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Lattice specific heats of cobalt and ruthenium

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The nearest-neighbor central-force model of Srinivasan and Ramji Rao has been used to calculate the lattice specific heats of cobalt and ruthenium as a function of temperature. The frequency distribution function needed for the specific-heat calculations has been drawn by constructing a histogram involving a total number of 19 380 frequencies. The theoretical C_V^l values are compared with C_V^l values obtained from experimental data on the specific heat at constant pressure C_P. There is reasonably good agreement between theory and experiment for both cobalt and ruthenium. The theoretical dispersion curves in the [0001] direction for ruthenium have been compared with the available experimental measurements and the agreement is fairly good except for one of the optical branches.

I. INTRODUCTION

Cobalt and ruthenium are metals which have the hexagonal-close-packed structure. The second-order elastic (SOE) constants of these metals have been measured as a function of temperature by Fisher and Dever.[1] The dispersion curves for ruthenium were measured only in the *c* direction by Smith *et al.*[2] The temperature dependence of the specific heat for these metals has also been reported and compiled.[3]

Srinivasan and Ramji Rao[4,5] proposed a central-force model with nearest-neighbor interactions to calculate the lattice dynamics, third-order elastic (TOE) constants, and thermal expansion of hcp metals. This model was used by the present authors to study the lattice dynamics, TOE constants, and thermal expansion of erbium,[6] cobalt,[7] ruthenium,[8] and scandium.[9] In this paper the temperature dependence of the lattice specific heat of cobalt and ruthenium has been calculated using this model and compared with experimental results. The lattice dynamics of ruthenium in the [0001] direction has also been compared with the experimental measurements.

II. FREQUENCY DISTRIBUTION FUNCTION FOR COBALT AND RUTHENIUM IN THE CENTRAL-FORCE MODEL

In this model the central interaction potential has the form

$$\Phi(r) = -a/r^m + b/r^n . \tag{2.1}$$

The normal-mode frequencies of the lattice vibrations are obtained as solutions of the determinant equation

$$| D_{ij}^{KK'}(\vec{q}) - \omega^2 \delta_{KK'} \delta_{ij} | = 0 . \tag{2.2}$$

$D_{ij}^{KK'}(\vec{q})$ are the coupling coefficients. The expressions for these coupling coefficients are given in Ref. 4 and they involve a parameter η which is defined

$$\eta = nb(n-m)/2MD^{n+2} . \tag{2.3}$$

Here M is the mass of the atom and D is the lattice constant in the basal plane. The experimental SOE constants C_{11} and C_{33} of the metal have been used to determine an average value of η. Figure 1 shows the comparison of the lattice dynamics of ruthenium[8] in the [0001] direction with the experimental data of Smith *et al.*[2]

The secular equation is solved for different wave vectors $\vec{q}$ and the corresponding normal-mode frequencies are obtained using a computer program (IBM 370/155). A grid of 213 points in the irreducible volume of the Brillouin zone is chosen for

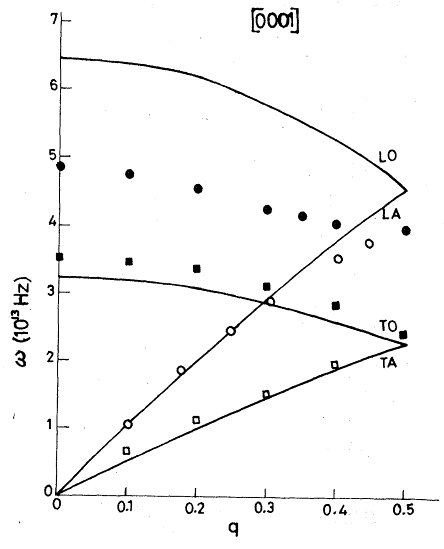

FIG. 1. Theoretical dispersion curves for ruthenium in the [0001] direction. Experimental points are denoted as ● LO, ■ TO, ○LA, □TA.

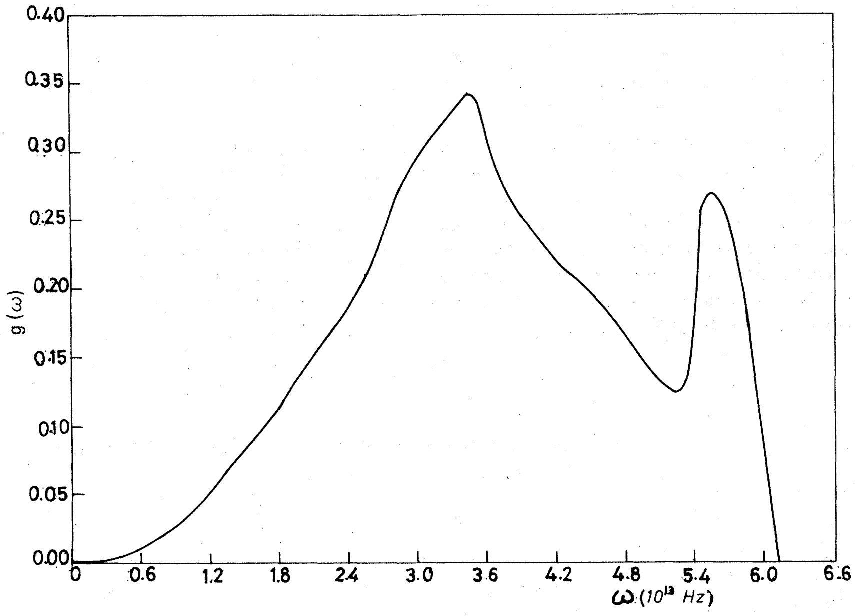

FIG. 2. Frequency distribution function for cobalt.

the wave vectors. This is equivalent to 3230 points in the entire volume of the Brillouin zone, taking into account the crystal symmetry. The density of points in the central region of the Brillouin zone is much higher than that in its peripheral region. The number of frequencies in each frequency interval ($\Delta\omega = 0.3\times10^{13}$ Hz) is counted and a histogram is constructed for $g(\omega)$. This is then used to draw a smooth curve, which encloses unit area with the frequency axis. The frequency distribution functions for cobalt and ruthenium obtained on this model are shown in Figs. 2 and 3, respectively.

III. RESULTS OF THE SPECIFIC-HEAT CALCULATIONS

The theoretical frequency distribution function has been used to calculate the lattice contribution to the specific heat as a function of temperature.

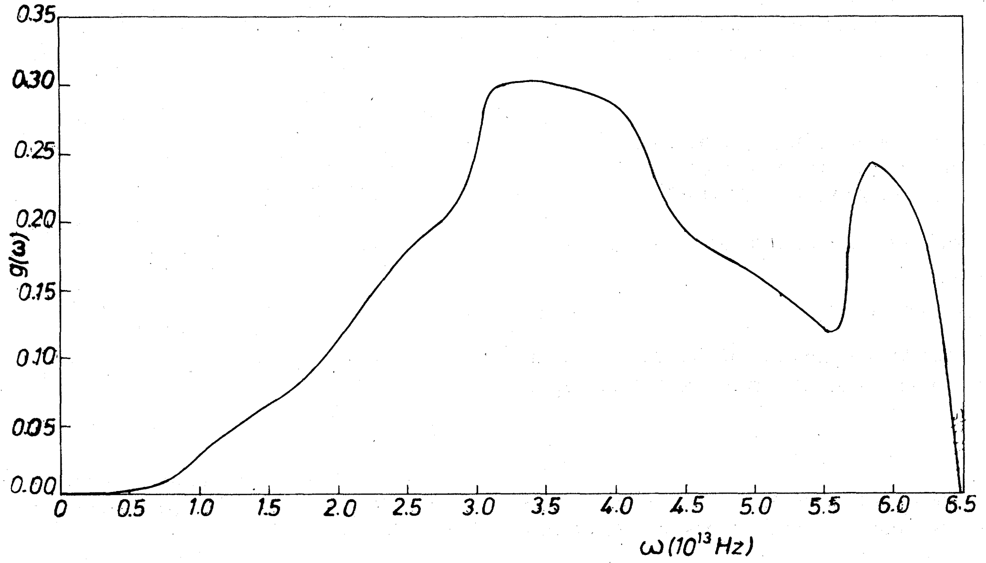

FIG. 3. Frequency distribution function for ruthenium.

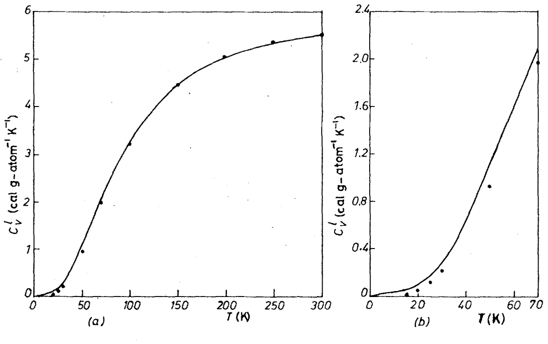

FIG. 4. (a) Specific heat of cobalt from 0 to 300 °K. (b) Specific heat of cobalt from 0 to 70 °K.

$$C_V^l(T)=3R\sum g(\omega)\,\sigma(\omega,T)/\sum g(\omega)\,, \qquad (3.1)$$

where $\sigma(\omega, T)$ is the Einstein specific-heat function and R is the gas constant expressed in calories/K mole. Figures 4 and 5 show the results of the present calculations for cobalt and ruthenium. The full circles in these figures are values of C_V^l calculated from the experimental measurements of C_P at different temperatures,[3] as described below.

The specific heat at constant pressure C_P, is related to the specific heat at constant volume C_V by the well-known thermodynamic relation

$$C_P=C_V+9\alpha^2TV/\chi\,. \qquad (3.2)$$

Thus to calculate C_V knowing C_P, one must also have a knowledge of α and χ at that temperature. However, if the second term which is called the dilation term C^d is written in the form

$$C^d=9\alpha^2TVC_P^2/C_P^2\chi\,, \qquad (3.3)$$

and letting

$$A=9\alpha^2V/\chi C_P^2\,, \qquad (3.4)$$

we have

$$C^d=AC_P^2T\,. \qquad (3.5)$$

It has been observed experimentally that A is almost constant over a wide range of temperatures. Hence it is sufficient if the value of A is known at room temperature for converting C_P to C_V. The electronic contribution to specific heat C_V^e given by

$$C_V^e=\gamma T\,, \qquad (3.6)$$

where γ is the electronic-specific-heat constant, is to be subtracted from C_V to finally yield C_V^l, the lattice contribution to the specific heat. The values of A and γ for cobalt and ruthenium have been taken from Gschneidner's compilation[10] and are given in Table I.

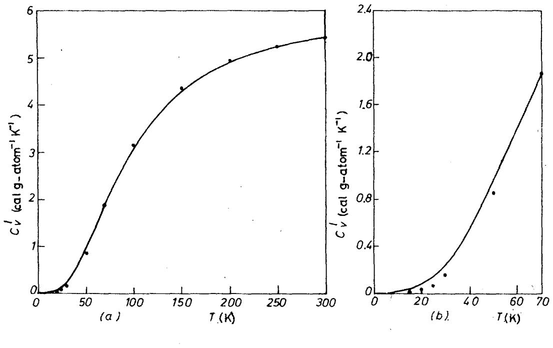

FIG. 5. (a) Specific heat of ruthenium from 0 to 300 °K. (b) Specific heat of ruthenium from 0 to 70 °K.

TABLE I. Values of the constants used in the present calculations.

Metal	10^5A (g-atom/cal)	$10^4\gamma$ (cal/g-atom K^2)
cobalt	1.196	11.3
ruthenium	1.472	7.9

IV. DISCUSSION

The phonon dispersion curves in the [0001] direction calculated on this model for ruthenium are found to be in fairly good agreement with experiment except for one optical branch, as seen in Fig. 1. The TA branch is in good agreement with experiment. The LA branch deviates from experiment above $q=0.3$ and at the zone boundary (A_1) the discrepancy is about 14%. The experimental frequencies are higher than the calculated frequencies for the TO branch and the difference is about 8%. The LO branch is higher than the experimental frequencies by about 25%, near the zone center.

Considering the fact that this model requires only a knowledge of the SOE constants of the metal, the agreement between theory and experiment is fairly good. This is further vindicated by the fact that the theoretical specific-heat values are in overall good agreement with the corresponding experimental values for both cobalt and ruthenium as seen from Figs. 4 and 5, respectively.

The agreement of the calculated C_V^l values using the frequency distribution functions of this model with those obtained from experimental C_P values is very good above 50 K for both metals. At temperatures below 50 K the agreement is poorer, in both cases. This could be due to the fact that the experimental measurements at low temperatures involve a greater degree of uncertainty, compared to the measurements at higher temperatures. Further, at low temperatures, the electronic contribution to the specific heat C_V^e is comparable to the lattice contribution C_V^l and any error in the determination of γ, the electronic coefficient, from low-temperature specific-heat data could result in an incorrect estimation of C_V^e. In view of these reasons one may conclude that this model provides a reasonably good description of the contributions of the phonons to the heat capacity of these two metals.

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