

Lattice dynamics of CePd_3

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The room-temperature phonon-dispersion curves of the mixed-valent compound CePd_3 were measured by inelastic neutron scattering techniques. No significant anomalies in either the phonon frequencies or in the widths of the measured neutron groups were observed. The phonon spectrum of CePd_3 resembles closely those of CeSn_3 and LaSn_3 . It is estimated that any lifetime effects due to the electron-phonon coupling in CePd_3 are certainly smaller than approximately 0.15 THz at room temperature. The force constants obtained by fitting the experimental data to a three-nearest-neighbor Born-von Kármán model were used to evaluate the phonon density of states, the lattice specific heat, and the atomic temperature factors of Ce and Pd in CePd_3 .

I. INTRODUCTION

The intermediate valence phenomena occurring in certain rare-earth compounds have been the subject of many experimental and theoretical investigations,¹⁻⁷ and interest in this area has considerably increased since the discovery in the last few years of the heavy-fermion compounds.⁸ Although there is an enormous wealth of experimental information on the intermediate valence materials, no theory can satisfactorily account for the physical phenomena.⁷

In the intermediate valence systems, the $f \leftrightarrow d$ electronic transitions are expected to affect both the lattice constants as well as the electronic density of states at the Fermi level. As a result, one would expect rather strong electron-phonon coupling that would affect the phonon frequencies. Actually, in Sm and Tm mixed-valence compounds and alloys that crystallize in the NaCl structure, pronounced phonon anomalies in the [111] longitudinal branches, have been observed.^{9,10} Several theoretical models reproduced the experimental results and demonstrated that the observed phonon anomalies are due to valence fluctuations.¹¹⁻¹³

In CeSn_3 that crystallizes in the Cu_3Au structure, on the other hand, no pronounced phonon anomalies have been observed.¹⁴⁻¹⁶ Entel and Sietz¹⁷ performed model calculations of the dispersion curves of CeSn_3 and CePd_3 and showed this is due simply to the fact that in the Cu_3Au structure, there is much larger free space available to the rare-earth ion than in the NaCl structure. We, therefore, felt that measurements of the dispersion curves of CePd_3 , one of the most extensively studied¹⁸⁻³¹ mixed-valence compounds, would establish the generality of their conclusions. Some preliminary data from the present work were compared with the results of an infrared study in a paper by Sham and Wilkins.³² In this

paper, we present a complete report of our measurements.

II. EXPERIMENTAL DETAILS

The measurements were performed on two large ($\sim 1-2 \text{ cm}^3$) single crystals of CePd_3 prepared by the Materials Preparation Center of the Ames Laboratory. The specimens were examined by standard neutron diffraction techniques and were found to be single crystals exhibiting the Cu_3Au structure. The mosaic spread (full width at half maximum) of the crystals was approximately 8 minutes of arc. This value was obtained by measuring the width of the (002) Bragg reflection, using a monochromatic neutron beam obtained by reflection from the (111) planes of a perfect Ge crystal.

The measurements were performed using three triple-axis spectrometers, one at the Oak Ridge Research Reactor (ORRR) and the other two at the High-Flux Isotope Reactor (HFIR) of the Oak Ridge National Laboratory. With few exceptions, the data were collected with the spectrometer in the constant-Q mode of operation (where Q denotes the neutron scattering vector) and with fixed scattered neutron energies E' of 14.9, 24.8, and 31 meV. In the case of $E' = 14.9 \text{ meV}$ a pyrolytic graphite filter was inserted upstream of the analyzer to attenuate higher-order contaminations. The following monochromator (reflecting plane) collimation before sample-collimation after sample-analyzer (reflecting plane) combinations were used: Be(002)-40'-40'-Be(002); Be(102)-40'-40'-Be(002); Be(002)-40'-40'-PG(002); PG(002)-40'-40'-PG(002); PG(004)-40'-40'-PG(002); PG(002)-40'-40'-PG(004); where PG denotes pyrolytic graphite. Be monochromator and analyzer were used for measurements in the 3-5 THz (12.4-20.7 meV) region where higher energy resolution was needed to resolve the struc-

ture of the dispersion curves. The phonon dispersion curves along the [100], [110], and [111] symmetry directions were obtained by measurements in the (100) and (110) symmetry planes.

Although CePd_3 does not oxidize in air as rapidly as CeSn_3 and LaSn_3 , the samples were kept under an inert gas atmosphere throughout the experiments. All phonon measurements were performed at ambient temperature.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Vibrations of the four atoms in the unit cell of a Cu_3Au -structure lattice result in a total of twelve phonon branches in each direction. By symmetry, the purely transverse branches (Δ_5 's) in the [100] direction and the transverse-like branches (Λ_3 's) in the [111] direction are doubly degenerate. To assign the measured phonon frequencies to the appropriate branches, the frequencies and phonon intensities were compared with calculations based on a three-nearest-neighbor Born-von Kármán force-constant model. We adopted the assignment for which we obtained the best agreement between the model calculations and the experimentally measured frequencies and intensities. We find that atomic force constants up to third nearest neighbors must be included to provide an adequate description of the data (the value of χ^2 in a least-squares analysis changes from 2.7 for a two-

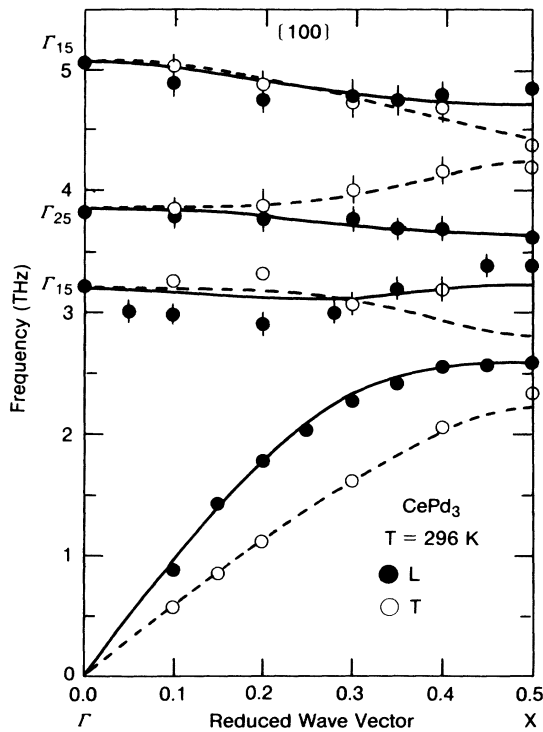


FIG. 1. Phonon dispersion curves of CePd_3 along the [100] symmetry direction at room temperature. The solid and dashed lines correspond to purely longitudinal (Δ_1 's and Δ_2) and purely transverse (Δ_5 's) branches, respectively, and were obtained by fitting the data to a three-nearest-neighbor Born-von Kármán model.

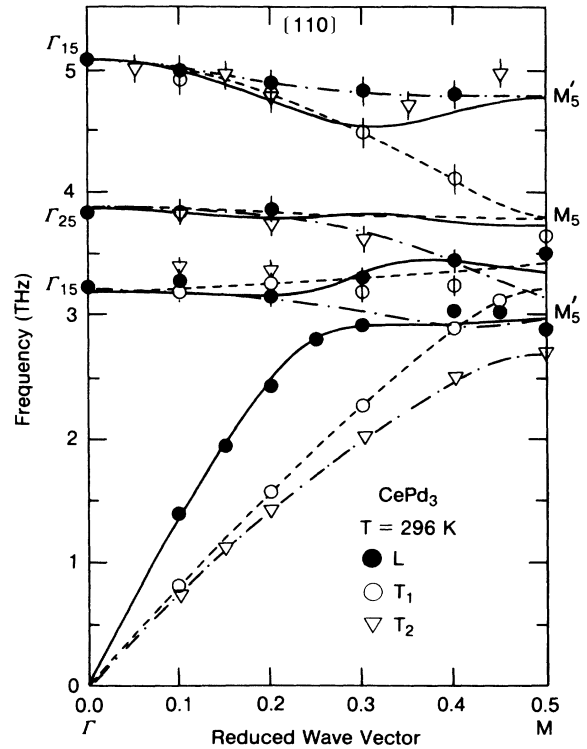


FIG. 2. Phonon dispersion curves of CePd_3 along the [110] symmetry direction at room temperature. The solid, dashed, and dot-dashed lines correspond to longitudinal-like (Σ_1 's) purely transverse (Σ_3 's and Σ_2), and transverse-like (Σ_4 's) branches, respectively, and were obtained by fitting the data to the model.

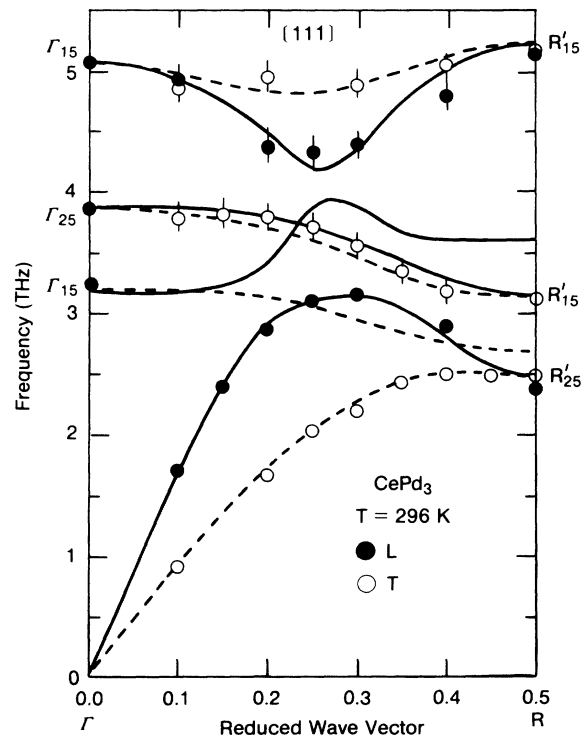


FIG. 3. Phonon dispersion curves of CePd_3 along the [111] symmetry direction at room temperature. The solid, dashed, and dot-dashed lines correspond to longitudinal-like (Λ_1 's), transverse-like (Λ_3 's), and purely transverse (Λ_2) branches, respectively, and were obtained by fitting the data to the model.

TABLE I. Atomic force constants and elastic constants obtained by fitting the data to a three-nearest-neighbor Born-von Kármán model.

Atomic force constants (10 ³ dyn/cm)		Elastic constants (10 ¹¹ dyn/cm ²)	
Ce-Pd 1XX	13.569±0.09	C ₁₁	17.40±0.09
Ce-Pd 1ZZ	-6.517±0.18	C ₄₄	5.84±0.38
Ce-Pd 1XY	12.916±0.16	C ₁₂	5.66±0.51
Pd-Pd 1XX	9.830±0.13		
Pd-Pd 1ZZ	1.746±0.13		
Pd-Pd 1XY	3.511±0.19		
Ce-Ce 2XX	21.565±0.57		
Ce-Ce 2YY	-0.096±0.45		
Pd-Pd 2YY	-0.001±0.16		
Pd-Pd 2XX	-4.316±0.12		
Ce-Pd 3XX	2.363±0.07		
Ce-Pd 3XZ	0.438±0.12		
Ce-Pd 3YY	-0.339±0.07		
Ce-Pd 3YZ	-0.785±0.09		
Pd-Pd 3XX	-0.339±0.04		
Pd-Pd 3XZ	0.963±0.07		
Pd-Pd 3YY	0.639±0.04		
Pd-Pd 3YZ	0.050±0.11		

nearest-neighbor to 1.1 for a three-nearest neighbor model). The measured phonon frequencies along the [100], [110], and [111] symmetry directions, and the calculated dispersion curves are plotted in Figs. 1–3. It can be seen that a three-nearest-neighbor Born-von Kármán model provides a satisfactory fit to the experimental data. The atomic force constants and the elastic constants obtained from the model are given in Table I. After we completed the phonon measurements, it was brought to our attention that a similar study of the lattice dynamics of CePd₃ has been carried out by Severing and co-workers.³³ Their room-temperature data agree, in general, with our results.

In general, the phonon dispersion curves of CePd₃ at room temperature resemble those of CeSn₃ and LaSn₃ if

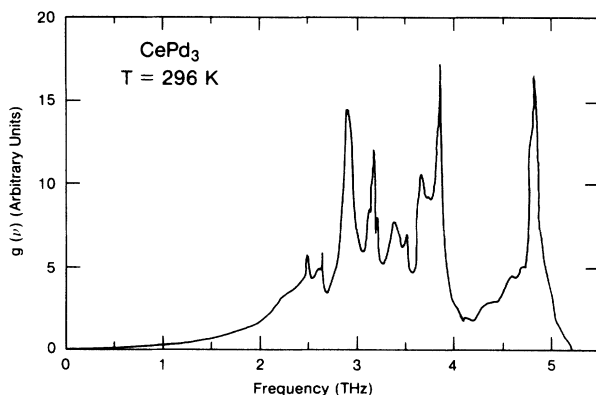


FIG. 4. Phonon density of states $g(\nu)$ of CePd₃ evaluated using the force constants listed in Table I.

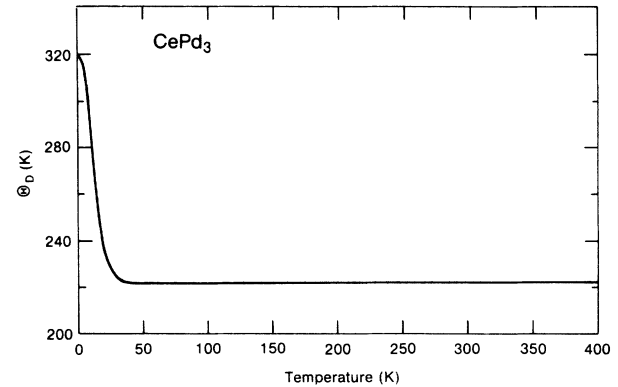


FIG. 5. Temperature dependence of the effective Debye temperature of CePd₃ evaluated using the phonon density of states plotted in Fig. 4.

one takes into account the difference in the atomic masses of Pd and Sn and in the melting temperatures of these materials. Differences in the dynamical behavior of these systems exist however and they are reflected in the details of their phonon density-of-states and in their atomic temperature factors (see Sec. IV below). The bulk modulus²⁰ of CePd₃ is almost twice as large as those of CeSn₃ and LaSn₃; the phonon frequencies of CePd₃ are expected to be higher than those of these isostructural compounds. Actually, from the measured phonon frequencies of these compounds, one obtains an estimate of 5.5 THz for the cutoff frequency of CePd₃. This estimate agrees well with the results of the present experiment (Figs. 1–3). The elastic constants deduced from the least-squares analysis of the phonon data (see Table I) are in good agreement with those obtained from ultrasonic measurements.¹⁷ It is noted that the elastic constants C_{12} and C_{44} are equal, to within experimental errors, as expected from the Cauchy relations for cubic crystals. This suggests that in the

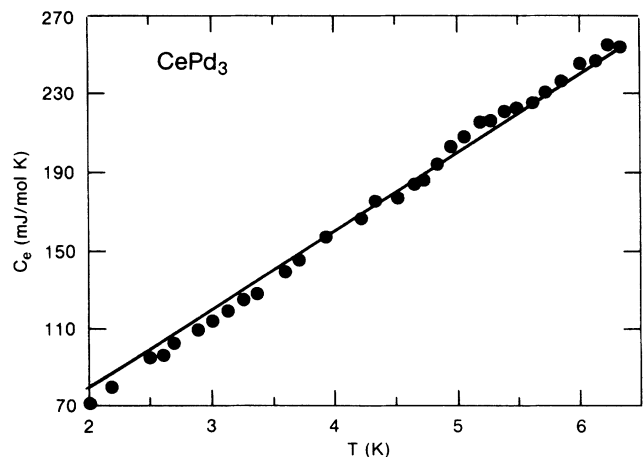


FIG. 6. Electronic specific heat, C_e , of CePd₃ obtained by subtracting the lattice contribution from the measured total specific heat (Ref. 18). The straight line was obtained by fitting these results to $C_e = \gamma T$.

context of this simple model a potential energy expressed in terms of two-body centrosymmetric interactions may adequately describe the lattice dynamics of the system. In addition, in CePd₃ the interaction between the longitudinal acoustic and the first longitudinal optic mode, near the midzone region along the [100] and [110] symmetry directions, appears to be weaker in comparison to that in CeSn₃ and LaSn₃.

In analyzing the phonon data, we have systematically examined the widths of the measured neutron groups. We find that in all cases the phonon widths of CePd₃ agree with the values expected from the energy resolution of the spectrometer. In fact, we estimated that, as in the cases of CeSn₃ and LaSn₃, any lifetime effects due to electron-phonon coupling are certainly smaller than approximately 0.15 THz, a limit set by the uncertainty in assessing the spectrometer resolution. This is in sharp contrast to the case of the mixed-valent alloy Sm_{0.75}Y_{0.25}S where large phonon widths of the order of 1 THz in conjunction with strong softening of the LA branch were observed⁹ at about $\frac{2}{3}$ of the Brillouin-zone boundary along the [111] symmetry direction. The experimental results are therefore in agreement with the theoretical predictions of Entel and Sietz¹⁷ and Kuramoto and Müller-Hartman.³⁴

IV. PHONON DENSITY OF STATES, LATTICE SPECIFIC HEAT, AND ATOMIC TEMPERATURE FACTORS

We have calculated the phonon density of states of CePd₃, $g(\nu)$, using the force constants listed in Table I. The tetrahedron method³⁵ was adopted for the necessary integration over the Brillouin zone. Using this phonon density of states (Fig. 4) the lattice specific heat has been calculated as a function of temperature, and the results, expressed in terms of an effective Debye temperature Θ_D , are plotted in Fig. 5. The electronic specific heat can be obtained by subtracting from the measured total specific heat the lattice contribution (the dilation term, estimated from the measured values of the thermal expansion and compressibility of CePd₃, introduces only an insignificant correction to the electronic contribution). Unfortunately, there are substantial differences between total specific-heat measurements²¹⁻²⁴ reported in the literature, reflecting presumably the sensitivity of the transport

properties of CePd₃ to sample stoichiometry and impurity content. Here, we have chosen to subtract the lattice specific heat evaluated in this work from the total specific-heat data of Hutchens *et al.*²¹ to obtain the electronic specific heat of CePd₃ (Fig. 6).

It can be seen (Fig. 6) that at low temperatures the electronic specific heat varies linearly with temperature with a slope γ of approximately 39.9 mJ/mol K². This value is to be compared with that (36.64 mJ/mol K²) obtained by extrapolation to 0 K of the C/T measurements.²¹ The large value of γ is consistent with the high density of states at the Fermi level in a mixed-valent system.

We also used our model to evaluate the atomic temperature factors of CePd₃ at room temperature. In CePd₃, the Ce atoms occupy positions with cubic point symmetry ($m\bar{3}m$), whereas the Pd atoms are at sites with tetragonal point symmetry ($4/mmm$). Within the harmonic approximation, the Ce temperature factor $B(\text{Ce})$ is isotropic whereas, in principle, two different temperature factors $B_{\perp}(\text{Pd})$ and $B_{\parallel}(\text{Pd})$ are necessary to characterize the thermal motion of the Pd atoms perpendicular to and in the cube faces, respectively. Using standard expressions³⁶ for the atomic temperature factors, we find that at room temperature $B(\text{Ce})=0.404$, $B_{\perp}(\text{Pd})=0.608$, and $B_{\parallel}(\text{Pd})=0.525$ Å. These values are in good agreement with the results of a detailed neutron diffraction study³⁷ of CePd₃. Thus in CePd₃, the Pd temperature factor is nearly isotropic ($B_{\perp}/B_{\parallel}=1.16$). Note, on the other hand, that the Sn temperature factors in CeSn₃ and LaSn₃ were found to be highly anisotropic^{15,38,39} ($B_{\perp}/B_{\parallel}=1.6$ and 1.95, respectively, for CeSn₃ and LaSn₃).

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