High-temperature specific heat of crystals

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The Monte Carlo method is used to estimate the specific heat of a model of rubidium. Both the specific heat at constant volume, C_v, and the specific heat at constant pressure, C_p, are obtained for a range of temperatures up to the instability point of this lattice. These results for the fully anharmonic perfect crystal are compared with those obtained by perturbation theory to lowest order in the anharmonicity, (i.e., only cubic and quartic anharmonic contributions to the Helmholtz free energy are considered). It is shown that the fully anharmonic Monte Carlo calculation yields a more rapidly increasing specific heat than the linear temperature dependence given by lowest-order perturbation theory in the high-temperature limit. The Monte Carlo calculations also indicate that, at temperatures much higher than the Debye temperature, large-scale atomic displacements can occur without disrupting the lattice. When this happens, there is a further increase in the specific heat.

I. INTRODUCTION

An anomalous rise in specific heat prior to melting has been observed in metals,[1-4] alkali halides,[5-7] and organic crystals.[8] The value of the specific heat at the melting point, T_m, may be from 20 to 100% greater than the classical (Dulong-Petit) value, the largest increases being observed in the refractory metals[1] and alkali halides.[5] The rise takes place over a considerable portion of the temperature range between the Debye characteristic temperature, Θ_D, and T_m. In the neighborhood of Θ_D and at lower temperatures, the specific heat can be quite well represented by lattice-dynamical theory,[9] but at significantly higher temperatures (i.e., $3\Theta_D$ or greater) the lowest-order anharmonic contribution to the specific heat is, in most cases, insufficient to account for the experimental values.[10,11] The balance ("excess" specific heat) is attributed to higher-order anharmonic effects[10] and to the vacancies which are expected to be present in a solid near its melting point.[1-3,5-7,12] To evaluate these two contributions to the specific heat is a not inconsiderable problem. The vacancy contribution depends on both the vacancy concentration, n_V, and the vacancy formation energy, E_f. Although reliable and consistent values of E_f can be derived from a variety of independent experimental investigations, e.g., tracer diffusion,[13,14] nuclear magnetic resonance,[15] electrical resistivity of quenched metals,[16,17] and ionic conductivity of alkali halides,[18] the estimates of vacancy concentration are less sure. The most reliable values of n_V are obtained by the simultaneous measurement of the lattice parameter (by x-ray dif-

fraction) and lattice dilatation.[19] These values are smaller, typically by an order of magnitude, than those needed to account for the anomalous rise in specific heat.[1] Estimates of n_V from quenching experiments are less certain because of vacancy loss during the quench, but they also give low values of n_V. In principle, n_V can also be obtained from studies of the lifetime for positron annihilation in metals,[20] but this promising method is in the early stages of development and reliable values are not yet available. Although there are now some arguments in favor of higher values for the vacancy concentration,[21] one cannot expect to resolve the problem of the excess specific heat without knowing the full anharmonic contribution to the specific heat. At present, a typical analysis[1,2,22] represents the electronic and lowest-order anharmonic contributions to the specific heat by a term, linear in temperature, which is fitted to the measurements at intermediate temperatures ($\sim\Theta_D$) and extrapolated to high temperatures. The excess specific heat above these extrapolated values is then treated in one of two ways: either (1) all the excess specific heat is attributed to vacancies and fitted to the appropriate exponential form, thus yielding values for E_f and n_V, or (2) values of E_f and n_V obtained from independent measurements such as those mentioned above are used to calculate the specific heat of the vacancies, and then any remaining excess specific heat is labeled "anharmonic." Consequently, the information gained from such an analysis will only be reliable if the linear approximation is a good one for the anharmonic effects. For this reason, it seems important to obtain, without approximation,

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the anharmonic contribution to the specific heat of a lattice. This is the subject to be discussed here. As a first step, we considered a perfect lattice. The parameters of the problem were chosen to represent rubidium. In Sec. IIA we give details of the Monte Carlo method used to calculate the fully anharmonic thermodynamic properties of this model lattice. In Sec. IIB, we outline the lowest-order perturbation theory calculation for the same system. The two sets of results are presented in Sec. III. In Sec. IV we discuss these results and compare them with experiment.

II. CALCULATIONS

A. Monte Carlo method

The model system consists of 250 particles interacting via a pair potential $\phi(r_{jk})$, where r_{jk} is the distance between particles j and k. The particles were located initially on bcc sites in a $5 \times 5 \times 5$ cube of unit cells with periodic boundary conditions applied at opposite cube faces to simulate an infinite system. The Monte Carlo method of Metropolis et al.[23] was used to compute the canonical ensemble averages for the potential part of the internal energy, U_i, and the pressure, P, according to the relations

$$U_i = \langle \Phi \rangle / N \tag{1}$$

and

$$P = \langle \pi \rangle = \left\langle \frac{N}{V} kT - \frac{1}{3V} \sum_{1 \leq j \leq k}^{N} \left(r_{jk} \frac{\partial \Phi}{\partial r_{jk}} + a \frac{\partial \Phi}{\partial a} \right) \right\rangle, \tag{2}$$

where $\Phi = \frac{1}{2} \sum_{j \neq k} \phi(r_{jk})$ is the potential energy of the lattice with N particles in volume V and a is the lattice constant. The second term in parentheses arises from the density dependence of the interatomic potential.[24] The specific heat at constant volume, C_v, was obtained in the course of the calculation from the relation[25]

$$C_v = \tfrac{3}{2}R + \langle (\delta \Phi)^2 \rangle / kT^2, \tag{3}$$

where $\delta \Phi = \Phi - \langle \Phi \rangle$ is the fluctuation in the potential energy of the lattice and R is the gas constant. The specific heat at constant pressure, C_p, was estimated from the relation

$$C_p = C_v - T \left(\frac{\partial p}{\partial T} \right)_V^2 \bigg/ \left(\frac{\partial p}{\partial V} \right)_T, \tag{4}$$

in which $(\partial p / \partial T)_V$ was also obtained directly by use of the relation[25]

$$\left(\frac{\partial p}{\partial T} \right)_V = \frac{Nk}{V} + \langle \delta \Phi \delta \pi \rangle / kT^2, \tag{5}$$

and $(\partial p / \partial V)_T$ was obtained graphically. The canonical ensemble averages are estimated from 10^6 samples obtained from 10^6 trials (with acceptance ratio $\sim\frac{1}{2}$) after an initial equilibration period of 10^5 trials. The resulting estimates are stable to a few parts in 10^4. We shall return to a discussion of the accuracy of our results in Sec. III. The interparticle potential, $\phi(r_{jk})$, is one appropriate for rubidium[26] and it is cut off at the sixth-neighbor distance. The parameters for this potential are given in Table I. Rubidium has been quite well studied experimentally.[3,10,27] The specific heat shows an anomalous rise over the last 100° prior to melting ($T_m = 312$ K) after a quite extensive region of linear temperature dependence above Θ_D ($\sim$55 K)[3].

The calculated pressures and internal energies are not the total pressures and energies for rubidium since the temperature-independent contributions from the electrons have not been included. These contributions are difficult to estimate reliably[28] so we have ignored them when determining the specific heats. For this reason, our estimates for C_p do not strictly apply to rubidium, but rather to the model lattice having the calculated pressure variation with volume.

B. Perturbation-theoretic method

The formal expressions for the cubic and quartic (lowest-order) terms in the Helmholtz free energy, F_3 and F_4, have been given by many authors.[29] Details of the computation of these terms for potentials of potassium and sodium in real space have been given in Ref. 30, and we have used the same method for rubidium with some modifications, to be described below, that speed up the cal-

TABLE I. Parameters of the Rb potential function for different lattice constants.

| v | Lattice const | $\dfrac{m^*}{m} = 0.89$ | | | |
		R_s^*	A	B	r_c
(cm³/mole)	(Å)				
54.638	5.661	4.687 87	1.009 83	0.244 21	2.45
55.776	5.700	4.720 17	1.010 31	0.243 50	2.45
56.914	5.739	4.752 47	1.010 78	0.242 80	2.45

culation. The interatomic potential is the same as that used in the Monte Carlo calculation with the cutoff at the sixth-neighbor distance. This enables us to compare the two calculations in a precise and meaningful way.

In the calculations of F_3 and F_4 [Eqs. (10) and (9), respectively, of Ref. 30], the eigenvalues $\omega(\vec{k}j)$ and the associated eigenvectors $\vec{e}(\vec{k}j)$ for the wave vector $\vec{k}$ and polarization (branch) index j are obtained from the dynamical matrix $D_{\alpha\beta}(\vec{k})$ for the sixth-neighbor model of Rb by the method described in Ref. 31. The high-temperature correlation function arising in F_4, viz

$$S_{\alpha\beta}(\vec{n}) = \sum_{\vec{k}j} \frac{e_\alpha(\vec{k}j)e_\beta(\vec{k}j)}{\omega^2(\vec{k}j)} (1 - \cos 2\pi a\vec{k}\cdot\vec{n}), \quad (6)$$

involves the sum $\vec{k}$ over the whole of the first Brillouin Zone (BZ) and the sum over the branch index j. The sum over the whole BZ in Eq. (6) for a direct lattice point $\vec{n}$ can be reduced to the $\frac{1}{48}$th portion or the irreducible sector of the zone by the method given in Shukla and Wilk.[32] We have checked the convergence of the BZ sum, $S_{\alpha\beta}(\vec{n})$, for a cubic mesh of different steplengths $Z = 20$, 25, and 30, which in general yields $2Z^3$ points in the whole zone, and found that the steplength $Z = 20$

gives the converged answer for $S_{\alpha\beta}(\vec{n})$ for the first six shells to better than 1 part in 10^3. Thus we have used $Z = 20$ (i.e., 16 000 points in the whole zone) in the calculation of F_4. The cubic term (F_3) has been computed for the steplength $Z = 6$. Use of a longer steplength is not warranted since considerable computer time (approximately 3 times greater) is needed for the steplength $Z = 7$ and there is only a very slight change (in the third significant digit) in the value of F_3 compared to its value calculated for $Z = 6$.

In evaluating the Fourier transforms of the anharmonic coefficients $\Phi(\vec{k}_1 j_1, \vec{k}_2 j_2, \vec{k}_3 j_3, \vec{k}_4 j_4)$ and $\Phi(\vec{k}_1 j_1, \vec{k}_2 j_2, \vec{k}_3 j_3)$ given by Eqs. (8) and (11), respectively, of Ref. 30, the direct lattice summations $(\vec{n})$ have been carried out to the sixth-neighbor distance.

III. RESULTS

A. Monte Carlo method

The specific heat has been computed for three volumes, $V = 54.638$, 55.776, and 56.914 cm³/mole (V_1, V_2, and V_3, respectively), and for a range of temperatures between 240 and 430 K. The results are shown in Table II. In order to examine the

TABLE II. Specific heat at constant volume C_v and specific heat at constant pressure C_p from Monte Carlo calculations; C_v^{anh} from lowest-order perturbation theory. All quantities are given in dimensionless units.

T	V_1 C_v/R	C_p/R	C_v^{anh}/R	V_2 C_v/R	C_p/R	C_v^{anh}/R	V_3 C_v/R	C_p/R	C_v^{anh}/R
240	3.03	· · ·	3.075						
250				3.25	3.34	3.082			
260							3.43	3.58	3.082
280	3.06	3.14	3.088						
290				3.32	3.44	3.095	3.32	3.46	3.092
							3.19	3.31	
320	3.20	3.30	3.100	3.46	3.61	3.105	3.48	3.66	3.101
350	3.27	3.39	3.109	3.12	3.23	3.115	3.33	3.49	3.111
							3.52 [a]	3.71 [a]	
370				3.38	3.54	3.121			
380	3.23	3.36	3.119	3.31	3.45	3.125	3.42	3.63	3.120
							4.02 [a]	4.37 [a]	
390				3.42	3.60	3.128			
400	4.20 [b]	4.49 [b]	3.125	3.74 [a]	3.98 [a]	3.131	4.05 [a]	4.39 [a]	3.127
	3.87								
410	3.76	3.98	3.128	3.75	4.01	3.135	3.90 [a]	4.26 [a]	3.130
				5.04 [b]	5.80 [b]		5.08 [b]	5.79 [b]	
415	3.46	3.65	3.130				4.67 [b]	5.30 [b]	3.131
420	3.77	4.04	3.131	6.34 [b]	7.54 [b]	3.138			
				6.41 [b]	7.26 [b]				
425				4.58 [a]	5.03 [a]	3.139			
				4.92 [b]	5.71 [b]				
430	3.99 [a]	· · ·	3.134						

[a] Moderate displacement of atoms from original sites during calculation.
[b] Extensive displacements (see text).

accuracy of these results, a number of calculations were repeated for given T and V but with a different starting point in the random number sequence. Although the energy and pressure stabilized in each case, in some cases the values at which they stabilized differed by as much as 5% from the first set of values, showing that the sampling was not uniform over a canonical ensemble even after 10^6 trials. The effect on C_v was particularly pronounced, e.g., 30% at V_2 and 410 K, corresponding to a 1% change in U_i and P. Fortunately, we have additional information which sheds light on this situation. During the course of the calculation, we have recorded the distribution of particles according to their distance from their initial positions. A histogram of this distribution is used to monitor the stability of the lattice structure.[33] When the lattice is stable, the distribution peaks at some value near the origin, and when the lattice is unstable, the distribution is spread out uniformly over a distance of several lattice spacings. This criterion determined the highest temperatures given in Table II. However, there can be an intermediate regime where some spreading of the main peak occurs, but subsidiary structure is observed for larger displacements. Such a result indicates that a significant number of atoms have moved from one site to another without destroying the lattice structure. We found that this situation obtained in some cases for our model lattice, with consequent increases in the energy, presssure, and specific heat over the values obtained when no migration had occurred. In Table II, we have denoted by footnote a those cases where the atomic displacements were moderate (~1 lattice spacing) and by footnote b those cases where the atomic
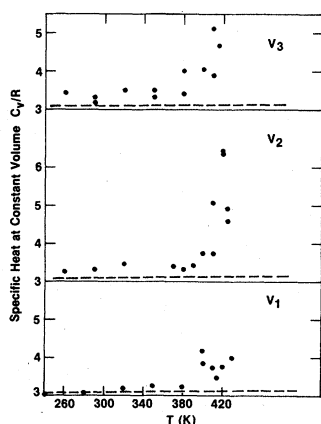
displacements were extensive (2 or more lattice spacings). The case V_1 (400 K) is special in that markedly different histograms were obtained from different portions of the same run. These showed that there was a large rate of migration in the first part of the run (6×10^5 trials) but thereafter the rate of migration was low. The lower C_v value given here was obtained from the last 4×10^5 trials. No subsidiary structure was observed in the histograms for the remaining cases studied.

We have plotted the results for C_v in Fig. 1. For cases with negligible atomic migration, the spread in C_v values is on the order of 5% of the mean value. When extensive migration takes place, the spread in C_v values is on the order of 20% of the mean value. The spread in C_p values is somewhat greater owing to the factor $(\partial p / \partial T)_V^2$ in Eq. (4).

B. Perturbation-theory method

The cubic and quartic anharmonic contributions to the Helmholtz free energy have been computed for volumes V_1, V_2, and V_3. The results are given in Table III. The coefficient A in this table is that given by

$$\frac{\Delta C_v^{\text{anh}}}{R} = -kT\frac{\partial^2 F}{\partial T^2} = -2kT(F_3 + F_4) \equiv AT. \quad (7)$$

Values of the total specific heat at constant volume

$$C_v^{\text{anh}}/R = 3 + AT \quad (8)$$

are given in Table II. The effect of volume change is insignificant. These results are plotted in Fig. 1, together with the results of the Monte Carlo calculations. In Fig. 2 we compare the calculations with the experimental results of Filby and Martin[3] plotted as $C_v^l/R = C_v/R - \gamma T/R$, where the electronic coefficient $\gamma = 2410$ μJK^{-2}mole^{-1}. The linear portion of this curve has a slope of 7.4×10^{-4} K^{-1}, i.e., about twice that of C_v^{anh}. The calculated C_v and C_v^{anh} at volume V_2 are also plotted here. Note that the constant volume in the experimental C_v is the equilibrium volume for temperature T_{r_1}

FIG. 1. Specific heat vs temperature. Monte Carlo calculations: C_v, ●. Perturbation theory calculations: C_v^{anh}, ---. (a) $V_1 = 54.638$ cm^3/mole, (b) $V_2 = 55.776$ cm^3/mole, (c) $V_3 = 56.914$ cm^3/mole.

TABLE III. Cubic, F_3, and quartic, F_4, anharmonic contributions to the Helmholtz free energy, and the coefficient A in C_v^{anh}. F_3 and F_4 are in units of $10^{12} N (kT)^2$ erg^{-1} and A is in units of 10^{-4} K^{-1}.

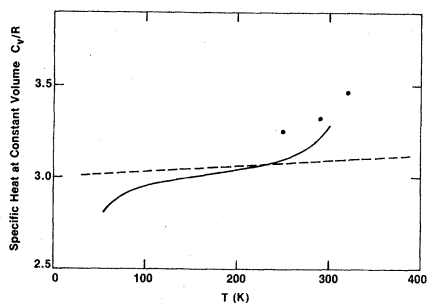| Lattice const. (Å)	F_3	F_4	A
5.661	−2.233 865	1.102 169	3.124 889
5.700	−2.416 396	1.228 109	3.281 150
5.739	−2.621 062	1.474 647	3.165 532

FIG. 2. Comparison with experimental C_v. Experimental results of Filby and Martin (Ref. 3), C_v^l, ——; C_v^{anh}, - - -; Monte Carlo at V_2, C_v, ● .

$V(T)$. V_2 is close to the volume of rubidium at room temperature $[V(293 \text{ K}) = 55.9 \text{ cm}^3/\text{mole}]$. We do not know how the melting temperature, T_m, of our model system is related to the temperature at which the lattice becomes unstable since the instability we observe is not melting (see Ref. 33 for a discussion of this question). Further, our model does not take account of the electrons explicitly, apart from their effect on the interatomic potential through the dielectric function, and we know that their presence is essential for the rubidium structure to be stable at the volumes observed. For these reasons, and since we are interested here in the specific heat of a *lattice* at high temperatures, the question of the model lattice's melting point is not pursued further.

IV. DISCUSSION

The results shown in Fig. 1 are, as far as we know, the first to enable a direct comparison to be made between lowest-order anharmonic theory and the fully anharmonic system as computed by the Monte Carlo method. At the lower temperatures there is fairly good agreement between the two sets of results, but at the higher temperatures there is a definite upward trend in the Monte Carlo values, even in those cases where no appreciable migration occurred, so we conclude that the fully anharmonic calculation does indeed account for some part of the anomalous rise in the specific heat. Further, the Monte Carlo results have much more interesting implications insofar as they associate high specific heat values with the migration of atoms from one site to another. Clearly such large-scale motion involving atom exchange cannot be dealt with in the context of classical lattice-dynamical theory. Much more extensive studies (a larger number of trials, more detailed sampling of the V-T space) need to be done to satisfy questions of stability and statistical significance, but even these limited results point in a direction which appears promising, namely a detailed study of the atomic motions at high temperatures. To this end, molecular-dynamics studies with one or two vacancies in the lattice are currently in progress.

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