Comparison of theories of anharmonicity applied to a model of copper*

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We have applied five different formulations for the calculation of thermodynamic properties of an anharmonic crystal to a simple model of copper, in order to investigate the range of validity of each theory for a weakly anharmonic system. The theories used are the quasiharmonic approximation, anharmonic perturbation theory, self-consistent phonon theory, improved self-consistent phonon theory, and the cell model. We find that perturbation theory, improved self-consistent theory, and the cell model give comparable results up to half the melting temperature, with perturbation theory diverging slightly above this.

I. INTRODUCTION

There exist at the present time several approximate schemes for the calculation of the thermodynamic properties of an anharmonic crystal. In particular we refer to the quasiharmonic approximation (QH), anharmonic perturbation theory (PT), self-consistent phonon theory (SC), the improved self-consistent phonon theory (ISC), and the cell model (CM). A large number of calculations have been carried out in which these methods are applied to a model of an inert-gas crystal, often involving a Lennard-Jones potential. A review of recent results has been given by Glyde and Klein.[1] The conclusion drawn from this work is that the quasiharmonic approximation is very unreliable, perturbation theory is useful only below about one-third of the melting temperature, and that the improved self-consistent theory is the only one giving at all satisfactory results. However, one of us[2] has applied the quasiharmonic and perturbation theories to a model of sodium chloride, with the finding that perturbation theory gave good results up to 70% of the melting temperature and that quasiharmonic theory was useful up to 30% of the melting temperature.

In these circumstances it seems useful to apply the various techniques to a model of a crystal with a completely different type of binding, and a metal is the obvious choice. The interatomic forces in many simple metals are long range and oscillatory, and in addition change as the crystal volume changes. While these effects can all be incorporated they do increase the magnitude of the calculation. For this reason we have chosen to apply the various theories to a model of copper. The interatomic forces in copper are known to exist primarily between nearest-neighbor atoms, and the largest contribution to the forces is a term arising from the overlap of the $3d$ orbitals on adjacent atoms, which is well represented by a phenomenological expression. It is thus possible to set up a model which is a fair representation of copper but which is computationally tractable.

We emphasize, however, that we are primarily interested in a comparison of the results of the various methods of calculation, rather than in a comparison with the experimental results for copper. The agreement with experiment in fact turns out to be not very good. The model is described in Sec. II, the different theories are given in Sec. III, and the numerical techniques and results in Sec. IV. The results are discussed in Sec. V.

II. THE MODEL

The model we have used is based initially on a calculation by Jaswal and Girifalco of the binding energy of copper.[3] They write the total energy per unit cell of the static crystal as a contribution $6E_{c-c}$ describing the overlap energy of nearest-neighbor ion cores, with

$$E_{c-c} = \alpha e^{\rho(r_0-r)/r_0} , \tag{1}$$

to which is added a complicated expression describing the kinetic, correlation, and electrostatic energies of the conduction electrons, and their interaction with the ion cores. This whole expression was left unchanged. The values of the three parameters appearing in E_{c-c} were changed very slightly in order to fit more recent experimental data. The values adopted are given in Table I.

The overlap energy E_{c-c} is the largest single contribution to the effective interatomic potential, but there is an additional contribution arising from the electronic-energy terms. Further, this contribution is a function of the volume of the crystal. We approximate it as follows. First we assume that only nearest-neighbor interactions are important. This is to some extent justified by direct calculations[4,5] of the electron-ion contribution to the forces, which indicate that the convergence is rapid, and by the fit to experimental phonon dispersion curves given by a nearest-neighbor model.[6] Next we assume, for simplicity, that for the nearest neighbors this contribution has the same spatial dependence as the overlap contribution (1). The

TABLE I. Parameters of the overlap energy.

Parameter	Unit	Value
α	10^{-12} ergs	0.154795
ρ	dimensionless	13.2377
r_0	Å	2.543

total interaction then has the same form as (1) but with a modified volume-dependent value for the coefficient α. The value at a given lattice spacing was obtained from the condition that the compressibility derived from the slopes of the phonon dispersion curves at long wavelengths should have the same value as that obtained from the second derivative of the total energy. The electron-ion contribution to the modified coefficient α turns out to be about 20% of the overlap term, and to be only weakly volume dependent. One test of the model is the calculation of phonon dispersion relations. At low temperatures the experimentally measured frequencies can be compared directly with the quasiharmonic frequencies. The frequencies calculated for the lattice spacing which corresponds experimentally to 80 K are in reasonable agreement with the measured values.[6] The mean ratio of calculated to experimental frequencies is 0.960, and the root-mean-square percentage deviation is 5.8%. At higher temperatures the comparison is less direct. Figure 1 shows dispersion curves measured for the two principal symmetry directions at 673 K.[7] The solid lines are the quasiharmonic calculation and the dashed lines are the first-order self-consistent frequencies, both at the experimentally measured lattice spacing. The two sets of curves differ by 10%, and the experimental points lie in between them. This is probably as much as could be expected.

The Helmholtz function for the crystal includes a thermal contribution arising from the electron gas. This was taken to be of the form $-\frac{1}{2}\alpha T^2$, with

α having the value (166.3 μcal/$^\circ$K^2 g atom),[8] independent of the crystal volume.

There are other models which we could have used. DeWette, Cotterill, and Doyama[9] have given the parameters for a Morse potential fitted to the compressibility, lattice spacing, and vacancy-formation energy. More recently, Moriarty[5] has tabulated a reciprocal-space form of the effective interaction. It is our hope that as far as the comparison of different methods of calculation is concerned, any of these models would lead to the same conclusions.

III. THE THEORIES

We have used the model described in the previous paragraph to calculate the Helmholtz function for copper, as a function of temperature and volume, using five different theoretical formalisms, which are here briefly reviewed.

A. Quasiharmonic theory (QH)

In this theory the Helmholtz function has the same form as for a harmonic crystal, namely

$$A_{QH} = (N/2)\sum_l \phi(\vec{R}_l)$$
$$+ kT\sum_{\vec{q}j} \ln\{2\sinh[\tfrac{1}{2}\beta\hbar\omega(\vec{q}j)]\}. \tag{2}$$

The first term is the static energy, the sum being over the neighbors of a particular atom. The second sum is over the $3N$ normal modes of vibration; k is Boltzmann's constant and β is $1/kT$. The anharmonicity manifests itself through the volume dependence of the static energy and of the frequencies, $\omega(\vec{q}j)$.

B. Perturbation theory (PT)

To lowest order in perturbation theory[10,11] the Helmholtz function is given by

$$A_{PT} = A_{QH} + A_3 + A_4,$$

where the cubic (A_3) and quartic (A_4) correction terms are given by

$$A_3 = -\frac{\hbar^2}{48N} \sum_{\vec{q}_1 j_1, \vec{q}_2 j_2, \vec{q}_3 j_3} \frac{\Delta(\vec{q}_1 + \vec{q}_2 + \vec{q}_3)|\Phi(\vec{q}_1 j_1, \vec{q}_2 j_2, \vec{q}_3 j_3)|^2}{\omega_1 \omega_2 \omega_3} f(\vec{q}_1 j_1, \vec{q}_2 j_2, \vec{q}_3 j_3),$$

$$f(\vec{q}_1 j_1, \vec{q}_2 j_2, \vec{q}_3 j_3) = \prod_{s=1}^{3} [1 - \exp(-\beta\hbar\omega_s)]^{-1} \left(\frac{1 - \exp[-\beta\hbar(\omega_1 + \omega_2 + \omega_3)]}{\omega_1 + \omega_2 + \omega_3} + 3\frac{\exp(-\beta\hbar\omega_3) - \exp[-\beta\hbar(\omega_1 + \omega_2)]}{\omega_1 + \omega_2 - \omega_3} \right),$$

$$\tag{3}$$

and

$$A_4 = \left(\frac{\hbar^2}{32N}\right) \sum_{\vec{q}_1 j_1, \vec{q}_2 j_2} \frac{\Phi(\vec{q}_1 j_1, -\vec{q}_1 j_1, \vec{q}_2 j_2, -\vec{q}_2 j_2)}{\omega_1 \omega_2} \coth(\tfrac{1}{2}\beta\hbar\omega_1) \coth(\tfrac{1}{2}\beta\hbar\omega_2).$$

Here N is the number of unit cells, and ω_1 has been written in place of $\omega(\vec{q}_i j_i)$ for brevity. $\Delta(\vec{q}_1 + \vec{q}_2 + \vec{q}_3)$ is unity if the argument is a vector of the reciprocal

lattice (including zero) and zero otherwise. $\Phi(\vec{q}_1 j_1, \vec{q}_2 j_2, \vec{q}_3 j_3)$ and $\Phi(\vec{q}_1 j_1, \vec{q}_2 j_2, \vec{q}_3 j_3, \vec{q}_4 j_4)$ are the Fourier transforms of the third- and fourth-order
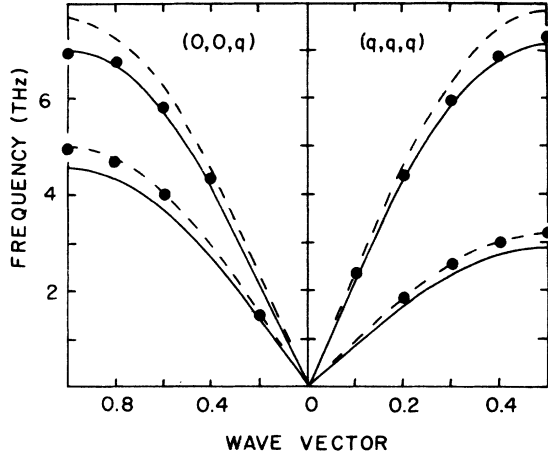
FIG. 1. Phonon dispersion relations for the two highest symmetry directions in copper at 673 K. Points are the experimental measurements of Ref. 7, solid lines are the quasiharmonic frequencies, dashed lines are the self-consistent frequencies.

atomic force constants. For a two-body force system they take the form

$$\Phi(\vec{q}_1 j_1, \ldots, \vec{q}_n j_n) = (1/2M^{n/2})$$

$$\times \sum_{l, \alpha \ldots \beta} \phi_{\alpha \ldots \beta}(\vec{R}_l) e_\alpha(\vec{q}_1 j_1) \cdots e_\beta(\vec{q}_n j_n)$$

$$\times \prod_{i=1}^{n} [1 - \exp(i\vec{q}_i \cdot \vec{R}_l)],$$

where M is the atomic mass.

C. Self-consistent phonon theory (SC)

In the first-order self-consistent phonon theory[12] (SC1) the eigenvalues, $\omega(\vec{q}j)$ and eigenvectors $\vec{e}(\vec{q}j)$ for a given $\vec{q}$ are obtained by iterating the following set of equations:

$$D_{\alpha\beta}(\vec{q}) = \frac{1}{M}\sum_l [1 - \cos(\vec{q}\cdot\vec{R}_l)]\langle\phi_{\alpha\beta}(\vec{R}_l)\rangle,$$

$$\langle\phi_{\alpha\beta}(\vec{R}_l)\rangle = (8\pi^3 \det\lambda_l)^{-1/2}$$

$$\times \int \exp(-\tfrac{1}{2}\vec{\tau}\cdot\lambda_l^{-1}\cdot\tau)\phi_{\alpha\beta}(\vec{R}_l + \vec{\tau}) d^3\tau, \quad (4)$$

$$(\lambda_l)_{\alpha\beta} = \frac{\hbar}{MN}\sum_{\vec{q}j}[1 - \cos(\vec{q}\cdot\vec{R}_l)]e_\alpha(\vec{q}j)e_\beta(\vec{q}j)$$

$$\times \coth[\tfrac{1}{2}\beta\hbar\omega(\vec{q}j)]/\omega(\vec{q}j).$$

$\phi_{\alpha\beta}(\vec{r})$ is the tensor derivative of the two-body potential, evaluated at the point $\vec{r}$.

The Helmholtz function is then calculated from

$$A_{\rm SC} = \tfrac{1}{2}N\sum_l\langle\phi(\vec{R}_l)\rangle + kT\sum_{\vec{q}j}\ln\{2\sinh[\tfrac{1}{2}\beta\hbar\omega(\vec{q}j)]\}$$

$$- \tfrac{1}{4}\hbar\sum_{\vec{q}j}\omega(\vec{q}j)\coth[\tfrac{1}{2}\beta\hbar\omega(\vec{q}j)]. \quad (5)$$

Except for the last term, this is the same as the quasiharmonic expression (2), with each quantity

replaced by its averaged, or smeared, value. The last term can be written in the alternative form

$$-\tfrac{1}{2}N\sum_{l,\alpha\beta}\langle\phi_{\alpha\beta}(\vec{R}_l)\rangle(\lambda_l)_{\alpha\beta}, \quad (6)$$

which occurs naturally in the derivation of self-consistent theory from perturbation theory.[13] We found this to be a useful alternative.

D. Improved self-consistent theory (ISC)

In the improved self-consistent theory[14] the Helmholtz function is given by the self-consistent value, $A_{\rm SC}$, to which is added a cubic correction term of the same form as A_3, in Eq. (3), but now $\omega(\vec{q}j)$ and $\vec{e}(\vec{q}j)$ are to be obtained from self-consistent theory, and $\phi_{\alpha\beta\gamma}(\vec{R}_l)$ is replaced by an averaged value similar to Eq. (4). Then

$$A_{\rm ISC} = A_{\rm SC} + \langle A_3\rangle.$$

E. Cell model (CM)

The Helmholtz function for the cell model[15] corresponds to that of N atoms each moving independently in the field due to its neighbors fixed at their equilibrium positions:

$$A_{\rm CM} = \tfrac{1}{2}N\sum_l\phi(\vec{R}_l) - \tfrac{3}{2}NkT\ln(2\pi mkT/h^2)$$

$$- NkT\ln G,$$

$$G = \int \exp[-\phi_1(\vec{u})/kT] d^3u,$$

$$\phi_1(\vec{u}) = \sum_l [\phi(\vec{R}_l - \vec{u}) - \phi(\vec{R}_l)].$$

The integral G is taken over a single Wigner-Seitz cell. The expression given above is derived from a classical theory, applicable only at high temperatures.

IV. NUMERICAL TECHNIQUES AND RESULTS

For each of the theoretical formalisms described in Sec. III the Helmholtz function was first calculated, at temperatures in 100-K steps to 1400 K, at three volumes, the volumes for each temperature being chosen to bracket the expected equilibrium volume. By interpolation between these results we could make a much better estimate of the equilibrium volume. The Helmholtz function was then calculated at this new volume and at six other points displaced slightly in temperature or volume or both. The various second derivatives of the Helmholtz function were then obtained as suitable second differences.

The sums over the normal modes occurring in $A_{\rm QH}$, $A_{\rm SC}$, and A_4 were each carried out over a simple cubic mesh of wave vectors in the irreducible part of the first Brillouin zone, corresponding to 13 500 wave vectors in the whole zone. The sums over wave vectors in A_3 and $\langle A_3\rangle$ were performed with a mesh of 256 wave vectors in the

whole zone. In the perturbation-theory calculation, the expression for A_3 was actually replaced by the first two terms in a high-temperature expansion, which gives adequate numerical accuracy with some saving in computation time. This was not done in the improved self-consistent calculation.

The smeared force constants defined in Eq. (4), and the smeared cubic force constants required in the calculation of $\langle A_3 \rangle$, were evaluated in several ways. In most of the calculations the integral was replaced by a summation over a simple cubic grid of 3375 points with a spacing which was automatically optimized for each temperature. We also used Gauss-Hermite quadrature formulas applied in three dimensions. This yielded more accurate results for a given number of points but was slightly less convenient to program. The two methods gave results which agreed to five or six figures. No precautions were taken to omit the area around the origin from the integration since the Born-Mayer potential remains finite in this region. A third method of evaluation which we investigated for the harmonic force constants was to expand the $\phi_{\alpha\beta}(\vec{R}_l + \vec{r})$ appearing in Eq. (4) as a Taylor series and to integrate term by term. For the Born-Mayer potential this was a practical method. The first three correction terms to the harmonic force constants yielded satisfactory results at all but the highest temperatures. However, the same procedure applied to the Lennard-Jones potential gave very poor results.

The self-consistent calculations were iterated until the self-consistent Helmholtz function was constant to seven figures. We also examined the convergence of the elements of the λ_l matrix. It is interesting that when Eq. (5) was used for the Helmholtz function, the rates of convergence of A_{SC} and of λ_l were very similar. If the modification to A_{SC} given by Eq. (6) was used the convergence of A_{SC} was greatly accelerated.

This is illustrated in Table II, which shows the values of some contributions to the Helmholtz function at one temperature and volume. The first three values are the quasiharmonic Helmholtz function, the quartic anharmonic contribution, and the sum of these two. The fourth and fifth values are the value of the self-consistent Helmholtz function on the first cycle, so that the quasiharmonic value of λ_l was used for the smearing, the two numbers corresponding to Eqs. (5) and (6), respectively. The number obtained from Eq. (6) is very similar to the sum in the third line, the difference representing the effect of higher-order contributions from even terms in the potential. The number obtained from Eq. (5) is quite different. Both formulas lead to the same converged answer for the Helmholtz function, the final value in the table, but if Eq. (6) is used this value is obtained in the third

TABLE II. Calculations of the Helmholtz function at 300 K, cell volume 11.62851 Å³.

Contribution	Value (J/mole deg)
A_{QH}	−1956.80
A_4	169.52
$A_{QH} + A_4$	−1787.28
A_{SC}[Eq. (5), first cycle]	−1462.48
A_{SC}[Eq. (6), first cycle]	−1797.02
A_{SC}(converged)	−1795.99

cycle, whereas if Eq. (5) is used six cycles are required. Note also that the difference between the last two numbers is not very large, indicating that the iterative procedure does not have much effect. If accurate eigenvectors and eigenvalues are required it is still necessary to converge the λ_l, but if A_{SC} is the only quantity required the use of Eq. (6) seems preferable.

The integration over the Wigner-Seitz cell occurring in the cell-model theory is also easily evaluated. The only difficulty which might be encountered is that at low temperatures the integrand is very strongly peaked at the origin. An efficient way around this is to replace the integration by a summation over a mesh of points with a spacing dependent on the temperature. We actually adopted the simpler approach of using a very dense mesh of points. The summation was carried out over a simple cubic grid of points in $\frac{1}{48}$ of the Wigner-Seitz cell corresponding to 54 000 points in the whole cell. Cell-model calculations were carried out only for temperatures of 300 K and higher.

From the values of the Helmholtz function the values of the lattice parameter (a_0), isothermal bulk modulus (B_T), linear thermal expansion coefficient (α_p), and heat capacities at constant volume (C_v) and constant pressure (C_p) were obtained from the equations

$$\frac{\partial A}{\partial a_0} = 0 \quad \text{at zero pressure},$$

$$B_T = V \frac{\partial^2 A}{\partial V^2},$$

$$\alpha_p = -\frac{\partial^2 A}{\partial V \partial T} \Big/ 3B_T,$$

$$C_v = -T \frac{\partial^2 A}{\partial T^2},$$

$$C_p = C_v + 9TVB_T \alpha_p^2.$$

Here V is the volume of the specimen. The results for the five models are shown in Figs. 2–6. In all except Fig. 5, which is plotted on a very expanded scale, it was not possible to separate the ISC and CM results. The experimental results[16–21] are also shown in the figures.
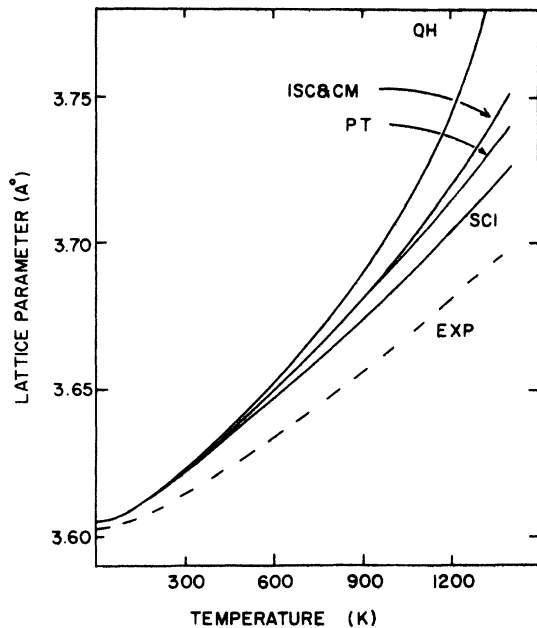
FIG. 2. Calculated and experimental values of the lattice parameter in copper.

FIG. 4. Calculated and experimental values of the isothermal bulk modulus.

V. DISCUSSION

We have used five different theoretical formalisms to calculate the thermodynamic properties of a model of copper, and the principal motivation of
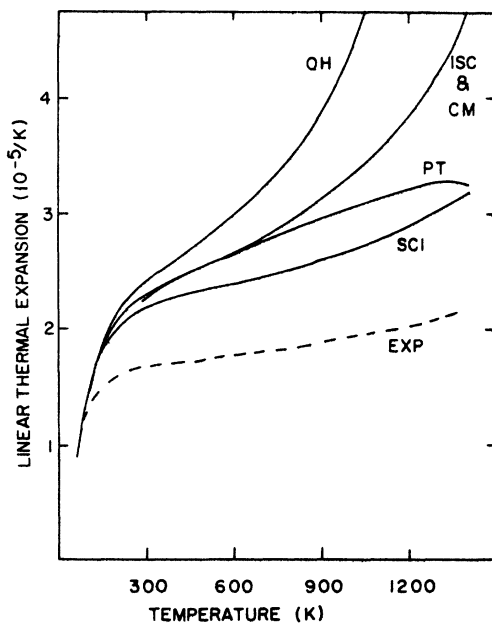

FIG. 3. Calculated and experimental values of the thermal expansion coefficient for copper.
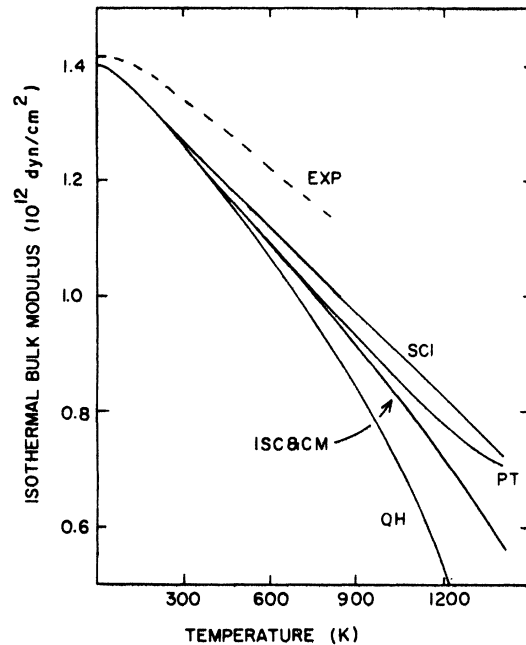
the work is to compare the results of the different theories. The model used was a plausible one, and we believe that the same qualitative conclusions would be obtained from any reasonable model of copper or of other metals with predominantly short range force systems.

The most sophisticated and time consuming of the theories is the improved self-consistent theory and we assume that the results of that calculation represent the correct values of the various properties. Then we can say that the much simpler perturbation theory gives good results for temperatures up to about half the melting temperature of 1350 K. The quasiharmonic and first-order self-consistent theories are much less satisfactory, discrepancies already being serious at one-fifth of the melting temperature. The simple cell model gives embarrassing agreement with ISC, though we believe that this is to some extent a coincidence. A perturbation treatment of the cell model shows that it gives an anharmonic contribution to the Helmholtz function closely equal to one-half of the quantity A_4 appearing in the conventional theory. For the model we have used A_3 is approximately minus one-half of A_4. The sum is then similar in magnitude to the cell model term. In some materials A_3 is as large as, or greater than, A_4 in magnitude, and the cell model would then not be so reliable.

As far as comparison with the experimental results is concerned the model is clearly inadequate.

The anharmonic contribution to C_v is of the wrong sign. Analysis of the experimental results indicates that the term A_3 should be slightly greater than A_4 in magnitude, instead of being half of it. At the same time the calculated thermal expansion is too large which we interpret as indicating that the third derivative of the potential is also too large. As discussed in Sec. II the model gives quite reasonable results for the phonon dispersion curves, so that the poor values obtained for the thermodynamic properties indicate a surprising sensitivity to the details of the model. The most serious weakness in the model is probably the assumption that the contribution to the interatomic forces arising from the electron-phonon interaction has the Born-Mayer form. An attractive component in this force would almost certainly have the effect of enhancing A_3 relative to A_4.

The experimental results shown in Figs. 2–6 all contain, at high temperatures, a contribution arising from point defects. The heat-capacity data have been analyzed by Brooks,[22] who concludes that the contribution to C_v arising from equilibrium lattice defects is negligible for temperatures below 800 K, rising to about 0.7 J/mole K at 1200 K. The subtraction of this contribution from the experimental curve would bring it into closer agreement with the quasiharmonic calculation, but would not
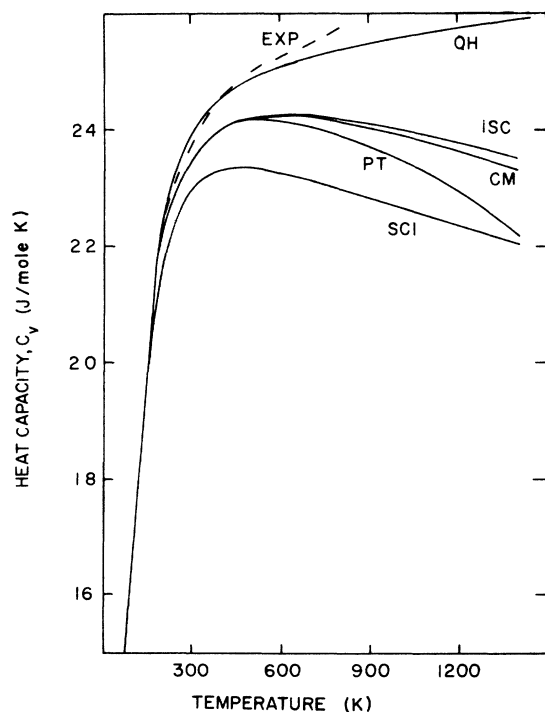

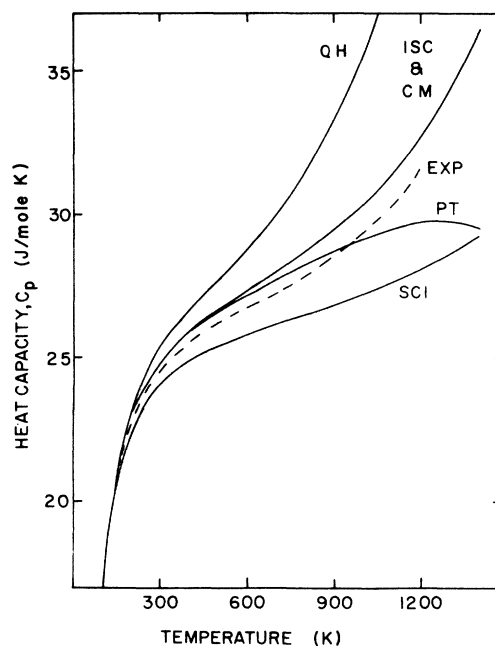FIG. 6. Calculated and experimental values of the heat capacity at constant pressure.

FIG. 5. Calculated and experimental values of the heat capacity at constant volume.

change the basic disagreement, that all the other models predict that C_v decreases with increasing temperature. Point defects make a similar contribution to C_p, and also make positive contributions to the bulk modulus and the thermal expansion coefficient. Presumably these contributions will also be negligible except at temperatures above about 800 K.

Any calculation of anharmonic properties requires the adoption of a model for the interatomic forces and of a theoretical technique for the calculation. It is then difficult to ascribe discrepancies between theory and experiment to either one source or the other. In this work we have shown that for a weakly anharmonic material, such as copper, several methods of calculation give similar results over a wide temperature range. In particular, anharmonic perturbation theory gives results comparable with those of the much more time-consuming improved self-consistent theory. It is now reasonable to apply the perturbation technique to several different models, with the knowledge that any variations in the results obtained do reflect real differences in the models. We intend to do this in the near future.

ACKNOWLEDGMENTS

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