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Lattice dynamics of hcp Hf

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Inelastic neutron scattering techniques have been used to study the lattice dynamics of hcp Hf. The phonon dispersion curves along the [001], [100] , and [110] symmetry directions were determined at 295 and 1300 K, and a selected number of phonon frequencies were measured also at 800 K. As the temperature decreases we observe a rather large increase in the frequencies of all but the [001] LO branch. The zone-center mode of the [001] LO branch, on the other hand, softens appreciably, and at room temperature this branch exhibits a dip at the zone center. These features of the phonon dispersion curves of Hf are similar to those of hcp Zr and Ti. The data were used to evaluate the lattice specific heat at constant pressure as a function of temperature. The calculated total specific heat, obtained by taking into account the electronic contribution, was found to agree, to within experimental uncertainties, with the results of specific-heat measurements. We find that the phonon anomalies (and their temperature dependence) in the dispersion curves of the superconducting elements of the IV column of the Periodic Table can be understood qualitatively as originating from the splitting about the Fermi level of doubly degenerate bands by the lattice distortion corresponding to the [001] LO mode. We argue that this mechanism may also be responsible for the phonon anomalies observed in other superconducting elements (Tc) and compounds ($LaSn_3$).

I. INTRODUCTION

Considerable effort has been directed, in recent years, towards a first-principles understanding of the anomalous features of the phonon dispersion curves of the transition metals and compounds. The electronic response to the ionic displacements is extremely difficult to evaluate in these systems, because of the atomiclike character of the d-electron wave functions near the ion cores. Thus, by necessity, only model calculations[1,2] have been performed to date based on the general theory of the lattice dynamics of metals. Unfortunately it is difficult using these models to clearly establish the dominant mechanism for the occurrence of the phonon anomalies.

An alternative approach to the problem is via band-structure calculations,[3,4] and has culminated in a novel formulation,[5] by Varma and Weber, of the lattice dynamics of transition metals and compounds. The basic premise of this work is that the occurrence of phonon anomalies is closely connected to the detailed topology of the electronic bands near the Fermi energy. More specifically, since a phonon anomaly will arise whenever a lattice distortion corresponding to a certain vibrational mode causes a reduction in electronic energy, pronounced anomalies will occur if the lattice distortion opens up a local gap in the electronic structure at the Fermi surface. A different approach,[6,9] closely related to the theory of Varma and Weber, consists of evaluating directly the change in electronic energy when a phonon is frozen into the lattice.

Measurements of the temperature dependence of the phonon dispersion curves of transition metals and compounds should help to clarify the physical picture emerging from the theoretical investigations of the lattice dynamics of these metals, since the effect of a change in temperature is largest for the electronic states near the Fermi level which play a dominant role in determining the electronic response to the nuclear motion. We initiated therefore a systematic study of the temperature dependence of the dispersion curves of the hcp (superconducting) transition elements of the fourth column of the Periodic Table.

The lattice dynamics of the transition metals of the fourth column of the Periodic Table is also relevant to an understanding of their thermophysical properties which exhibit rather remarkable features at high temperatures.[10–13] In particular, the heat capacity[12] at constant pressure for the hcp phase increases more rapidly with increasing temperature than one would expect from a simple consideration of anharmonic and electronic corrections to the Dulong-Petit law.

In our studies[14–16] of the temperature dependence of the phonon dispersion curves of hcp Zr and Ti we have found, in particular, that the zone-center mode of the [001] LO branch softens appreciably as the temperature decreases, and at room temperature this mode is considerably softer than expected from its behavior in nonsuperconducting hcp elements. To establish whether this anomalous behavior is characteristic of all the superconducting transition elements of the IV column of the Periodic Table we extended our studies to metallic hafnium. Preliminary results of this study were reported in an earlier communication.[17] In this paper we present a complete report of these experiments.

II. EXPERIMENTAL DETAILS

The single crystals used in the present experiments were prepared from high-purity Hf by the same technique[15] utilized in the preparation of the hcp Zr and Ti crystals. The measurements were performed using a vacuum furnace (described in Ref. 15) mounted on the sample goniometer of a triple-axis neutron spectrometer. At the highest temperature (1300 K) reached in our experiments the temperature was controlled to within a few degrees and the vacuum was approximately 10^{-5} Torr.

The data were taken using two triple-axis spectrometers, one at the Oak Ridge Research Reactor (ORR) and the other at the High-Flux Isotope Reactor (HFIR) of the Oak Ridge National Laboratory. Pyrolytic graphite reflecting from the (002) planes was used for both monochromator and analyzer and all data were collected with the spectrometer in the constant-Q mode of operation (where $\vec{Q}$ denotes the neutron scattering vector). Most of the data were collected at a constant scattered neutron energy of 6 THz (24.82 meV) and neutron groups scattered with energy loss were detected. This rather high scattered neutron energy was chosen (as a compromise between the requirements of good energy resolution and an acceptable rate of data collection) because of the large $1/\sqrt{E}$ (where E is the neutron energy) absorption cross section of Hf. We used a 40′ collimation of the neutron beam before the sample and collimations after the sample of 60′ and 40′ for the ORR spectrometer and the HFIR instrument, respectively. A large number of phonon frequencies was determined using both instruments and they were found to agree to within experimental precision.

III. EXPERIMENTAL RESULTS: LATTICE SPECIFIC HEAT

The phonon dispersion curves of hcp Hf were determined along the [001], [100], and [110] symmetry directions at 295 and 1300 K. The frequencies of a selected number of phonons were measured also at 800 K. The measured phonon frequencies at 295, 800, and 1300 K are listed in Table I and the room-temperature dispersion curves are plotted in Fig. 1. The measured phonon frequencies of hcp Hf are in fair agreement with the values estimated from the measured[15,16] phonon frequencies of hcp Zr and Ti by taking into account the differences in mass, interatomic spacing, and melting temperatures of these elements. Thus the phonon frequencies of these elements follow quite well the Lindemann homology rule.[18]

TABLE I. Measured frequencies (THz) of hcp Hf. The symbols ⊥ and || refer to polarizations perpendicular and parallel to the basal plane, respectively.

ξ	$T = 295$ K	$T = 800$ K	$T = 1300$ K
		TA[00ξ]	
0.1	0.42 ± 0.01		
0.2	0.90 ± 0.02	0.76 ± 0.02	0.71 ± 0.02
0.3	1.21 ± 0.03	1.16 ± 0.02	1.08 ± 0.03
0.4	1.58 ± 0.03	1.47 ± 0.04	1.39 ± 0.02
0.5	1.9 ± 0.10	1.75 ± 0.06	1.61 ± 0.03

TABLE I. *(Continued).*

ξ	$T = 295$ K	$T = 800$ K	$T = 1300$ K
TO[00ξ]			
0.0	2.7 ± 0.16	2.46 ± 0.08	2.15 ± 0.15
0.1	2.74 ± 0.12		
0.15			2.12 ± 0.12
0.2	2.54 ± 0.12		
0.3	2.46 ± 0.12	2.1 ± 0.09	1.97 ± 0.06
0.4	2.16 ± 0.10		
0.5	1.9 ± 0.10	1.75 ± 0.06	1.61 ± 0.03
LA[00ξ]			
0.1	0.76 ± 0.02		0.68 ± 0.03
0.2	1.6 ± 0.04	1.48 ± 0.06	1.31 ± 0.10
0.3	2.1 ± 0.10		1.92 ± 0.12
0.4	2.6 ± 0.10		2.6 ± 0.10
0.5	3.0 ± 0.15	3.15 ± 0.10	3.2 ± 0.10
LA[ξ00]			
0.1	1.31 ± 0.02		1.21 ± 0.05
0.2	2.36 ± 0.10		2.3 ± 0.12
0.3	3.29 ± 0.10	3.25 ± 0.10	3.12 ± 0.15
0.4	3.8 ± 0.15		3.47 ± 0.12
0.5	3.85 ± 0.15	3.77 ± 0.10	3.63 ± 0.12
TA$_{\parallel}$[ξ00]			
0.15	1.2 ± 0.05		0.83 ± 0.03
0.2	1.41 ± 0.04		1.08 ± 0.04
0.3	1.73 ± 0.03		1.48 ± 0.10
0.4	2.03 ± 0.15		1.71 ± 0.10
0.5	2.08 ± 0.06		1.85 ± 0.10
TO$_{\perp}$[ξ00]			
0.0	3.1 ± 0.15	3.57 ± 0.10	3.65 ± 0.15
0.05	3.12 ± 0.12		
0.1			3.69 ± 0.12
0.15	3.21 ± 0.2		
0.2	3.23 ± 0.15		3.57 ± 0.12
0.25	3.37 ± 0.2		
0.3	3.52 ± 0.1		3.54 ± 0.10
0.4	3.45 ± 0.1		
0.5	3.5 ± 0.12		3.57 ± 0.15
TA$_{\perp}$[$\xi\xi$0]			
0.05			0.6 ± 0.02
0.1	1.37 ± 0.07		1.09 ± 0.03
0.15			1.5 ± 0.04
0.2	2.28 ± 0.15		1.92 ± 0.06
0.25			2.3 ± 0.06
0.333	3.13 ± 0.15		2.82 ± 0.1
0.4			3.2 ± 0.15
0.5	3.5 ± 0.15		3.57 ± 0.1

TABLE I. *(Continued).*

ξ	$T = 295$ K	$T = 800$ K	$T = 1300$ K
		LA[$\xi\xi 0$]	
0.054	1.5		
0.1	2.27 ± 0.2		1.81 ± 0.1
0.15	2.63 ± 0.10		
0.2	2.90 ± 0.10		
0.25	3.15 ± 0.10		
0.3	3.4 ± 0.15		
0.35	3.5 ± 0.15		
0.4	3.52 ± 0.15		3.28 ± 0.15
0.45	3.58 ± 0.12		
0.5	3.62 ± 0.12		3.35 ± 0.15
		LO[$\xi\xi 0$]	
0.0	2.7 ± 0.16	2.46 ± 0.08	2.15 ± 0.15
0.1			2.70 ± 0.1
0.15	3.6 ± 0.15		3.31 ± 0.1
0.2			3.48 ± 0.15
0.25	3.72 ± 0.12		3.5 ± 0.2
0.5	3.85 ± 0.15		3.63 ± 0.12
		LO[00ξ]	
0.0	3.1 ± 0.15	3.57 ± 0.1	3.65 ± 0.15
0.05	3.15 ± 0.15		
0.1	3.1 ± 0.2		3.71 ± 0.10
0.2	3.4 ± 0.15		
0.25	3.58 ± 0.15		
0.3	3.7 ± 0.15		
0.35	3.56 ± 0.15		3.65 ± 0.10
0.4	3.5 ± 0.10		
0.45	3.4 ± 0.10		
0.5	3.0 ± 0.15	3.15 ± 0.10	3.2 ± 0.10
		TA$_\perp$[$\xi 00$]	
0.1	0.79 ± 0.03		0.75 ± 0.03
0.15	1.18 ± 0.02	1.11 ± 0.03	1.0 ± 0.02
0.2	1.48 ± 0.02		
0.25	1.78 ± 0.03		
0.3	1.91 ± 0.04		1.74 ± 0.03
0.4	2.16 ± 0.12		2.12 ± 0.10
0.5	2.35 ± 0.15	2.3 ± 0.2	2.26 ± 0.12
		TO$_\perp$[$\xi 00$]	
0.0	2.7 ± 0.16	2.46 ± 0.08	2.15 ± 0.15
0.1	2.7 ± 0.2		2.3 ± 0.10
0.15	2.78 ± 0.12		
0.2	2.9 ± 0.15		2.69 ± 0.06

TABLE I. *(Continued)*.

ξ	$T = 295$ K	$T = 800$ K	$T = 1300$ K
$\mathrm{TO}_{\parallel}[\xi 00]$			
0.3	3.4 ± 0.15		3.07 ± 0.10
0.35	3.5 ± 0.15		
0.4	3.55 ± 0.15		
0.5	3.62 ± 0.12		3.35 ± 0.15
$\mathrm{LO}[\xi 00]$			
0.0	2.7 ± 0.16		2.15 ± 0.15
0.05	2.75 ± 0.10		
0.1	2.95 ± 0.10	2.66 ± 0.08	2.55 ± 0.10
0.15	3.25 ± 0.10		
0.2	3.45 ± 0.10		3.1 ± 0.10
0.25	3.7 ± 0.10		
0.3	3.8 ± 0.10		3.55 ± 0.15
0.5	4.27 ± 0.05	3.88 ± 0.12	3.77 ± 0.15
$\mathrm{TA}_{\parallel}[\xi\xi 0]$			
0.05	0.61 ± 0.03		
0.1	1.39 ± 0.02		1.14 ± 0.04
0.15	1.87 ± 0.05		
0.2	2.56 ± 0.06		2.28 ± 0.08
0.25	2.97 ± 0.1		
0.33	3.32 ± 0.16		3.04 ± 0.10
0.4	2.9 ± 0.06		
0.5	2.08 ± 0.06		1.85 ± 0.09
$\mathrm{TO}_{\perp}[\xi\xi 0]$			
0.0	3.1 ± 0.15	3.57 ± 0.1	3.65 ± 0.15
0.1	3.16 ± 0.12		
0.2	3.57 ± 0.12		3.52 ± 0.12
0.4	2.82 ± 0.10		2.50 ± 0.1
0.5	2.32 ± 0.1		2.62 ± 0.12
$\mathrm{TO}_{\parallel}[\xi\xi 0]$			
0.0	2.7 ± 0.16	2.46 ± 0.08	2.15 ± 0.15
0.15	3.3 ± 0.1		
0.4	4.03 ± 0.15		3.7 ± 0.1
0.5	4.27 ± 0.05		

It can be seen from Table I and Fig. 2 that the frequencies of all but the [001] LO branch of hcp Hf decrease with increasing temperature. This behavior is similar to that observed[15,16] in hcp Zr and Ti and, moreover, the observed relative frequency changes with varying temperature for these elements are approximately of the same magnitude. The experimentally measured frequency shifts in these metals are, however, approximately 5 times larger than those estimated from the thermal expansion of the lattice. This implies that the relatively large frequency shifts with varying temperature observed in these metals are mainly due to an explicit temperature dependence of the phonon frequencies,

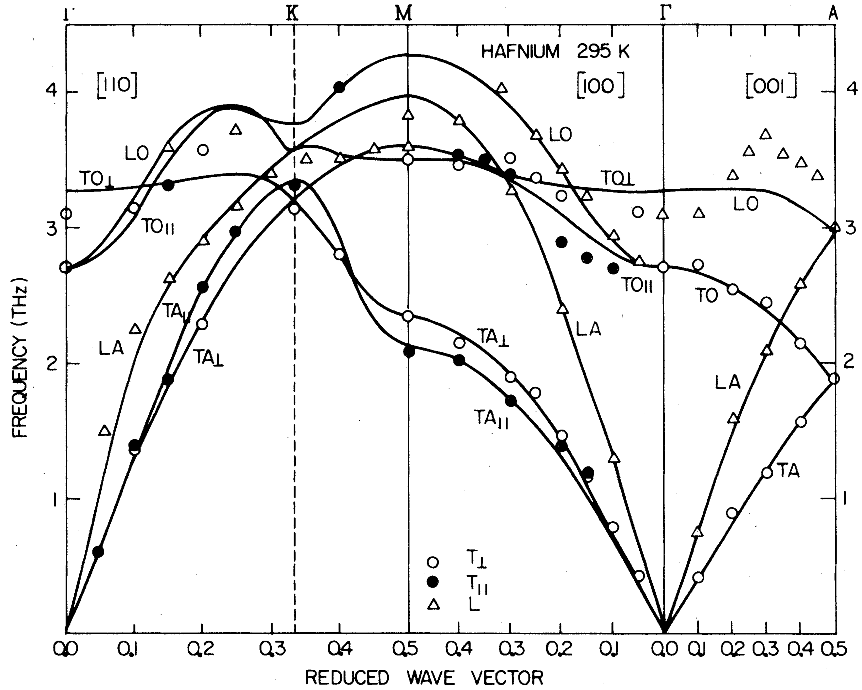

FIG 1. Phonon dispersion curves of hcp Hf along the [001], [100], and [110] symmetry directions at 295 K. The solid lines were obtained by fitting the data to the force-constant model of DeWames *et al.* (Ref. 24).

a conclusion consistent with the results obtained from measurements[19] of the pressure dependence of the elastic moduli of hcp Ti and Zr. In regard to the origin of these rather large frequency changes with varying temperature, it should be noted that measurements[13] of the temperature dependence of the elastic constants of Hf, Zr, and Ti show that the softening of the acoustic branches near $q = 0$ is, in general, more pronounced than that observed in the neutron experiments for the finite wave-vector acoustic modes. This observation implies that in hcp Hf, Ti, and Zr the frequency changes with varying temperature are mainly due to changes in the long-range interatomic forces, which are largely determined by the density and electronic character of states near the Fermi level.

It can be seen (Fig. 2) that the temperature dependence of the frequencies of the [001] LO branch of hcp Hf is anomalous. The frequency of the zone-center mode of this branch softens significantly as the temperature decreases and at room temperature the [001] LO branch exhibits a dip at the zone center. The anomalous dispersion and temperature dependence exhibited by the [001] LO branch of hcp Hf are similar to those observed[15,16] in hcp Zr and Ti. Actually the anomalies observed in the dispersion curves of the superconducting transition elements of the IV column of the Periodic Table may be characteristic of all hcp superconducting transition elements. In fact neutron scattering measurements of the dispersion curves of superconducting hcp Tc revealed that the [001] LO branch of this element also exhibits anomalous dispersion[20] (Fig. 3) and similar temperature dependence[21] as found in our experiments on hcp Zr, Ti and Hf.

As in the case of hcp Zr and Ti, no dramatic changes in the phonon frequencies or the widths of the measured neutron groups were observed as the hcp → bcc transformation temperature was approached from below. This observation suggests that the hcp → bcc transition in Hf, as in Zr and Ti, is of the first order. Actually the hcp → bcc transformation is these metals is generally believed to be of the martensitic variety.

In summary, the general features of the lattice dynamics of hcp Hf bear a striking resemblance to those of hcp Zr and Ti. This is not surprising in view of the similarity of the electronic structures (as well as many of the other physical properties of these metals).

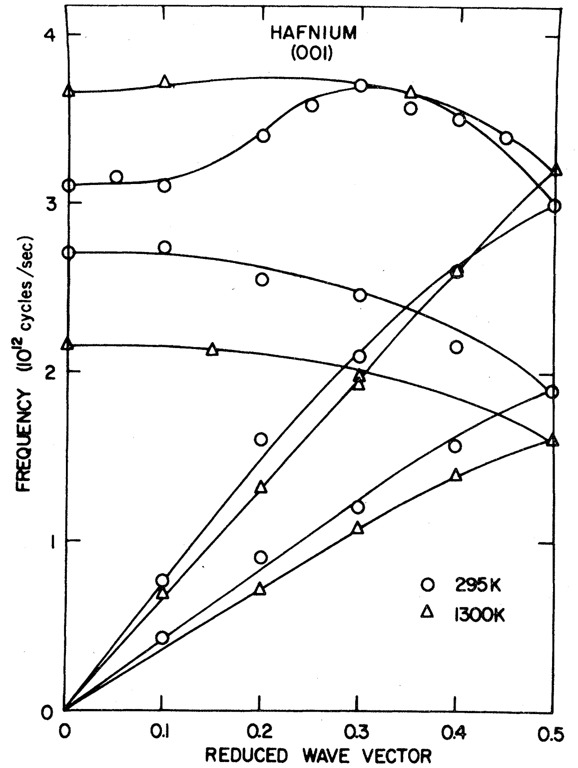

FIG 2. Room-temperature and 1300-K measurements of the dispersion curves of hcp Hf along the [001] symmetry direction.

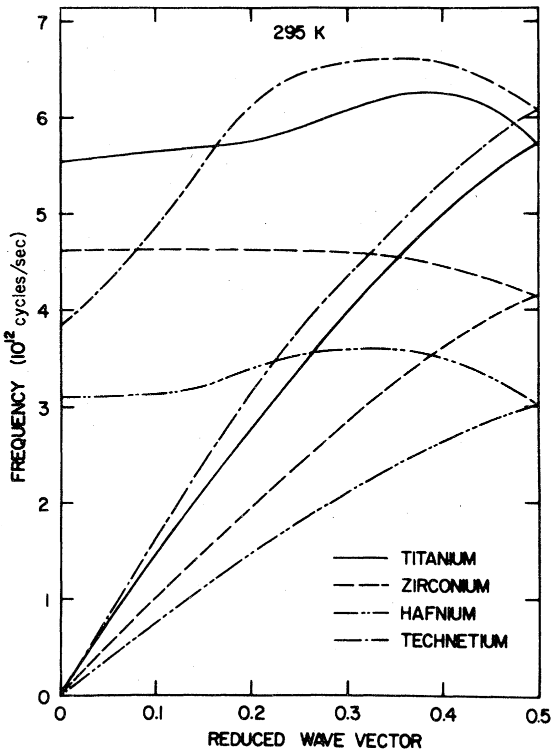

FIG 3. Comparison of the room-temperature dispersion curves of Hf, Zr (Ref. 15), Ti (Ref. 16), and Tc (Ref. 20), along the [001] direction. The transverse branches are not shown for the sake of clarity.

Before we discuss these results in terms of the electronic structure of Hf, it is instructive to examine whether the observed temperature variation of the phonon frequencies can account for the temperature dependence of the measured specific heat. Since the lattice specific heat has been evaluated by the same method[22] as that described in Refs. 15 and 16 (see also references therein), only a brief outline of the calculations will be presented in this paper.

The lattice specific heat at constant pressure $C_p^{(l)}$ can be obtained [see Eq. (2) of Ref. 16], once the room-temperature phonon spectrum $g(\omega,T_1)$ and an analytic expression $f(T)$ for the temperature dependence of the phonon frequencies have been determined from the experimental data. The present analysis is considerably simplified since the experimental frequencies vary to a good approximation linearly with temperature (Fig. 4) and thus $f(T)$ can be written as $1-A(T-T_1)$ with the constant A determined from the measured phonon frequencies.[23] To determine the room-temperature phonon spectrum $g(\omega,T_1)$, the phonon frequencies measured at room temperature were fitted to the modified axially symmetric force-constant model of DeWames *et al.*[24]. It can be seen from Fig. 1 that this model provides a satisfactory fit to the experimentally determined room-temperature dispersion curves. The force constants determined by fitting the experimental results to the model are listed in Table II. Using these force constants the frequency spectrum at room temperature was calculated by the interpolation method[25] of Raubenheimer and Gilat. This frequency distribution, together with $f(T)$, was then used in Eq. (2) of Ref. 16 to evaluate the lattice specific heat at constant pressure as a function of temperature.

The calculated lattice specific heat at constant pressure $C_p^{(l)}$ is plotted in Fig. 5 together with the quasiharmonic lattice specific heat $C_p^{(l)}$ (QH). As expected the latter approaches the classical value at high temperatures. It can be seen from Fig. 5 that there is a large contribution to the lattice specific heat arising from the explicit temperature dependence of the phonon frequencies. To compare the results of the present analysis with the measured total specific heat of Hf, we evaluated the electronic contribution to the specific heat using the electronic density of states obtained by Jepsen *et al.*[26] in their band theoretical calculation of the electronic structure of Hf. The use of the bare electronic density of states in evaluating the electronic specific heat is justified, since at the relatively high temperatures of interest here the electron-phonon mass enhancement is negligible.[27] The calculated electronic specific heat $C_v^{(e)}$ is plotted in Fig. 6. It can be seen from this figure that at high temperatures the calculated electronic specific heat is considerably larger than expected by linear extrapolation from low temperatures. This is due to the increase with increasing temperature of the effective electronic density of states at the Fermi level. The total specific heat, obtained by adding to the lattice specific heat the electronic contribution, is compared in Fig. 7 with experimental measurements[28-30] of the total specific heat of Hf. It can be seen from this figure that the agreement between the results obtained in the present analysis and the measurements of the specific heat of Hf is quite satisfactory. Thus the observed "anomalous" temperature dependence of the specific heat of Hf at high temperatures can be accounted for by the temperature dependence of the lattice and electronic specific heats.

IV. DISCUSSION

The dispersion curves and the temperature dependence of the phonon frequencies of hcp Hf bear a striking resemblance to those of hcp Zr and Ti, as expected from the similarity of the electronic structures[26,31] (as well as many other properties) of these metals. We find in particular that the following properties are characteristic of the lattice dynamics of the transition metals of the IV column of the Periodic Table. (i) The frequencies of all but the [001] LO branch decrease with increasing temperature considerably more than expected by taking into account the thermal expansion of the lattice. This explicit temperature dependence of the phonon frequencies gives rise to a considerable contribution (Fig. 6) to the lattice specific heat and together with the electronic contribution accounts for the "anomalous" temperature dependence of the specific heat of these metals at high temperatures. (ii) The most interesting feature of the lattice-dynamical properties of these transition metals is the anomalous temperature dependence of the [001] LO branch. The zone-center mode of this branch softens appreciably with decreasing temperature and as a result the [001] LO branch exhibits a dip at the zone center, at room temperature in Ti and Hf, and at 5.5 K in Zr. Actually this type of phonon anomaly may be characteristic of all hcp superconducting transition elements. In fact the [001] LO

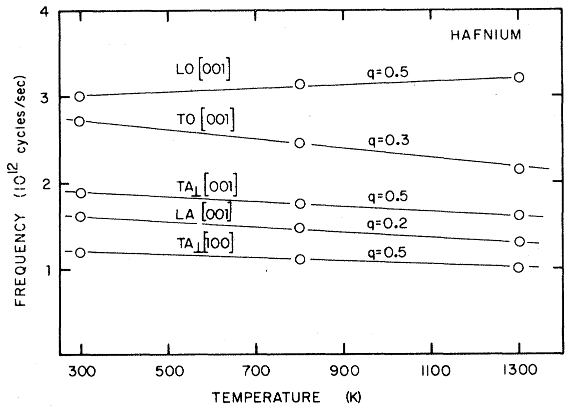

FIG 4. Temperature dependence of the frequencies of some normal modes of hcp Hf.

TABLE II. Force constants (10^3 dynes/cm) obtained by fitting the 295-K data of hcp Hf to the DeWames model (Ref. 24). The notation is that of Ref. 24.

$K(1,1-2)$	43.01
$C_{BX}(1,1-2)$	-2.44
$C_{BZ}(1,1-2)$	-16.54
$K(2,1-1)$	25.86
$C_{BX}(2,1-1)$	-0.49
$C_{BZ}(2,2-1)$	6.19
$K(3,1-2)$	-5.63
$C_{BX}(3,1-2)$	1.54
$C_{BZ}(3,1-2)$	-1.50
$K(4,1-1)+C_{BZ}(4,1-1)$	11.95
$C_{BX}(4,1-1)$	0.17
$K(5,1-2)$	1.40
$C_{BX}(5,1-2)$	0.71
$C_{BZ}(5,1-2)$	0.66
$K(6,1-1)$	1.22
$C_{BX}(6,1-1)$	0.22
$C_{BZ}(6,1-1)$	-0.27

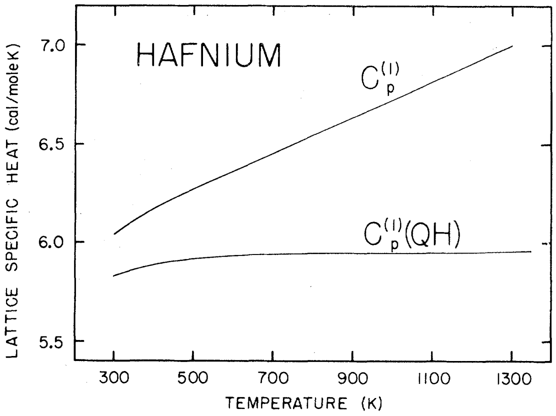

FIG 5. Temperature dependence of the calculated lattice specific heat at constant pressure $C_p^{(l)}$. C_p^l (QH) is the quasiharmonic lattice specific heat.

branch of technetium, which has the highest superconducting transition temperature ($T_c \sim 8$ K) of the hcp elements, also exhibits anomalous dispersion (Fig. 3) and similar temperature dependence as found in Zr, Ti, and Hf. In addition since it is generally believed[5] that the occurrence of phonon anomalies depends on the detailed topology of the electronic bands near the Fermi level, the simple type of phonon anomaly observed in Zr, Ti, Hf, and Tc may also occur in superconducting compounds with different crystal structures. Experimental evidence for this has been found in a recent study[32] of the lattice dynamics of the superconducting ($T_c \simeq 6.4$ K) compound $LaSn_3$ which crystallized in the Cu_3Au structure. In fact the temperature dependence of the frequency of the first Γ_{15} mode in $LaSn_3$ was found to be anomalous and quite similar to that of the zone-center [001] LO mode in the hcp superconducting elements Zr, Ti, Hf, and Tc.

A fundamental understanding of the experimental results on Hf, Zr, and Ti and their relation to the detailed electronic structure of these metals could in principle be obtained within the framework of the theory[5] of the lattice dynamics of transition metals as formulated by Varma and Weber. Unfortunately, however, in the present stage of development of this theory no realistic calculations at finite temperature have been attempted. However, as we show in the following discussion (see also Refs. 15—17), considerable insight into the origin of the phonon anomalies in these metals may be obtained from frozen phonon band theoretical calculations.

Since similar phonon anomalies were observed in the dispersion curves of Hf, Zr, and Ti, it is natural to attribute their origin to the electronic band structure[26,31] of these metals. In hcp metals, the energy bands in the AHL plane are doubly degenerate. Symmetry considerations show that the presence of a lattice distortion, corresponding to the zone-center [001] LO mode, will lift the degeneracy of the bands. For bands close to the Fermi level this splitting will reduce the electronic energy and a phonon anomaly will occur. In this simple picture the tem-

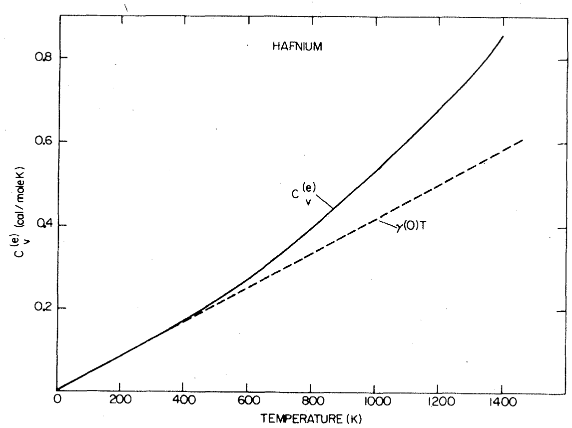

FIG 6. The electronic contribution to the specific heat $C_V^{(e)}$ evaluated using the electronic density of states obtained by Jepsen *et al.* (Ref. 26) $\gamma(0)T$ is the electronic specific heat obtained by extrapolation from low temperatures.

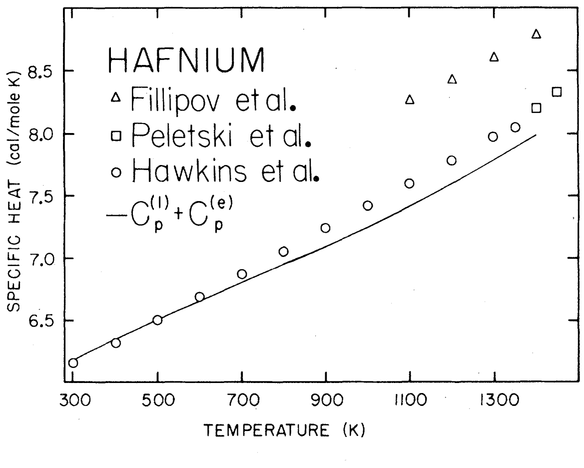

FIG 7. Comparison of the specific heat at constant pressure C_p, obtained by adding $C_p^{(e)}$ to $C_p^{(l)}$, with the experimental results obtained by various workers (Refs. 28—30).

perature dependence of the zone-center [001] LO mode can be understood as arising from the disorder and thermal repopulation which at higher temperatures reduces the effectiveness of the band splitting in lowering the electronic energy. To assess the validity of this interpretation we performed band theoretical calculations[33] for hcp Zr with the nuclei frozen in the positions obtained by the zone-center [001] LO mode. These calculations show that in fact this mode is particularly effective in splitting the double degenerate bands in the AHL plane and that the splitting of these bands results in a substantial decrease in the electronic energy, since the band which is lowered in energy remains occupied while the other band is raised above the Fermi level and becomes unoccupied. Our frozen phonon band theoretical calculations show also (assuming[34] the validity of the rigid band model) that the band splitting at the Fermi level is considerably larger for Tc than for Zr, a result consistent with the observation of a pronounced phonon anomaly in Tc (Fig. 3). Thus the phonon anomalies in the hcp superconducting elements Zr, Ti, Hf, and Tc can be accounted for qualitatively on the basis of this simple model. This mechanism, the splitting of degenerate bands near the Fermi level by lattice distortions, may also be responsible for the anomalous behavior[32] of the optical modes in the vicinity of the first Γ_{15} point in the superconducting compound $LaSn_3$. In fact, it is clear that the doubly degenerate Δ_5 bands[36] of $LaSn_3$ will be split by the lattice distortions corresponding to the zone-center optical modes. To summarize, the experimental results on Zr, Ti, Hf, Tc, and $LaSn_3$, as well as frozen phonon band theoretical calculations, suggest that the splitting of degenerate bands about the Fermi level by the lattice distortions may be responsible for the occurrence of phonon anomalies in the dispersion curves of a large number of superconducting elements and compounds.

A detailed quantitative analysis of the experimental results necessitates an accurate evaluation of the total energy for the phonon-distorted lattice. Such calculations have been performed recently[9] and have demonstrated that in the case of Si the phonon frequencies can be evaluated with the necessary accuracy. Similar calculations for Nb and Zr are presently in progress in this laboratory.

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