The constant term α is a direct measure of the number of clusters N or $\alpha = N k$. For CrB_2, $N = 3.6 \cdot 10^{20}$ clusters/mole-CrB_2. Further the moment on each cluster can be determined by measuring the magnetization as a function of field. TYAN [22] found for these samples $dM/dH = 1.1 \cdot 10^{-3}$ cm/mole at 4.2 K which corresponds to about 240 Bohr magnetons per cluster. If we assume that the clusters are due entirely to iron impurity atoms, each with 2.2 aligned spins, then we calculate that 110 Fe atoms are in each cluster and that the needed impurity concentration is 50,000 ppm. This is an unreasonable result since it is far greater than the results of chemical and neutron activation analysis. Furthermore, no anomalies were observed in the other Cr and V borides prepared in the same manner from the same material.

Thus, if we are to retain the notion of the cluster model, it is necessary to propose a new type of cluster other than those caused by impurities. These would result primarily from a random fluctuation of localized boron concentration in the diboride. The diborides are known to exist over a range of compositions, in contrast to the more metallic borides, which have narrower composition ranges. Thus it is possible that boron-poor and boron-rich regions coexist in the diborides. These regions coupled with small impurity concentrations of ferromagnetic elements could result in a spontaneous magnetization and account for the anomaly. Presently we are preparing samples with different impurity concentrations to determine the effect on the anomaly and the magnetization and we will report on these results at a later date.

Vibration Spectra and Debye Temperatures of Some Transition Metals

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The lattice vibration spectra and the associated constant volume specific heats of the transition metals niobium, tantalum, chromium, and palladium have been determined by using Sharma and Joshi's three-force constant model which includes the effect of electrons on lattice vibrations in metals. The calculated values of the specific heats and the equivalent Debye temperatures are compared with available calorimetric data. The frequency versus wave vector dispersion relations along the three major symmetry directions of chromium and palladium are determined and compared with curves deduced from recent neutron scattering experiments. Reasonably satisfactory agreement between theory and experiment is obtained.

I. Introduction

With the development of inelastic neutron scattering technique, in recent years a considerable amount of work has been devoted to the study of lattice vibrations in transition metals by measuring the frequency versus wave vector dispersion relations along the symmetry directions [1]. This has stimulated much interest in their thermodynamic properties, in particular the lattice specific heat. During the last few years, a number of models [2] have been worked out for calculating the phonon frequencies of metals by taking cognizance of electrons as a compressible gas. One of the authors (P. K. S.) and JOSHI [3, 4] have propounded a successful theory of this type by considering the volume

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forces due to the compressibility of conduction electrons and their interaction with ions by an average over a Wigner-Seitz sphere. This model has provided a plausible description of phonon dispersion relations [5-7], and thermal [8-10] and transport [11, 12] properties of a number of cubic metals.

In this paper, we present a computation of vibration spectra and the associated constant volume lattice specific heats of the transition metals niobium, tantalum, chromium, and palladium on the basis of SHARMA and JOSHI's model [3, 4] of electron-ion interaction. The phonon dispersion relations along the symmetry directions of chromium and palladium are determined and compared with curves deduced from recent neutron scattering experiment. The phonon dispersion in niobium and tantalum has already been studied [7] on this model. It was therefore thought proper to evaluate the lattice specific heats of these metals. For niobium and chromium, the Debye-Waller factors are also determined from the computed spectrum.

II. Secular Determinant

The secular determinant determining the angular frequency ω of the normal modes of vibration in a cubic metal can be written as

$$| D(\mathbf{q}) - M \omega^2 I | = 0 , \qquad (1)$$

where M is the mass of an ion in the lattice and I is a 3×3 unit matrix. The elements of the dynamical matrix $D(\mathbf{q})$ on SHARMA and JOSHI's model [3, 4] are given by

$$D_{ii}(\mathbf{q}) = 8 a_1 (1 - C_1 C_2 C_3) + 4 a_2 S_i^2 \\ + 4 K_e a^3 g^2(q r_s) q_i^2 , \qquad (2 \text{ a})$$

$$D_{ij}(\mathbf{q}) = 8 a_1 S_i S_j C_k + 4 K_e a^3 g^2(q r_s) q_i q_j , \quad (\text{bcc})$$

$$D_{ii}(\mathbf{q}) = 4 a_1 (2 - C_i C_j - C_i C_k) + 4 a_2 S_i^2 \\ + 2 K_e a^3 g^2(q r_s) q_i^2 , \qquad (2 \text{ b})$$

$$D_{ij}(\mathbf{q}) = 4 a_1 S_i S_j + 2 K_e a^3 g^2(q r_s) q_i q_j , \quad (\text{fcc})$$

where

$$S_i = \sin(q_i a) , \qquad C_i = \cos(q_i a) , \\ g(x) = 3 (\sin x - x \cos x)/x^3 . \qquad (3)$$

In these equations q_i is the i-th Cartesian component of the phonon wave vector $\mathbf{q}$; r_s is the radius of the Wigner-Seitz sphere; a is the semi-lattice parameter; K_e is the bulk modulus of electron gas; and a_1 and a_2 are the central force constants for the first and second nearest neighbour interaction, respectively. The parameters a_1, a_2 and K_e are related to the three independent elastic constants (C_{11}, C_{12}, C_{44}) of a cubic metal through the relations:

$$a_1 = a C_{44} , \quad a_2 = a(C_{11} - C_{12}) , \\ K_e = C_{12} - C_{44} , \quad (\text{bcc}) \qquad (4 \text{ a})$$

$$a_1 = a C_{44} , \quad a_2 = (a/2) (C_{11} - C_{12} - C_{44}) , \qquad (4 \text{ b}) \\ K_e = C_{12} - C_{44} . \quad (\text{fcc})$$

III. Numerical Computation

The evaluation of the vibration spectrum of niobium, tantalum, chromium, and palladium has been made by root sampling technique for a discrete subdivision of wave vector space [13] as discussed in the earlier studies [9, 10]. In order to have a fairly large number of frequencies, we have considered a mesh of equally spaced 64 000 wave vectors in the first Brillouin zone. For this purpose, the translation vector of the reciprocal space was divided into 40 equal parts. From symmetry considerations, vibration frequencies were determined at nonequivalent points lying within the irreducible trihedral angle of the reciprocal space of a cubic crystal. Each frequency was weighted according to the number of similar points associated with it. The number of frequencies falling into intervals of 0.05×10^{13} rad/sec were counted and from these the histogram of frequency distribution was obtained. Figure 1 shows the calculated frequency histograms for the four metals. The units of $G(\omega)$ are arbitrary, but the curves are normalized to the same area. For chromium and palladium, the frequency versus wave vector dispersion relations along the symmetry directions [100], [110], and [111] are determined from the solutions of secular Eq. (1) along these directions.

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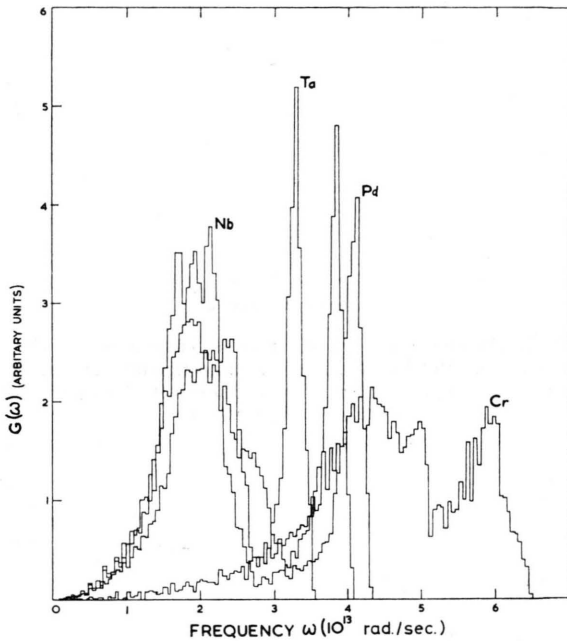
Fig. 1. The lattice vibrational spectra of the four transition metals.

Fig. 3. The dispersion curves for palladium in the three major symmetry directions. L and T represent the longitudinal and transverse polarization modes. The circles (○, ●) and crosses (×) show the experimental measurements of Miiller and Brockhouse.

The calculated dispersion curves are displayed in Figs. 2 and 3 along with the experimental values obtained from recent neutron scattering experiments (l. c. [14-16]).

Using the frequency distributions plotted in Fig. 1, the lattice specific heats C_v at constant volume and the Debye-Waller factors of the metals considered were determined in the usual manner by numerical
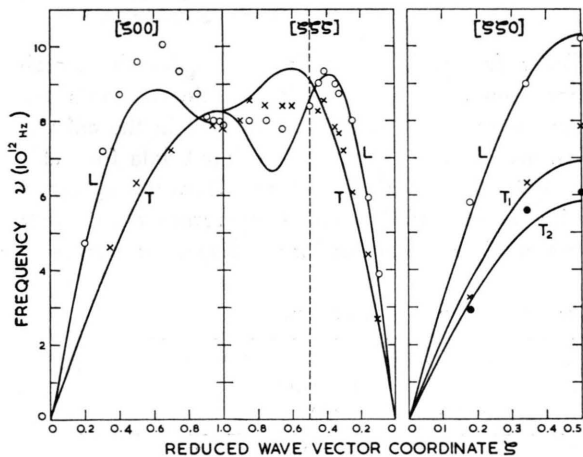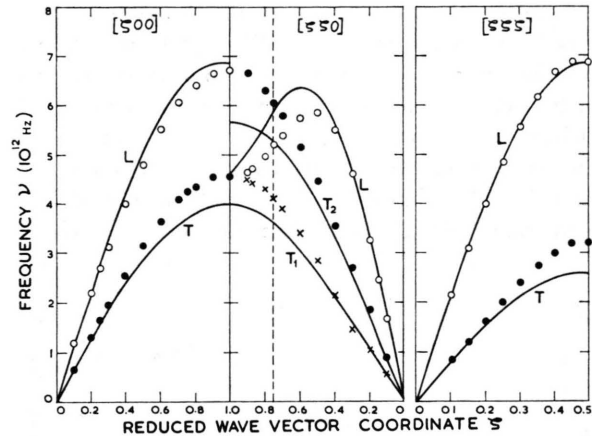

Fig. 2. The dispersion curves for chromium in the three major symmetry directions. L and T label the longitudinal and transverse polarization modes. The circles (○, ●) and crosses (×) are the experimental points of Möller and Mackintosh.
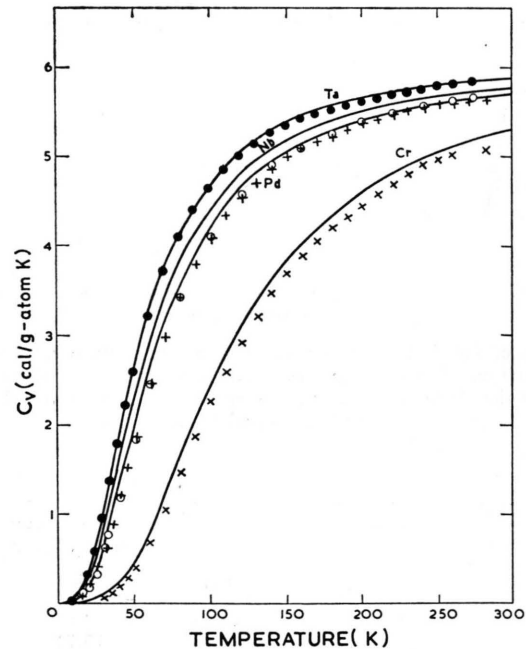

Fig. 4. Comparison of the calculated and observed lattice specific heats of the four transition metals. Experimental points: + niobium; ● tantalum; × chromium; ○ palladium.

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integration. In Fig. 4 the calculated and observed specific heats are plotted at different temperatures. Another more sensitive comparison with the calorimetric data is made in terms of the equivalent Debye temperature Θ. The Θ versus T curves for the four metals are shown in Figs. 5 – 8 where the empirical data have also been plotted. The Debye temperature Θ_M, which characterizes the Debye-
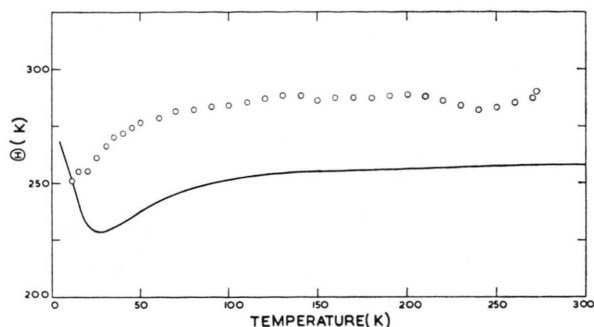
Fig. 7. The Debye temperature against temperature for chromium. The solid line is based on our computations and the circles ($\bigcirc$) represent the experimental specific heat data due to Clusius and Franzosini.

Fig. 5. The Debye temperature of niobium as a function of temperature. The solid line shows the present calculations and the circles ($\bigcirc$) are the experimental values obtained from the specific heat data of Clusius, Franzosini and Piesbergen.

Fig. 8. Variation of the Debye temperature of palladium with temperature. The solid line depicts our calculations and the circles ($\bigcirc$) are the experimental values calculated from the specific heat data of Clusius and Schachinger.
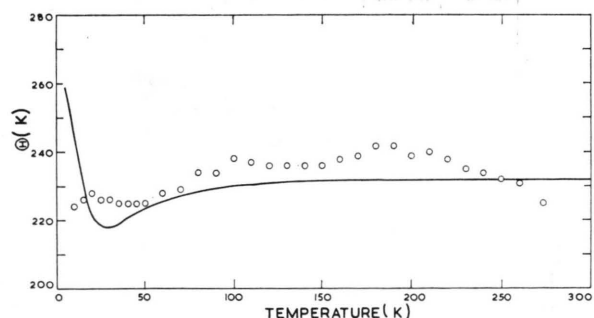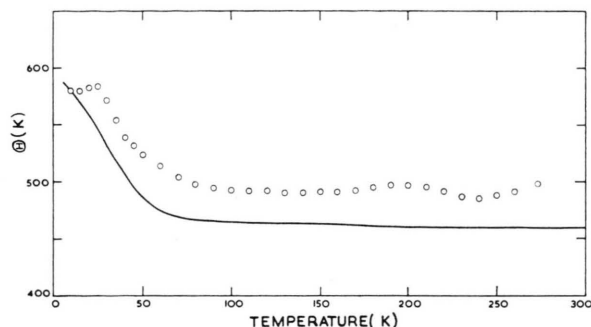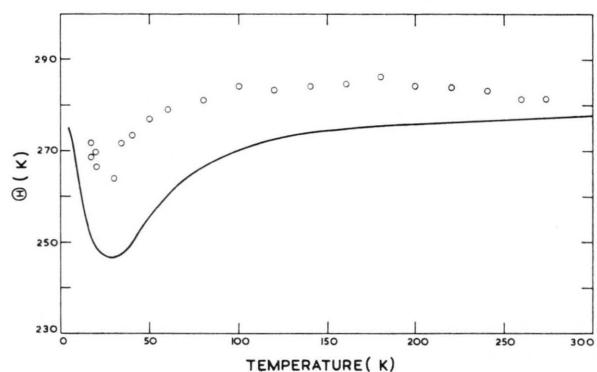
Fig. 6. The Debye temperature versus temperature curve for tantalum. The solid line represents the present calculations and the circles ($\bigcirc$) show the experimental specific heat data of Clusius and Losa.

Waller factor. is shown in Fig. 9 for the metals chromium and niobium. The elastic constants and other parameters of the metals used in the calculation are given in Table 1. The input data for palladium in the calculation of the vibration spectrum refer to 0 K, while room temperature elastic data were used in the evaluation of dispersion curves.

Table 1. Constants for the transition metals used in the calculation.

Metal	Elastic constants (10^{11} dynes/cm^2)			Density (gm/cm^3)	Lattice parameter (Å)	Temperature * (K)
	C_{11}	C_{12}	C_{44}			
Niobium [a]	23.50	12.10	2.82	8.57	3.301	298
Tantalum [b]	26.10	15.74	8.18	16.655	3.303	300
Chromium [c]	35.00	6.78	10.08	7.19	2.88	298
Palladium [d]	23.41	17.61	7.12	12.132	3.872	0
	22.70	17.59	7.17	12.00	3.89	296

* Temperature at which elastic constants are measured.
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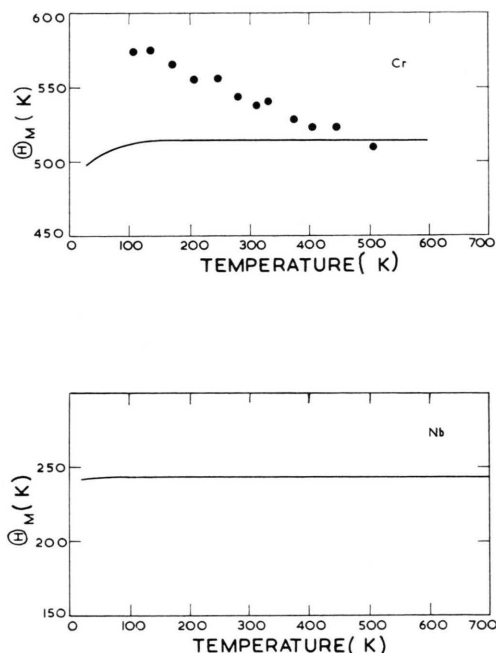d J. A. RAYNE, Phys. Rev. 118, 1545 [1960].

Fig. 9. The Debye-Waller factor characteristic temperature of chromium and niobium as a function of temperature. The solid curves show present calculations. The circles (●) depict the experimental measurements of Wilson et al. for chromium.

IV. Discussion

MÖLLER and MACKINTOSH [14] have experimentally determined the dispersion curves at room temperature for chromium along the symmetry directions from inelastic neutron spectrometry. Because of the relative sparseness of data, these dispersion curves did not receive much attention in the literature. Recently FELDMAN [17] has analyzed them in terms of fourth-neighbour Born-von Kármán model. The detailed study of phonon dispersion relations in palladium at 296 K has recently been made by MIILLER and BROCKHOUSE [15, 16] by means of inelastic neutron scattering. They have also tabulated the values of frequencies for selected modes. For the purpose of the present comparison, these neutron measurements are plotted in Figs. 2 and 3. It will be seen that he calculated dispersion curves are in broad agreement with the experimental data. Along the [111] direction beyond $\zeta = \frac{1}{2}$ the calculated dispersion cur-

ves for chromium, however, show marked discrepancies. For palladium, the observed transverse mode frequencies are somewhat higher than the theoretical values, and the discrepancy increases with phonon wave vector.

The experimental data for the specific heats of metals considered are taken from the measurements of CLUSIUS and his coworkers [18-21]. These have been plotted after correction for the $C_p - C_v$ and the electronic specific heat contributions. The values of γ, the coefficient of electronic specific heat, used for this purpose are given in Table 2. These are

Table 2. Electronic specific heat coefficient of transition metals.

Metal	γ (μcal/g-atom K^2)	
Niobium	2050	(up to 20 K)
	520	(above 20 K)
Tantalum	760	
Chromium	360	(up to 20 K)
	1380	(above 60 K)
Palladium	2251	(up to 40 K)

taken from the low temperature calorimetric measurements of CLUSIUS et al. [18-20]. For palladium, the electronic specific heat C_e deviates from the usual γT dependence at temperatures above 40 K; it tends to saturate in the high temperature region above 200 K. In the present work, we have used the recent estimate of C_e given by MIILLER and BROCKHOUSE [16]. For temperatures below 40 K, their C_e are in good agreement with those predicted by γT with $\gamma = 2251$ μcal/g-atom K^2 reported by VEAL and RAYNE [22]. It is seen in Figs. 5 – 8 that the nature of the theoretical and experimental $\Theta - T$ curves is similar. The agreement is particularly very satisfactory for tantalum. For other metals, the experimental Θ are uniformly higher than the theoretical values, the maximum discrepancy of about 17% being in the case of niobium.

In Fig. 9 the calculated $\Theta_M - T$ curve for chromium shows reasonable agreement with the effective characteristic temperature obtained by WILSON et al. [23] from Bragg's x-ray intensity measurements, although there are large uncertainties in the experimental measurements. No such experimental data are available for niobium.

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The discrepancies between theory and experiment may be ascribed to the neglect of temperature variation of elastic constants and other anharmonic effects. At lower temperature, the discrepancies are attributable to the coarseness of the frequency spectrum and the uncertainty in the electronic contribution to the specific heat. The disagreement is also partly attributable to the approximate description of electron-ion interaction and to the assumption of short range interatomic interaction in the theory.

The analyses of phonon dispersion relations on Born-von Kármán force models show that atoms beyond the second neighbour interact appreciably, particularly in niobium.

Interdiffusion Studies in Molten Alkali Nitrates

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Interdiffusion of anions in fused alkali nitrates has been studied with a plane source diffusion technique; the concentration gradients in the diffusion cell being measured with a wave-front-shearing interferometer. By choosing the same cations in the experiments the diffusional mixing of different anions at low concentrations into three alkali nitrates has been studied. The diffusion coefficients of F^- and Br^- in $LiNO_3$; F^-, Br^-, I^-, CO_3^{2-}, and SO_4^{2-} in $NaNO_3$; and I^- and CO_3^{2-} in $RbNO_3$ were obtained over a temperature range of some 100 °C above the melting point of the different solvents.

A development of experimental procedures has been in progress during the last couple of years, which enables the use of optical interferometry for studying density gradients at temperatures up to 300 °C [1-6]. As a part of this work a new method for studying interdiffusion has been suggested and proved successful. The experimental arrangement has resembled that of a plane diffusion source in a semiinfinite medium or often refered to as bottom layer diffusion. The initial plane source has been obtained by dropping a solid crystal to the bottom of a diffusion vessel containing the solvent. The melting points of the chosen solutes are generally much higher than those of the alkali nitrates used as solvents, which favourably eliminates an eventual partial disintegration of the crystal before reaching the bottom of the container. Because of the large

density and refractive index differences between the solvents and solutes it has been possible of work with rather small crystals, which implies a very slight disturbance of the liquid at the beginning of the experiment because of the temperature difference between the solvent and the crystal being dropped from room temperature.

The concentration differences are given for a number of representative experiments in Table 1. The reason why it was possible to work with such low differences is the comparatively large dependence of refractive index on concentration. The dependence being estimated according to a theory given elsewhere [5]. The concentration increase due to the diffusing solute is so small that the diffusion coefficient may be considered as that at infinite dilution.

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