

Observation of phonon anomalies in the intermediate-valence compound CePd_3

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We report measurements of the phonon dispersion relation in intermediate-valence CePd_3 . The longitudinal-acoustic modes show a distinct softening above 100 K and a temperature-dependent broadening and splitting at higher temperatures. Especially in the $\langle 100 \rangle$ direction the longitudinal modes differ from those of other Cu_3Au structures. A good fit of the room-temperature dispersion curves is given by a 16-parameter Born-von Kármán model with a breathing force as an additional degree of freedom.

INTRODUCTION

The valence instability of $4f$ intermediate-valence (IV) systems due to fluctuations between the $4f^n$ and the $4f^{n+1}$ configurations was expected to result in a wealth of phonon anomalies because of the large volume difference ($\sim 20\%$) between the two valence states.^{1,2} Because of this volume difference the valence fluctuations are accompanied by large volume fluctuations. If the volume fluctuations or the "breathing" of the rare-earth atoms occur on a time scale comparable with typical lattice response times, an influence on the phonon system like the damping of certain phonon modes may be expected. So far, direct experimental evidence for such phonon anomalies is scant. Indeed, while strong phonon anomalies were found in IV $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$, SmS , and TmSe ,³⁻⁵ i.e., in materials which are strongly of mixed valence and whose fluctuation frequencies are of the same order of magnitude as the phonon frequencies, there is as yet very little direct evidence for phonon anomalies in other valence-unstable materials.⁶ There are three nearly-integral-valence (γ -type IV) cerium compounds whose phonon dispersion has been studied in the past: CeSn_3 ,⁷ CeAl_2 ,⁸ and CeNi .⁹ CeSn_3 does not exhibit phonon anomalies at room temperature, and phonon measurements performed under pressure¹⁰ did not bring clear evidence for anomalous electron-phonon interaction. The absence of phonon anomalies in CeSn_3 might be due either to the fact that the fluctuation temperature of $T_f = 290$ K (Ref. 11) is larger than the Debye temperature $\Theta_D = 205$ K,¹² i.e., the valence fluctuations are faster than lattice response times, or to the fact that the cerium ion is of nearly integral valence. In CeAl_2 and CeNi phonon softenings as function of temperature have been observed, but in CeAl_2 the effect was interpreted as a

crystal-field phonon resonance, and in CeNi the softening might occur because of a nearby crystallographic phase transition.¹³ On the other hand, there is strong indirect experimental evidence for anomalous electron-phonon coupling in many cerium Kondo-type and IV compounds at low temperatures, e.g., from anomalies of the bulk moduli of CeSn_3 ,¹² CeAl_3 ,¹⁴ and CeBe_{13} .¹⁵ To study this type of electron-phonon coupling within the Brillouin zone by inelastic neutron scattering, one needs large single crystals. The difficulty of producing these has been the true bottleneck for progress in detecting the expected phonon anomalies directly by inelastic neutron scattering.

In this paper we present detailed neutron-scattering experiments of IV CePd_3 (cubic Cu_3Au structure). CePd_3 is the only known α -type cerium-like compound [valence 3.23 (Ref. 16)] with a rather low fluctuation temperature [$T_f = 220$ K (Ref. 11)] in comparison to the Debye temperature [$\Theta_D = 292$ K (Ref. 12)].

EXPERIMENTS AND RESULTS

The single crystals used in our investigations were grown by the Czochralski technique and the lattice constants agree with values found in the literature [$a = 4.126$ Å (Ref. 17)]. One of the crystals has a volume of about 0.5 cm³ and a mosaic spread of less than 0.8° . Most of the measurements presented here were performed on this crystal. Recently, another larger crystal became available (size about 3.0 cm³, mosaic spread $\leq 0.5^\circ$). This crystal was used for the verification of some of the results obtained on the first crystal.

We measured the phonon dispersion curves at room temperature and investigated the temperature dependence of several selected acoustic modes. Preliminary

measurements of the acoustic branches at room temperature and at 12 K were performed on the triple-axis spectrometers UNIDAS and SV4 at the FRJ2 reactor at Kernforschungsanlage Jülich (KFA) and on the IN3 spectrometer at the high flux reactor (HFR) in Grenoble. The optical phonons at room temperature and the temperature dependence of the acoustic modes, which are discussed here, were measured on the 2T1 spectrometer at the ORPHEE reactor in Saclay. We used a pyrolytic graphite monochromator and analyzer, a 25'-31'-49'-49' collimation, and a graphite filter placed between sample and analyzer in order to suppress second-order scattering. The measurements were performed with fixed final energy $E_f = 14.7$ meV.

Figure 1 shows the room-temperature phonon dispersion curves of CePd₃ for the three main symmetry directions. The crystallographic structure of CePd₃ gives rise to 12 phonon branches in each direction. In the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions the transverse modes are twofold degenerate. The solid and open circles in Fig. 1 represent longitudinal and transverse modes, respectively. The triangles in the [110] direction indicate the transverse modes vibrating in a (110) plane, whereas the open circles represent the transverse modes with polarization vectors within a (100) plane. The lines in Fig. 1 are the results of two different fits which will be discussed later. The slopes of the acoustic branches for $q \rightarrow 0$ agree well with the ultrasonic data at 250 K.¹² The same is valid for the slopes of the 12-K measurements. Moreover, the room-temperature values for the two infrared-active Γ -point modes (14.5 and 21.5 meV) concur well with earlier infrared-absorption measurements.¹⁸

Measurements of the longitudinal-acoustic (LA) phonons as a function of temperature show that the most interesting temperature range is above 100 K instead of the low-temperature range. As displayed in Fig. 2, the LA phonons in the [111] direction show an unusual behavior

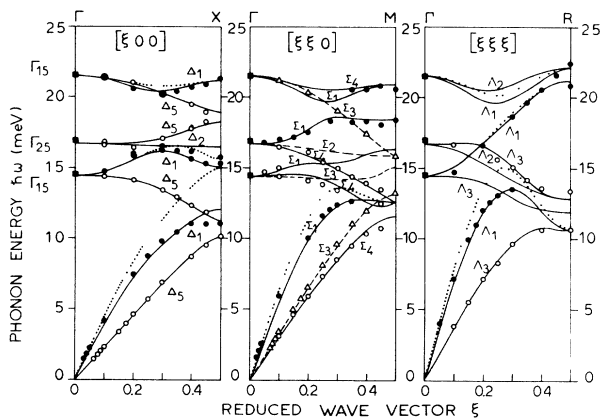


FIG. 1. Room-temperature phonon dispersion of CePd₃. Symbols: ●, longitudinal modes; ○, transverse modes. In the [110] direction: △, transverse polarized in (110) plane; ○, transverse polarized in (100) plane. The solid and dashed lines [transverse polarized in a (110) plane] represent a Born-von Kármán fit which includes an additional breathing parameter S . The dotted lines are the resulting fit when the breathing is turned off ($S=0$). For more details, see the text.

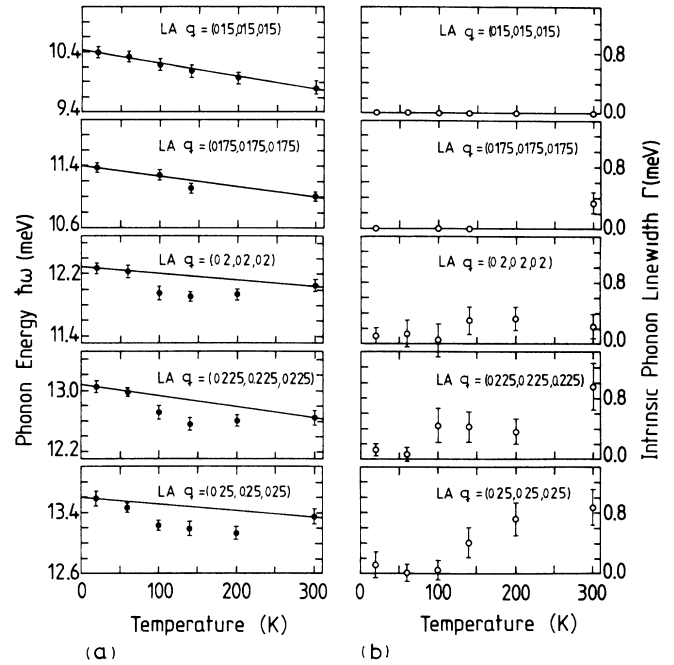


FIG. 2. (a) Phonon energies vs temperature for several LA modes in the [111] direction. (b) Intrinsic phonon linewidths of the corresponding modes vs temperature (see the text).

as function of temperature. Figure 2(a) shows the phonon energies and Fig. 2(b) the corresponding intrinsic phonon linewidths [full width at half maximum (FWHM)] versus temperature for five different q vectors at $T=20, 60, 100, 140, 200,$ and 300 K. For $q=(0.175, 0.175, 0.175)$ there appears a smooth dip in the phonon energy between 100 and 200 K. The dip becomes more pronounced with increasing q . As shown in Fig. 2(b) intrinsic phonon linewidths show up in this temperature range. We were not able to extend these investigations to q values beyond $q=(0.25, 0.25, 0.25)$; the structure factors become so weak due to mode crossing that no reliable values for energy shifts and linewidths can be given for this region. Scans of one phonon measured at different temperatures were obtained with the same instrumental resolution, i.e., they are directly comparable. In order to determine intrinsic phonon linewidths, the data were fitted with a Lorentzian, which describes the intrinsic phonon line shape, convoluted with a Gaussian of constant width for each q vector due to the finite spectrometer resolution. The points in Fig. 2(b) without error bars reflect a fit without a Lorentzian. These scans were well described by the spectrometer resolution alone so that no intrinsic phonon lifetime was assumed. In the [110] direction we made measurements for just one q vector [$q=(0.275, 0.275, 0)$] and the same temperature behavior was observed.

An even more pronounced anomaly occurs in the LA branch in the [100] direction. Figure 3 shows the scans of longitudinal-acoustic modes in the [100] direction for $q=(0.4, 0, 0), (0.45, 0, 0),$ and $(0.5, 0, 0)$ (the zone boundary). The lines are guides to the eye only. These results have been obtained with the larger crystal. At 13 K and

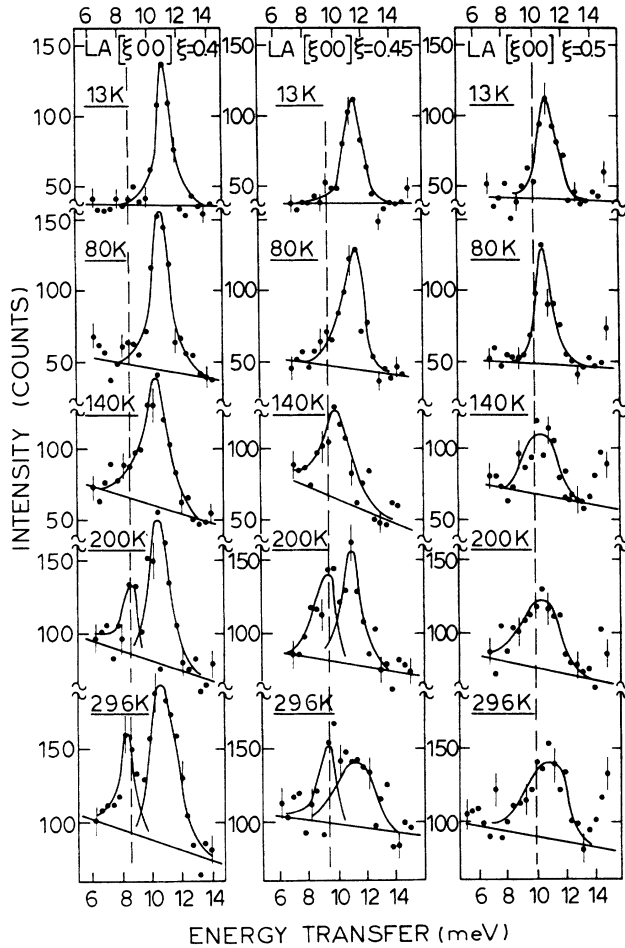


FIG. 3. Scans of several LA modes in the [100] direction for different temperatures (see the text). The vertical dashed lines indicate the positions of the corresponding TA modes at room temperature as measured from a transverse configuration.

still at 80 K all three peaks look very narrow. At 140 K there is already enhanced scattering intensity at the low-energy side of the peaks and above 200 K the phonon groups look like double-peak structures. It is surprising that the low-energy peaks appear close to positions where the transverse-acoustic modes are expected, even though we measured in a purely longitudinal configuration. In Fig. 3 the positions of the transverse branches have been marked by vertical dashed lines. In order to rule out the possibility of spurious scattering, involving transverse phonons, we performed checks with reduced vertical divergence in the beam and a different crystallographic

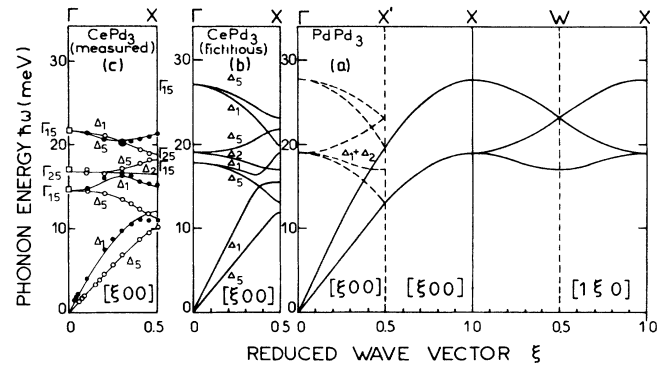


FIG. 4. (a) Phonon dispersion of PdPd₃ (Cu₃Au structure) in the [100] direction as constructed from the measured dispersion of fcc palladium (Ref. 19). (b) Phonon dispersion of CePd₃ as constructed from PdPd₃ by replacing the mass of every fourth palladium by the mass of cerium. (c) The [100] direction of the measured phonon dispersion of CePd₃ (see Fig. 1).

orientation. These modifications of the experimental conditions left the line shapes essentially unchanged. Further insight can be obtained from an analysis of the temperature dependence of the intensities. Table I lists the intensities of the observed phonon groups (including the peaks on the low-energy side) in relative units after subtraction of the background and division by the Bose occupation factor. For $q=(0.4, 0, 0)$ the values are constant within the accuracy of the experiment, as should be expected for a normal spectrum. For $q=(0.45, 0, 0)$ there is a slight decrease with increasing temperature which is more pronounced at the zone boundary. We have to admit that there are considerable uncertainties in the determination of the background especially at $q=(0.5, 0, 0)$. Nevertheless, there is no indication at all for additional scattering intensity at higher temperatures, which must be expected if there were contaminations by parasitic scattering processes. Thus we are led to the conclusion that the unusual line shapes are an intrinsic property of the LA phonons in CePd₃. Previous studies of the temperature dependence of the [100] LA phonons using the other crystal led essentially to the same results. The observation of longitudinal-acoustic modes near the zone boundary measured in a transverse configuration is ruled out because the structure factor of the lowest-lying transverse-optical branch increases towards the zone boundary.

ANALYSIS AND DISCUSSION

At first sight, the dispersion curves of CePd₃ seem to be quite normal without pronounced structures in the

TABLE I. The values of peak intensity times the half-width corrected for the Bose factor are listed for the modes shown in Fig. 3.

q	13 K	80 K	140 K	200 K	296 K
(0.4, 0, 0)	11.9	12.5	11.3	11.6	11.2
(0.45, 0, 0)	10.8	11.2	8.7	10.1	7.0
(0.5, 0, 0)	10.2	8.2	7.2	6.3	5.5

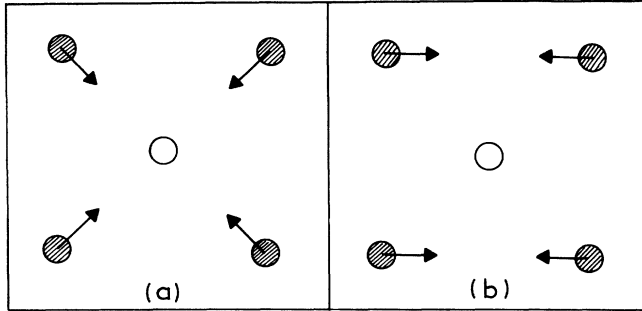


FIG. 5. Elongation pattern within the (100) plane (a) for the breathing deformation and (b) for the LA mode at $\mathbf{q}=(0.5, 0, 0)$.

phonon branches. However, the broadening and splitting effects which were observed above 100 K give strong hints that anomalous features exist in the phonon dispersion of CePd_3 , even at room temperature. This can be demonstrated without detailed analysis and it turns out that these effects agree quite well with the breathing idea of valence-fluctuating cerium ions. With this in mind we consider the close relationship between fcc and Cu_3Au lattices: one ends up with the CePd_3 structure by replacing every fourth palladium atom by a cerium atom in pure fcc palladium metal. Figure 4(a) shows the dispersion curves in the [100] direction for PdPd_3 (Cu_3Au structure) as constructed from the corresponding Brillouin zones of fcc palladium.¹⁹ The optic branches are generated by projecting the direction $X-X'$ and the zone-boundary directions $X-W$ and $W-X$ onto $\Gamma-X'$. Substituting another atom for every fourth palladium atom lifts the degeneracies at Γ and X , as demonstrated by Fig. 4(b). In this example the mass of every fourth palladium atom is replaced by that of cerium without changes in the interatomic forces. Because of the different lattice constants (PdPd_3 , 3.891 Å; CePd_3 , 4.126 Å) this construction cannot yield the CePd_3 phonon spectrum quantitatively, but it describes the overall feature of a Cu_3Au phonon dispersion. That the latter is indeed true is shown by a

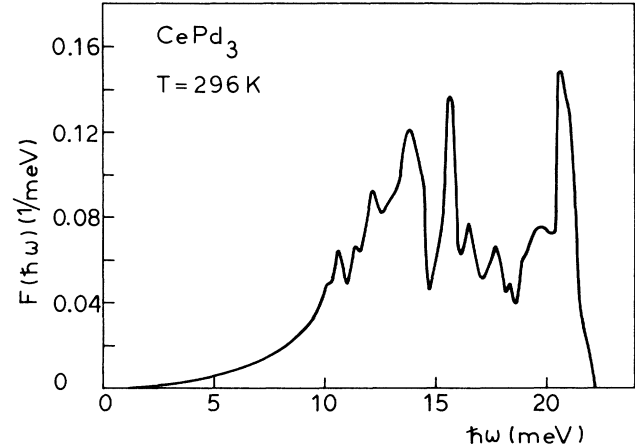


FIG. 6. Phonon density of states at room temperature calculated from the lattice-dynamical model including the breathing force.

comparison of the fictitious spectrum with the spectra of other Cu_3Au compounds [such as CeSn_3 , LaSn_3 ,⁷ Ni_3Al ,²⁰ Pt_3Mn ,²¹ and Pd_3Fe (Ref. 22)]. Therefore qualitative differences between this fictitious dispersion spectrum of CePd_3 and the measured dispersion relations must be due to electronic properties of cerium in CePd_3 . Comparing Fig. 4(b) (fictitious CePd_3) with the measured CePd_3 phonon dispersion spectrum [Fig. 4(c)] some differences appear: In CePd_3 the interaction between the highest longitudinal-optic (LO_3) and the LA branch towards the zone boundary is so strong that the LO_3 branch lies above the transverse branch, in contrast to other Cu_3Au structures. This is consistent with a large energy split of these two branches. It implies that not only the position of the LO_3 is anomalously high, but also that the LA is softened as well. The conclusion that the LA branch in the [100] direction is anomalous goes along with the observation of anomalous phonon line shapes towards the zone boundary (see Fig. 3).

We have used lattice-dynamical models of various complexity to reproduce the measured phonon data. The

TABLE II. Force constants of the Born-von Karman fit with an additional breathing term of the room-temperature dispersion of CePd_3 and CeSn_3 . r/a gives the nearest-neighbor (NN) distance in units of the lattice constants. F and G are the longitudinal and transverse force constants, and S is the breathing force constant in units of dyn/cm.

r/a	NN	CePd_3		CeSn_3		G (Ref. 7)
		F	G	F	G	
0.7071	Ce-Pd	27 813	-2321	Ce-Sn	24 720	-2700
0.7071	Pd-Pd	22 425	1546	Sn-Sn	12 340	-2080
1.0	Ce-Ce	20 912	-7591	Ce-Ce	630	1720
1.0	Pd-Pd	638	6	Sn-Sn	900	-150
1.225	Ce-Pd	1703	-348	Ce-Sn	-640	-430
1.225	Pd-Pd	67	141	Sn-Sn	1800	-200
1.414	Ce-Ce	6660	-75	Ce-Ce	-4830	1380
1.141	Pd-Pd	-454	-98	Sn-Sn	2620	-740
		$S = 20\,000$		$S = 9480$		

most satisfactory fit was obtained with a 16-parameter Born–von Kármán model with an additional breathing term. This breathing term accounts for an extra degree of freedom due to the breathing deformability of the IV rare-earth atom. In our model the breathing contribution to the dynamical matrix is represented by a term $D_{br} = -S\mathbf{a}\cdot\mathbf{a}'$, where S is the breathing force constant and \mathbf{a} is a twelve-dimensional vector with subvectors of the form $(0,0,0)$ for cerium and $(\sin(\pi q_x)\cos(\pi q_y), \cos(\pi q_x)\sin(\pi q_y), 0)$ for the palladium atoms in the (001) plane. The other elements are derived by cyclic permutations. This expression results from a breathing deformation as shown in Fig. 5(a). It should be pointed out that a vibration pattern of exactly this type does not occur in the Cu_3Au structure. The strongest influence of D_{br} is obtained at $\mathbf{q}=(0.5, 0, 0)$ with an elongation pattern that is depicted in Fig. 5(b). Furthermore, it should be mentioned that the model does not yield information about line shapes. It is still based on the harmonic approximation, i.e., it yields energy shifts but no intrinsic phonon linewidths or line splittings. The result of this 17-parameter fit is shown in Fig. 1. The solid lines represent longitudinal and transverse modes and, the dashed lines in the $[110]$ direction represent the transverse modes vibrating in a (110) plane. In Table II the resulting fit parameters are listed. Figure 6 shows the phonon density of states calculated from the lattice-dynamical model. The Debye temperature calculated from the theoretical phonon density of states is in good agreement with the Debye temperature determined from the room-temperature slopes of the acoustic branches ($\Theta_D=289$ K). The ultrasonic data give a value of $\Theta_D=292$ K.¹² This comparison verifies that our model calculations reflect the lattice dynamics in a proper way.

A model of this type was used by Pintschovius *et al.*⁷ to describe the phonon dispersion of CeSn_3 . For comparison the force constants of CeSn_3 are given in Table II as well. The difference in the Ce–Ce force constants of both compounds is striking. The Ce–Ce interactions are very large in comparison to CeSn_3 . In particular, the breathing force constant S is large and not negligible in order to obtain a reasonable fit of the LA branch in the $[100]$ direction. In contrast to this, the additional breathing force in CeSn_3 did not improve the fit to the data significantly.⁷ We believe that this is another indication of the anomalous influence of IV cerium in CePd_3 . In order to study the influence of the breathing term on the phonon dispersion curves, the breathing has been turned off ($S=0$), whereas all other parameters were kept constant. The result is shown by the dotted lines in Fig. 1. For clarity we have not marked the rather small changes in the optical branching of the $[110]$ direction. It turns out that a strong influence of the breathing term on the dispersion spectrum is where we indeed observed the anomalous effects. It softens the LA branches of the $\langle 111 \rangle$ and $\langle 110 \rangle$ directions in the middle of the Brillouin zone. A comparison with our data shows that in these regions of the zone intrinsic linewidths exist [Fig. 3 and $\mathbf{q}=(0.275, 0.275, 0)$], i.e., additional interactions are indeed taking place. The strongest softening influence of

the breathing force is on the LA branch in the $[100]$ direction towards the zone boundary. In this region of the spectrum we have observed the mode splitting (see Fig. 3) and have demonstrated the existence of a softening by comparing the measured spectrum with a spectrum constructed from PdPd_3 (see Fig. 4). Intuitively, one would expect that the upward bending of the highest Δ_1 branch and the depression of the LA branch towards the zone boundary are related. As can be seen from Fig. 1 our form of the breathing term does not provide such a correlation. In our model the unusual behavior of the highest Δ_1 branch is reflected in the rather large longitudinal Ce–Ce force constants.

We do not believe that ordinary phonon-phonon annihilation and creation processes are responsible for the observed anomalous line shapes and broadenings. Comparable effects are absent in CeSn_3 . CeSn_3 is a much softer material than CePd_3 [the bulk moduli differ roughly by a factor of 2 (Ref. 12)]. Therefore phonon lifetime reduction due to phonon-phonon interaction resulting in a broadening of the phonon linewidth should be more dramatic in CeSn_3 , but at room temperature CeSn_3 does not show any detectable intrinsic phonon linewidths.⁷ This leads to the conclusion that phonon line broadenings in CePd_3 must have their origin in an additional interaction, other than phonon-phonon coupling. Possibly a damping of the harmonic phonon modes by a breathing of the IV rare-earth atoms occurs as observed in other IV materials with NaCl structure.^{3–5} The phonon anomalies in CePd_3 occur in different parts of the Brillouin zone and they are less pronounced. Differences in size and position due to the different crystallographic structure have been predicted by Entel and Sietz.²³

Our data seem to reflect two different temperature regions, the low-temperature region ($T < 100$ K) with normal line shapes and the region $T \geq 140$ K with anomalous line shapes and intrinsic linewidths. We do not have an explanation for this behavior yet. However, we point out that quite generally the temperature of about 140 K is characteristic for cerium in CePd_3 as well as in other IV cerium compounds. For example, the static susceptibility of CePd_3 shows its maximum at about 140 K,²⁴ and in the magnetic neutron-scattering response an inelastic hump appears in addition to the quasielastic line below that temperature.²⁵ Transport measurements of CePd_3 show structure at the same temperature scale. For CePd_3 the electrical resistivity and thermopower exhibit a maximum at about 130 K and the thermal conductivity goes through a minimum there.²⁶ Furthermore, anomalies in the elastic properties of other cerium compounds like CeSn_3 (Ref. 12) and CeBe_{13} ,¹⁵ i.e., the minimum in the bulk modulus, occur at this temperature and the γ - α transition in pure cerium metal occurs at about 140 K.²⁷ This implies that not only the phonon spectrum but also other physical properties show two distinct temperature regions. The corresponding temperature scales of the phonon dispersion and other physical properties support the idea that the intermediate-valence character of cerium in CePd_3 is responsible for the observed phonon anomalies, although the mechanism responsible is not yet clear.

CONCLUSION

We have observed several anomalous features in the phonon-dispersion spectrum of CePd₃. The highest Δ_1 branch in the [100] direction shows, in contrast to other Cu₃Au spectra, an upward curvature which can only be fitted with large Ce-Ce force constants. On the other hand, the LA branch in this direction is fairly low, which results in a large breathing term in our model calculation. Measurements as function of temperature show a softening of some acoustic modes at about 140 K and the existence of intrinsic phonon linewidths. In particular, the LA modes of the [100] direction show a very anomalous line shape towards the zone boundary; they appear to split. All the observed anomalies led to the assumption that the mixed-valence state of cerium in CePd₃ causes these unusual features. Therefore the qualitative picture of a volume-fluctuating rare-earth atom whose breathing couples to certain phonon modes seems to be a good

starting point for understanding the phonon dispersion of CePd₃.

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