

Simple Description of Anharmonic Phenomena in Cubic Crystals

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Abstract

A simple spherically symmetric single-atom potential expression in the form of a series expansion in the atomic displacement is assumed to describe the potential energy of each atom in monatomic cubic crystals from room temperature to their melting point. Expressions are derived to account for thermal properties such as melting point and thermal expansion. Calculated results for 13 cubic metals are compared with experimental values. The model accounts for the broad trends in the experimental data and provides an estimate of the extent of anharmonicity to be found in these simple solids.

Introduction

Various thermal properties of crystals may be calculated in lattice dynamical theory in terms of anharmonic or higher order contributions to the total lattice potential energy expanded as a power series in the atomic displacement. It has been found recently that X-ray diffraction data from monatomic anharmonic cubic solids can be readily interpreted by assuming a single-atom anharmonic potential expansion model for the crystal (e.g. Willis 1969; Field and Medlin 1974). In this paper we derive expressions on the basis of this simple single-atom model for various thermodynamic properties considered to be consequences of anharmonicity, in order to determine whether the model offers a reasonable means of estimating the extent of anharmonicity present in simple crystals.

Theory

We consider the potential energy expansion to fourth order given by

$$V(r) = \frac{1}{2}\alpha r^2 + \gamma r^4, \quad (1)$$

where $r^2 = x^2 + y^2 + z^2$ and x, y, z are the components of the displacement from the mean position. The parameter γ is taken to be negative. The function in equation (1) has a turning point at

$$r_{tp} = (-\alpha/4\gamma)^{\frac{1}{2}} \quad (2)$$

and the height of the well at the turning point is given by

$$V(r_{tp}) = -\alpha^2/16\gamma. \quad (3)$$

The potential energy function $V(r)$ is shown in Fig. 1.

It is assumed that $V(r)$ is an adequate representation of the potential well in which the atom vibrates from room temperature to melting point, and we now proceed to derive relations for various thermal quantities.

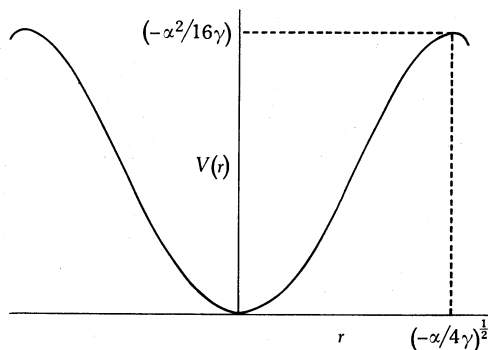


Fig. 1. Single-particle fourth order anharmonic potential function $V(r)$ defined by equation (1).

The r.m.s. amplitude of vibration of the atom can be calculated by taking the thermal average of r^2 as

$$\langle r^2 \rangle = \iiint_{-\infty}^{\infty} r^2 \exp\{-\beta V(r)\} dx dy dz / \iiint_{-\infty}^{\infty} \exp\{-\beta V(r)\} dx dy dz, \quad (4)$$

where $\beta = (k_B T)^{-1}$, k_B being the Boltzmann constant and T the absolute temperature. Using the approximation for small vibrations

$$\exp\{-\beta V(r)\} = \exp\{-\frac{1}{2}\alpha\beta r^2\} (1 - \beta\gamma r^4), \quad (5)$$

equation (4) reduces to

$$\langle r^2 \rangle = \frac{3k_B T \alpha^{-1} - 105 \gamma k_B^2 T^2 \alpha^{-3}}{1 - 15 \gamma k_B T \alpha^{-2}}. \quad (6)$$

Thermal expansion is a manifestation of anharmonicity which can be considered in a rigorous lattice dynamical model in terms of the temperature change of the mean displacement of the atoms due to third and higher order components of the potential energy expansion for the lattice. In the present case of a one-atom potential, the elements for which calculations have been made are face-centred or body-centred cubic with each atom at a centre of symmetry. Then the third and higher odd-order anharmonic terms in the potential energy expansion are zero and the mean atomic displacement is zero. However, an approximate linear thermal expansion coefficient α_l may be derived from the single-atom anharmonic potential model by considering the variation of the anharmonic part $\langle r_A^2 \rangle$ of $\langle r^2 \rangle$ with temperature and taking

$$\alpha_l = a_0^{-1} \partial \langle r_A^2 \rangle^{\frac{1}{2}} / \partial T,$$

where

$$\langle r_A^2 \rangle = \langle r^2 \rangle - \langle r_H^2 \rangle = \langle r^2 \rangle - 3k_B T / \alpha,$$

$\langle r_H^2 \rangle$ being the harmonic part of the mean square displacement and a_0 the room temperature lattice parameter. For the fourth order potential expansion model, omitting terms of order γ^2/α^5 and higher, we have

$$\alpha_l \sim a_0^{-1} (-60 \gamma k_B^2 / \alpha^3)^{\frac{1}{2}}. \quad (7)$$

The heat capacity of the anharmonic solid may be estimated by making use of the partition function Z (Kittel 1971). This is calculated for the atom in the anharmonic well as

$$Z = \iiint_{-\infty}^{\infty} \exp(-\beta p^2/2m) dp_x dp_y dp_z \\ \times \iiint_{-\infty}^{\infty} \exp\{-\frac{1}{2}\alpha\beta r^2\} (1-\beta\gamma r^4) dx dy dz,$$

where the approximation of equation (5) has been used. Here p_x , p_y and p_z are the components of the momentum p and m is the mass. The average energy of the oscillator at temperature T is then

$$\langle E \rangle = k_B T^2 d(\ln Z)/dT$$

and the specific heat is given by

$$C = d\langle E \rangle/dT.$$

Using the potential energy function (1), the specific heat becomes, ignoring higher order terms,

$$C = 3k_B \{1 - 10 \gamma k_B T / \alpha^2\}. \quad (8)$$

Melting can be taken into account if a suitable judgment is made as to a melting criterion. The Lindemann formula works satisfactorily on the criterion that the solid melts when the amplitude of vibration reaches a certain fraction of the lattice spacing. If it is accepted that a liquid has short-range order, but not long-range order, and that the potential well for each atom will be modified when sufficient numbers of atoms have sufficient thermal energy to create vacancies in the lattice, that is, that there is a certain probability that each atom will escape from its potential well, then the selection of a criterion for melting becomes the selection of a critical probability for the formation of a vacancy. Now, at the melting point T_m the probability P that the atom has energy greater than E_m is given by

$$P = \exp\{-E_m/k_B T_m\}$$

and, according to the criterion stated above, $E_m = V(r_{tp})$. Thus

$$P = \exp\{-V(r_{tp})/k_B T_m\},$$

which yields

$$T_m = -V(r_{tp})/k_B \ln P = \alpha^2/16 \gamma k_B \ln P \quad (9)$$

for the potential function of equation (1).

Results

Calculations have been carried out for five b.c.c. metals and eight f.c.c. metals. In the previous discussion it has been assumed that temperatures at or above room temperature are sufficiently high for anharmonic effects to be present and to be representable by the single-atom potential model for the 13 metals considered here. Generally this is taken to be true for $T \geq \theta_D$, where T is the temperature of interest

and θ_D the Debye temperature. Measured values of the X-ray θ_D together with their sources are contained in Table 1 for each element. Although the Debye temperatures of a number of the metals in this table are above room temperature, the assumption is justified over the range from room temperature to the melting point.

Table 1. X-ray Debye temperatures for 13 metals

Metal	Structure	θ_D (K)	Reference
Tungsten	b.c.c.	377 ± 11	Walford (1969)
Niobium	f.c.c.	284 ± 6	Linkoaho (1971)
Vanadium	b.c.c.	372 ± 6	Linkoaho (1971)
Platinum	f.c.c.	236 ± 5	Alexopoulos <i>et al.</i> (1965)
Nickel	f.c.c.	417 ± 12	Linkoaho (1971)
Iron	b.c.c.	398 ± 9	Herbstein and Smuts (1963)
Copper	f.c.c.	307 ± 3	Linkoaho (1971)
Silver	f.c.c.	200 ± 3	Linkoaho (1971)
Gold	f.c.c.	188 ± 8	Synecek <i>et al.</i> (1970)
Aluminium	f.c.c.	393 ± 1	Dingle and Medlin (1972)
Lead	f.c.c.	85 ± 6	Alexopoulos <i>et al.</i> (1965)
Sodium	b.c.c.	134 ± 1	Field and Medlin (1974)
Potassium	b.c.c.	81	Bednarz (personal communication)

Values of the Debye parameter B have been calculated from the values for θ_D in Table 1 by the usual method, and values of the potential parameter α have been determined according to the relation (Willis 1969)

$$\alpha = 8\pi^2 k_B T/B.$$

It has been assumed that the depth of the potential energy well $V(r_{tp})$ can be given by the activation energy E_a for self-diffusion in the metals, since E_a is a measure of the potential well from which an atom must escape in order to produce diffusion by vacancy formation. From equation (3), values of the anharmonic parameter γ have been determined via the relation

$$\gamma = -\alpha^2/16 E_a.$$

Data for E_a were taken from Peterson (1968).

Various thermodynamic properties have been calculated from the α and γ values so obtained and the results are shown in Table 2a. Corresponding experimental values are listed in Table 2b; here r_n represents the radius associated with the atomic volume in the crystal. In the case of the melting temperature, the probability P chosen to use in equation (9) was 3×10^{-8} .

Discussion

The very anharmonic nature of the metals that we are trying to describe has limited the accuracy of the α parameters since these have been determined from data analysed on a 'quasiharmonic' theory. However, the α values obtained are regarded as being the most accurate available in terms of experimental technique and the application of appropriate correction factors for effects such as thermal diffuse scattering. Further, the range of measured values of E_a for some of the metals is

Table 2. Comparison of calculated and experimental thermal properties

(a) Calculated Results							
Metal	α (eV \AA^{-2})	γ (eV \AA^{-4})	r_{tp} (\AA)	$V(r_{\text{tp}})$ (eV)	$\langle r^2 \rangle^{**}$ (\AA)	α_i^* (10^{-6} K^{-1})	T_m (K)
W	14.8	-2.1	1.33	6.63	0.0726	5.4	4340
Nb	4.31	-0.28	1.96	4.17	0.135	12	2730
V	3.94	-0.30	1.81	3.20	0.141	15	2090
Pt	6.32	-0.84	1.37	2.96	0.111	9.8	1980
Ni	5.62	-0.67	1.45	2.95	0.118	12	1930
Fe	4.99	-0.63	1.41	2.49	0.125	17	1630
Cu	3.44	-0.34	1.59	2.15	0.150	17	1410
Ag	2.52	-0.21	1.73	1.92	0.175	19	1260
Au	4.07	-0.57	1.34	1.81	0.138	15	1180
Al	2.36	-0.28	1.45	1.25	0.181	24	818
Pb	0.884	-0.043	2.27	1.13	0.296	34	740
Na	0.243	-0.0084	2.69	0.438	0.565	120	287
K	0.152	-0.0034	3.34	0.423	0.714	120	277
(b) Experimental Values							
Metal	Structure	r_n (\AA)	E_n (eV)	$\langle r_n^2 \rangle^{**}$ (\AA)	α_i^* (10^{-6} K^{-1})	T_m (K)	
W	b.c.c.	1.56	6.63	0.0724	4.3	3653	
Nb	f.c.c.	1.63	4.17	0.134	7.1	2741	
V	b.c.c.	1.49	3.20	0.140	7.8	2183	
Pt	f.c.c.	1.53	2.96	0.111	8.9	2042	
Ni	f.c.c.	1.38	2.95	0.117	13	1726	
Fe	b.c.c.	1.41	2.49	0.125	12	1810	
Cu	f.c.c.	1.42	2.15	0.150	17	1356	
Ag	f.c.c.	1.60	1.92	0.175	19	1234	
Au	f.c.c.	1.59	1.81	0.138	14	1336	
Al	f.c.c.	1.58	1.25	0.181	23	933	
Pb	f.c.c.	1.93	1.13	0.296	30	601	
Na	b.c.c.	2.11	0.438	0.565	68	371	
K	b.c.c.	2.63	0.423	0.714	83	336	

* At 300 K.

significantly wide, although the values selected in the review by Peterson (1968) are claimed to be the best available.

Despite the above uncertainties, the general trends in the results are clear. The elements are listed in Table 2 in order of increasing anharmonicity, as given by the ratio of the potential parameters γ/α^2 (or the inverse of E_a). This is also the order, with some exceptions, of decreasing α , increasing r.m.s. amplitude of vibration at room temperature, increasing expansion coefficient and decreasing melting temperature. The values of T_m , α_l and r_{tp} compared with r_n have been estimated to average deviations of about 11, 30 and 14 % over ranges of values involving factors of about 12, 20 and 3 respectively.

The agreement for the f.c.c. metals is in general better than for the b.c.c. metals. Iron is slightly anomalous because it undergoes two phase changes at higher temperatures. Sodium and potassium are known to exhibit evidence of anisotropy in

the single-atom potential energy (Field and Medlin 1974; B. Bednarz, personal communication). Further, in b.c.c. metals there is some probability of divacancy as well as monovacancy formation near the melting point.

The melting criterion used here is approximately equivalent to the usual Lindemann supposition for melting. Suppose that there is a critical r.m.s. amplitude of vibration r_c for which melting occurs and that r_c is the same fraction of the potential radius r_{tp} for all metals. Although r_{tp} is not directly comparable with the lattice parameter, it has been compared with the atomic radius, an indirect measure of the lattice spacing. It can be seen from Table 2 that the r.m.s. vibration amplitude is one of the quantities least affected by anharmonicity. Now, from equations (1) and (2) it can be shown that the following relation holds

$$V(r_c)/V(r_{tp}) \sim 1 - (1 - r_c^2/r_{tp}^2)^2. \quad (10)$$

Thus the supposition that melting occurs when the r.m.s. amplitude of vibration reaches a critical fraction of the atomic radius leads, on the potential model used here, to the result that the potential energy corresponding to the critical radius is the same fraction of the depth of the well in which each atom is vibrating for all metals, that is, the probability that the atoms can escape from the potential well at the melting point is the same for each metal.

It is difficult to determine accurate values of heat capacity at constant volume C_v from experimental values of C_p , the constant pressure heat capacity, and a comparison of C with C_v has not been made. However, the model predicts a first order contribution $\sim T$, as for more rigorous models, and the same behaviour for all metals as T/T_m , with a contribution $\sim 4\%$ at the melting point.

Higher order terms in the potential energy would account qualitatively for the observed increase of α_l with temperature.

In conclusion, the model is seen to provide a description of the broad features observed in the thermal properties surveyed for the simple metals, and it may be useful in providing an estimate of the anharmonicity to be found in those metals.

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