

Thermal properties of cubic metals in anharmonic approximation

O P GUPTA

Physics Department, J Christian College, Allahabad 211 003, India

MS received 17 February 1984; revised 10 May 1984

Abstract. Expressions for thermal properties such as thermal expansion, specific heat and melting point are obtained by employing the usual quadratic-quartic form of the potential energy. Computed results for nineteen cubic metals are presented and compared with the experimental values. The model describes the broad features observed in the thermal properties and an estimate of the anharmonicity in cubic metals.

Keywords. Thermal properties; cubic metals; anharmonic approximation.

PACS No. 65.40 – f; 65.70 + y

1. Introduction

In the theory of lattice dynamics of solids, thermal properties can be calculated by employing the anharmonic *i.e.*, higher order contribution to the potential energy expanded as a power series in the atomic displacement. Experimental data on x-ray diffraction from monatomic anharmonic cubic solids have been analysed and explained on the basis of a single-atom anharmonic potential expansion model of the crystal (Willis 1969; Field and Medlin 1974; Field and Bednarz 1976). In the recent theoretical study of Thomchick *et al* (1978) it has been shown that the quadratic-quartic form of the potential energy closely approximates the physical situation in various areas of physics.

In the present paper, we employ the spherically symmetric single-atom potential expression in the form of series expansion in the atomic displacement *i.e.*, quadratic-quartic form of the potential energy of each atom in monatomic cubic crystals from room temperature to their melting point, to derive expressions for thermal properties such as thermal expansion, specific heat and melting point. Numerical results for nineteen cubic metals are presented and compared with experimental values.

2. Theory

Assuming the anharmonic potential of the quadratic-quartic form to be

$$U(r) = 0.5Ar^2 + Br^4 \quad (1)$$

where A and B are potential parameters, $r^2 = x^2 + y^2 + z^2$ and x , y , z are the components of the displacement from the mean position. The function $U(r)$ of (1) has a turning point at

$$r_{tp} = (-A/4B)^{0.5} \quad (2)$$

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

$$U(r_{ip}) = -A^2/16B. \quad (3)$$

2.1 Thermal expansion

The root-mean-square (rms) amplitude of vibration of the atom is calculated by taking the thermal average of r^2 as

$$\langle r^2 \rangle = \frac{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} r^2 \exp(-U(r)/k_B T) dx dy dz}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \exp(-U(r)/k_B T) dx dy dz}, \quad (4)$$

where k_B is the Boltzmann constant and T the temperature. For small vibrational amplitudes

$$\exp(-U(r)/k_B T) = (1 - Br^4/k_B T) \exp(-0.5Ar^2/k_B T) \quad (5)$$

Using this approximation, (4) can be written as

$$\langle r^2 \rangle = \frac{3k_B A^2 T - 105Bk_B^2 T^2}{A^3 - 15k_B A B T}. \quad (6)$$

However, the coefficient of linear thermal expansion α_l can be obtained in the present case of single-atom anharmonic potential model by taking the variation of the anharmonic part $\langle r_A^2 \rangle$ of $\langle r^2 \rangle$ with temperature as

$$\alpha_l = (1/a_n) d\langle r_A^2 \rangle^{0.5}/dT, \quad (7)$$

where

$$\langle r_A^2 \rangle = \langle r^2 \rangle - \langle r_H^2 \rangle = \langle r^2 \rangle - 3k_B T/A. \quad (8)$$

Here $\langle r_H^2 \rangle$ is the harmonic part of the mean square displacement and a_n the lattice constant at room temperature. Neglecting terms of the order of B^2/A^5 and higher, (7) reduces to

$$\alpha_l = (k_B/a_n) (-60B/A^3)^{0.5}. \quad (9)$$

2.2 Specific heat

The specific heat is given by

$$C = d\langle E \rangle/dT \quad (10)$$

where $\langle E \rangle$ is the average energy of the oscillator at temperature T . The average energy can be written as

$$\langle E \rangle = k_B T^2 d(\ln Z)/dT. \quad (11)$$

Here Z is the partition function (Kittel 1971) and can be calculated for the atom in the anharmonic well as

$$Z = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \exp(-p^2/2mk_B T) dp_x dp_y dp_z \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \exp(-U(r)/k_B T) dx dy dz \quad (12)$$

Here m is the mass and p_x, p_y, p_z are the components of the momentum p . Using (5) and (10)–(12) and omitting higher order terms, the specific heat becomes

$$C = 3k_B(1 - 10k_B T B/A^2). \quad (13)$$

2.3 Melting point

To incorporate melting in the present work, an appropriate melting criterion is necessary. The Lindemann melting law (Gupta 1982) suggests that a solid melts when the ratio of the mean square displacement of thermal vibration to the square of the interatomic spacing reaches a certain constant value. Assuming that a liquid has short-range order, and that, the potential well for each atom is modified when adequate number of atoms have adequate energy to create vacancies in the lattice, *i.e.*, there is a certain probability for each atom to escape from its potential well, then the choice of a melting criterion turns the choice of a critical probability for a vacancy formation. Therefore, at the melting point T_m the probability P that the atom has energy greater than E_m can be written as

$$P = \exp(-E_m/k_B T_m). \quad (14)$$

But, according to the above stated criterion, we have $E_m = U(r_{tp})$. Therefore, (14) takes the form

$$P = \exp(-U(r_{tp})/k_B T_m). \quad (15)$$

Making use of (3), (15) transforms to

$$T_m = (A^2/16Bk_B \ln P). \quad (16)$$

3. Results

Values of the Debye-Waller factor $B(T)$ have been borrowed from our recent lattice dynamical model (Gupta and Hemkar 1977; Gupta and Hemkar 1978a, b; Gupta *et al* 1978a, b; Gupta 1978; Gupta and Kharoo 1979) to evaluate the anharmonic potential parameter A from the relation (Willis 1969)

$$A = 8\pi^2 k_B T/B(T). \quad (17)$$

Since the activation energy E_a is a measure of the potential well from which an atom must escape to produce diffusion by vacancy formation, the depth of the potential energy well $U(r_{tp})$ can be given by the activation energy for self-diffusion in metals. Using (3), the anharmonic potential parameter B can be determined from the following relation

$$B = -A^2/16E_a. \quad (18)$$

Data for E_a have been taken from Peterson (1968). Various thermal properties as derived in §2 are computed from the knowledge of A and B values so obtained and the theoretical results for nineteen cubic metals are presented in table 1(a). All the calculations have been carried out at room temperature, *i.e.*, $T = 300$ K. The specific heat values obtained from (13) are expressed in equivalent Debye temperature Θ_D . The probability value P used in (16) to evaluate the melting temperature has been chosen as

Table 1(a). Theoretical results for the thermal properties of cubic metals.

Metal	A (Jm^{-2})	B (10^{19}Jm^{-4})	r_{rp} (nm)	$U(r_{rp})$ (10^{-19}J)	$\langle r^2 \rangle^{0.5}$ (pm)	α_i (10^{-6}K^{-1})	Θ_D (K)	T_m (K)
W	48.77	-13.984	0.2952	10.630	15.999	11.7	390	4445
Nb	170.58	-272.612	0.1250	6.671	13.266	7.5	278	2789
Mo	61.23	-36.572	0.2045	6.407	14.302	13.0	446	2679
Th	68.78	-55.545	0.1759	5.323	13.504	8.6	164	2225
Cr	83.44	-84.971	0.1566	5.121	12.264	14.2	625	2141
V	43.47	-23.075	0.2170	5.118	16.990	18.0	275	2140
Pt	95.45	-120.155	0.1409	4.739	11.470	10.1	250	1982
Ni	93.31	-115.168	0.1423	4.725	11.502	11.4	460	1975
Co	78.82	-82.544	0.1545	4.704	12.623	12.3	450	1966
Pd	72.56	-74.464	0.1560	4.419	13.161	12.1	271	1847
Fe	123.12	-237.980	0.1137	3.981	10.110	13.3	459	1665
Cu	98.71	-176.820	0.1181	3.444	11.302	12.7	370	1440
Ag	43.14	-37.814	0.1688	3.076	17.111	17.9	230	1286
Au	58.71	-74.362	0.1405	2.897	14.674	15.8	170	1211
Al	34.21	-36.627	0.1528	1.997	19.298	25.2	416	835
Pb	53.23	-97.839	0.1166	1.810	15.490	17.4	100	756
Li	18.24	-22.191	0.1433	0.937	26.783	58.0	336	392
Na	16.01	-22.853	0.1323	0.701	28.816	59.5	142	293
K	5.589	-2.883	0.2201	0.677	32.301	83.1	90	283

Table 1(b). Experimental values for the thermal properties of cubic metals.

Metal	S	r_n (nm)	E_a (10^{-19}J)	$\langle r_H^2 \rangle^{0.5}$ (pm)	α_i (10^{-6}K^{-1})	Θ_D (K)	T_m (K)
W	bcc	0.0857	10.630	15.961	4.6	400	3683
Nb	bcc	0.0950	6.671	13.268	7.1	275	2688
Mo	bcc	0.0852	6.407	14.245	5.0	450	2883
Th	fcc	0.1251	5.323	13.440	11.2	163	2023
Cr	bcc	0.0982	5.121	12.203	8.4	630	2148
V	bcc	0.0873	5.118	16.906	8.3	380	2173
Pt	fcc	0.1217	4.739	11.409	9	240	2042
Ni	fcc	0.1093	4.725	11.539	12.7	450	1726
Co	fcc	0.1101	4.704	12.555	12.4	445	1768
Pd	fcc	0.1206	4.419	13.086	11.5	274	1825
Fe	bcc	0.0978	3.981	10.046	11.7	470	1810
Cu	fcc	0.1412	3.444	11.219	16.7	343	1356
Ag	fcc	0.1594	3.076	16.971	19.2	225	1234
Au	fcc	0.1593	2.897	14.547	14.1	165	1336
Al	fcc	0.1097	1.997	19.058	23.1	428	933
Pb	fcc	0.1218	1.810	15.278	29.0	105	600.3
Li	bcc	0.1714	0.937	26.100	45.0	344	453.5
Na	bcc	0.2087	0.701	27.858	70.6	158	370.8
K	bcc	0.2573	0.677	28.386	83.0	91	336.7

3×10^{-8} . For a comparative study between the theoretical and experimental values, corresponding experimental values are listed in table 1(b); here r_n is the radius of the atomic volume. The source of experimental values for coefficient of linear thermal expansion, Debye temperature, and melting point are respectively Gschneidner (1964), Kittel (1976), and Moffatt *et al* (1964). All the physical quantities in tables 1(a, b) are written in SI units.

4. Discussion

The anharmonic behaviour of the metals in the present study has limitations over the accuracy of the A parameters because these are determined from the theoretical values of Debye-Waller factors analysed on the basis of a harmonic theory. However, the A values determined are supposed as being the most accurate since the employed theoretical lattice dynamical model is based on sound physical principles as evidenced by the recent studies (Gupta and Hemkar 1977; Gupta and Hemkar 1978a, b, c; Gupta *et al* 1978a, b; Gupta 1978; Gupta and Kharoo 1979; Gupta 1982, Gupta 1983a, b, c). Further, the range of the measured E_a values for some metals is significantly wide, in spite of the fact that the values compiled by Peterson (1968) are the best available.

The average error in the theoretical values of r_{tp} , α_l , Θ_D and T_m have been estimated to be about 20%, 6%, 2% and 3% respectively.

We have made use of the melting criterion approximate equivalent to that due to Lindemann (Gupta 1982). We assume that there is a critical rms amplitude of vibration r_c at the melting point temperature and that r_c is the same fraction of the anharmonic potential radius r_{tp} for all the metals. Although r_{tp} is not directly comparable with the lattice constant, it has been compared with the radius of the atomic volume, an indirect measure of the lattice constant: The rms vibration amplitude is least affected by anharmonicity as can be seen from tables 1(a) and 1(b). Using (1), (2) and (3), the following relation holds

$$U(r_c)/U(r_{tp}) = 1 - (1 - r_c^2/r_{tp}^2)^2. \quad (19)$$

That is, the probability that the atoms can escape from the anharmonic potential well at the melting point is the same for all the metals.

In the present work, anharmonicity is considered by treating the crystal as a system of independent anharmonic oscillators, with each atom vibrating in a potential field whose symmetry conforms with the site symmetry of the atom. By treating the crystal as an Einstein solid, whereby each atom vibrates in a potential field which is not affected by the motion of the neighbouring atoms, the extension of the anharmonic analysis to fcc and bcc type of crystal structures made possible the present work.

Despite the above uncertainties and limitations, the general trends in the results are clear. In conclusion, the present approach provides a satisfactory description of the broad features observed in the thermal properties surveyed for the cubic metals, and it may be useful in providing an estimate of the anharmonicity to be found in those metals.

Acknowledgements

The author wishes to record his gratitude to the learned referees and the editor for their useful and valuable comments and suggestions.

References

- Field D W and Medlin E H 1974 *Acta Crystallogr.* **A30** 234
Field D W and Bednarz B 1976 *Acta Crystallogr.* **A32** 315
Gschneidner K A 1964 *Solid State Phys.* **16** 275
Gupta O P and Hemkar M P 1977 *Z. Naturforsch.* **a32** 1495
Gupta O P and Hemkar M P 1978a *Physica* **B94** 319
Gupta O P and Hemkar M P 1978b *Il. Nuovo Cimento* **B45** 255
Gupta O P and Hemkar M P 1978c *J. Phys. Soc. Jpn* **45** 128
Gupta O P, Kharoo H L and Hemkar M P 1978a *Pramana* **11** 111
Gupta O P, Kharoo H L and Hemkar M P 1978b *Can. J. Phys.* **56** 447
Gupta O P 1978 *Lattice dynamical study of solids* D. Phil. Thesis Allahabad University Allahabad
Gupta O P and Kharoo H L 1979 *Indian J. Pure Appl. Phys.* **17** 245
Gupta O P 1982 *Acta Phys. Polo.* **A62** 225
Gupta O P 1983a *Acta Phys. Polo.* **A64** 269
Gupta O P 1983b *Physica* **B122** 236
Gupta O P 1983c *J. Phys. Soc. Jpn* **52** 4237
Kittel C 1971 *Introduction to solid state physics* 4th (edn) (New York: Wiley)
Kittel C 1976 *Introduction to solid state physics* 5th (edn) (New York: Wiley)
Moffatt W G, Pearsall G W and Wulff J 1964 *The structure and properties of materials* Vol. 1 (New York Wiley)
Peterson N L 1968 *Solid State Phys.* **22** 409
Thomchik J, McKelvey J P and Elliott Jr C F 1978 *Phys. Lett.* **A66** 86
Willis B T M 1969 *Acta Crystallogr.* **A25** 277