,[4] and Sommer and McCarroll.[5] In a recent paper,[6] hereafter referred to as I, we have presented the preliminary determination of the optical constants of purple K_3Sb using a Kramers–Kronig (KK) dispersion analysis of the transmittance data. The present paper describes detailed optical properties of K_3Sb; this compound has two modifications, the purple hexagonal and the brown cubic form.[5] The optical constants of Na_3Sb and Na_2KSb are also presented. The results provide the important information needed for the future systematic study of the electronic structure of alkali-antimony compounds.

II. EXPERIMENTAL PROCEDURE

A. Materials Preparation

The preparation of K_3Sb was presented in I, so that only a brief description is given here. Antimony is evaporated on a quartz substrate of 1-mm thickness at a pressure of less than 1×10^{-6} Torr. The evaporated Sb film is then exposed to K vapor at 160 °C until peak sensitivity to white light is obtained. At the photosensitivity peak, the resistance decreases to a value of two or three orders of magnitude less than the peak value. The film shows pure purple color in transmitted light. On the basis of the transmittance spectrum, this film is believed to be K_3Sb of hexagonal structure. In fact, it has been reported that the K-Sb system has the chemical composition of K_2Sb at the resistance peak[7] and K_3Sb at the photoemission peak.[5] The K_3Sb film thus obtained is *n* type, in agreement with previous work.[3,5,7] Thus conductivity type was determined by a thermoelectromotive-force measurement. It has been suggested that *n*-type conductivity is due to the stoichiometric excess K metal.[5] When the activation process of the evaporated Sb film with K vapor is continued beyond the photoemission peak, the resistance continues to decrease by about one order of magnitude and then it shows no change or only a very slow in-