

Anomalous lattice dynamics in intermediate-valence CeNi

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(Received 15 December 1997)

The low-energy phonon modes of the intermediate-valence system CeNi and the isostructural reference compound LaNi have been measured at room temperature by inelastic neutron scattering in the scattering planes (001) and (100). In general, the frequencies of the acoustic and lower optical-phonon branches are found to be appreciably lower in CeNi. This effect is especially dramatic for the acoustic modes propagating along the *a* and *b* directions. Maximum softening was observed near the zone boundary, where it can exceed 20% for some of the branches. These data represent the most pronounced effect of electron-lattice coupling in a Ce-based intermediate-valence compound that we are aware of. [S0163-1829(98)51514-7]

Intermediate-valence (IV) rare-earth compounds, in which a lanthanide ion (typically Ce, Sm, Eu, Tm, or Yb) can be regarded as fluctuating between two different valence states, are prone to display anomalies in their vibrational properties because changes in the 4*f*-shell occupancy are associated with large differences in the ionic radius. Therefore, the possibility of a strong coupling between valence fluctuations and the lattice dynamics of such materials has been contemplated early in the development of this field, causing numerous experimental studies to be undertaken on a variety of systems (see Ref. 1 and references therein). But whereas significant phonon anomalies have been found in Sm- and Tm-based IV systems, such as (Sm,Y)S,² SmB₆,³ or TmSe,⁴ only a few indications have been reported so far in the case of Ce, possibly due to some mismatch between the characteristic energy scales for lattice vibrations and charge fluctuations.⁵ The first conclusive results were obtained by Severing *et al.*⁶ for CePd₃, where unusual temperature effects were observed in the LA modes along [111]. The authors argued that the room-temperature spectra contained anomalies which they accounted for by introducing an extra "breathing term" in the model calculation. However, the interpretation of these anomalies was not supported by an independent study of Loong *et al.*,⁷ who described their phonon spectra of CePd₃ using a three-nearest-neighbor Born-von Kármán force-constant model without any breathing term. Up to now, no

measurements of an isostructural reference system, e.g., LaPd₃, have been reported. More recently, definite softening of the lowest LO phonon branch at the Γ point of the Brillouin zone was discovered in CeNi₅,⁸ showing a decrease in frequency by 0.17 THz in comparison with the reference systems LaNi₅ and PrNi₅.

The intermetallic compound CeNi (orthorhombic space group *Cmcm*) exhibits typical IV properties. At low temperatures, it behaves as an enhanced Pauli paramagnet with a maximum near $T_{\max} = 140$ K in the *T* dependence of the magnetic susceptibility.⁹ The characteristic Kondo energy was estimated on the basis of macroscopic measurements to be about 100–150 K. Unique to this compound is the strong temperature change of its valence state from $\nu = 3.15$ at $T = 80$ K to 3.07 at $T = 300$ K.¹⁰ Anomalies have been found in the linear thermal-expansion coefficients, which go through a pronounced maximum (*a* and *c* directions) or minimum (*b* direction) at temperatures of the order of 100 K.^{11,12} The elastic constant c_{11} derived from inelastic neutron scattering experiments¹¹ also exhibits a minimum at about the same temperature, resulting from an anomalous softening of the LA phonon branch in the [100] direction near the zone center. From time-of-flight measurements on polycrystalline materials,¹³ it turned out that the phonon spectrum of CeNi is rather soft (cut off in the density of states at about 6 THz) in comparison with the phonon spectra of other Ni-based sys-

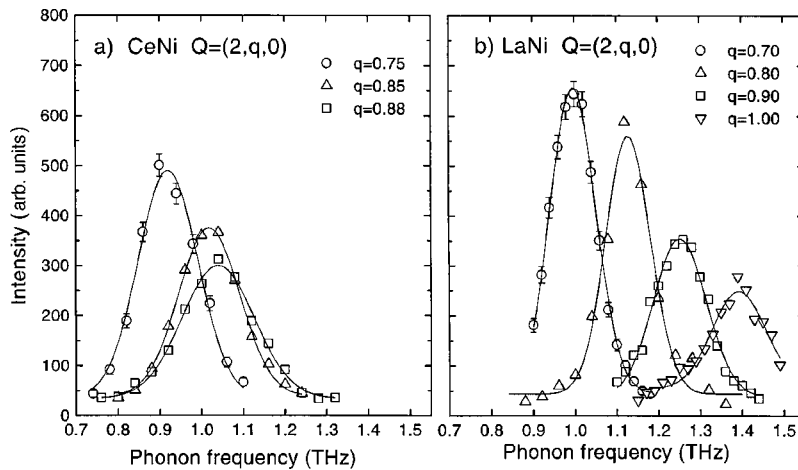


FIG. 1. Room-temperature scans of $[0\xi 0]$ TA phonon modes (open circles in Fig. 2) for CeNi (a) and LaNi (b) measured at fixed $k_f = 2.66 \text{ \AA}^{-1}$. q denotes the reduced phonon wave vector. Counting times are approximately 60 sec.

tems: CeNi₅, for instance, has a maximum phonon frequency of the order of 10 THz.

In view of the physical properties outlined above, it can be concluded that the energies of valence fluctuations and lattice vibrations are close to each other in CeNi and, therefore, sizeable effects of the electronic instability on the phonon modes can be anticipated. In order to sort out the effects of electron-phonon coupling associated with the valence fluctuations, one needs to estimate the normal lattice dynamics expected for this material. The latter may be calculated as in Ref. 6 but, for systems with a low symmetry, it is more reliable to proceed by comparison to a reference compound. In this paper, we describe inelastic neutron scattering experiments performed on CeNi and LaNi single crystals. The lower branches along several high-symmetry directions have been determined for both compounds. Their comparison reveals striking differences, which are discussed in connection with the anomalous electronic properties of cerium in CeNi. A more complete survey of the phonon spectra of CeNi and LaNi, including optical branches and temperature dependences, will be the subject of a forthcoming paper.

Single crystals of CeNi and LaNi with volumes of approximately 0.7 cm^3 were grown by the Czochralski technique. The orthorhombic lattice parameters were determined by neutron and x-ray diffraction [$a=3.784(2) \text{ \AA}$, $b=10.543(4) \text{ \AA}$, $c=4.363(4) \text{ \AA}$ for CeNi, and $a=3.913(2) \text{ \AA}$, $b=10.808(4) \text{ \AA}$, $c=4.394(4) \text{ \AA}$ for LaNi], and found to be in good agreement with previous determinations.

The phonon-dispersion relations were measured on the triple-axis spectrometer 4F2, installed on a cold neutron source at the reactor Orphée (LLB, Saclay). Constant- Q and constant-energy scans with fixed final neutron energies of $E_f=14.7 \text{ meV}$ and $E_f=8.05 \text{ meV}$ ($k_f=2.66 \text{ \AA}^{-1}$ and $k_f=1.97 \text{ \AA}^{-1}$, respectively) were used in the experiments, with corresponding energy resolutions [full width at half maximum (FWHM)] of 0.90 meV and 0.44 meV (0.22 THz and 0.11 THz) at the elastic position. A pyrolytic graphite filter was placed between sample and analyzer in order to suppress second-order contamination. In this configuration, the accessible neutron energy-transfer range was $0 < E < 13.5 \text{ meV}$ (photon frequencies up to 3.4 THz). All measurements reported here were carried out at $T=300 \text{ K}$.

The crystallographic structure of CeNi (four ions per primitive cell) gives rise to 12 phonon branches, which are nondegenerate along the orthorhombic directions. Experimental data were collected along four high-symmetry directions ($[100]$, $[010]$, $[001]$, and $[110]$) within the a - b and b - c scattering planes. Figure 1 shows typical scans of TA phonon modes in CeNi and LaNi. Acousticlike phonon branches measured along the above-mentioned directions are plotted in Fig. 2. The results for CeNi are in excellent agreement with the more limited set of data (along the $[100]$, $[010]$, and $[110]$ directions near the center of the Brillouin zone) previously reported by Gignoux *et al.*¹¹ The most striking feature of the results is a general softening of the phonon frequencies in CeNi, as compared to LaNi. This effect is particularly clear for the acoustic modes propagating along $[010]$. Strong changes also occur along $[100]$ and $[110]$ but their analysis is more delicate (see below). For some particular directions, huge deviations occur near the zone boundary, e.g., the phonon frequency is reduced by as much as 20% in CeNi for $\mathbf{q}=(1,1,0)$. Even though only limited information is as yet available for the optical modes, we have found that some of them also exhibit considerable softening. It should be emphasized that these effects are by far the strongest ever reported for a Ce-based compound: in Ce_{0.9}Pr_{0.1}Ni₅, the maximum softening of the lowest optical mode at the zone center did not exceed 10%.

Before discussing the physical origin of these effects, a comment should be made regarding the identification of the above branches as ‘‘acoustic.’’ It is clear, for instance, that the zone-boundary points in the $[100]$ and $[010]$ directions are actually identical (Z point in Slater, Koster, and Wood’s notation). This implies that, in Fig. 2, an additional branch, with a frequency of 1.6 THz at the zone boundary, must also exist in the $[\xi 0 0]$ direction. To understand this behavior, one needs to assume that the LA branch along $[100]$ intersects a low-lying optical branch with negative slope belonging to the same irreducible representation and, due to their mutual interaction, folds down to reach the zone boundary at the above frequency. Therefore, the continuation of the branch denoted LA in the figure becomes, strictly speaking, an optical branch, even though these modes will retain predominant acoustic character. A similar effect occurs for the TA

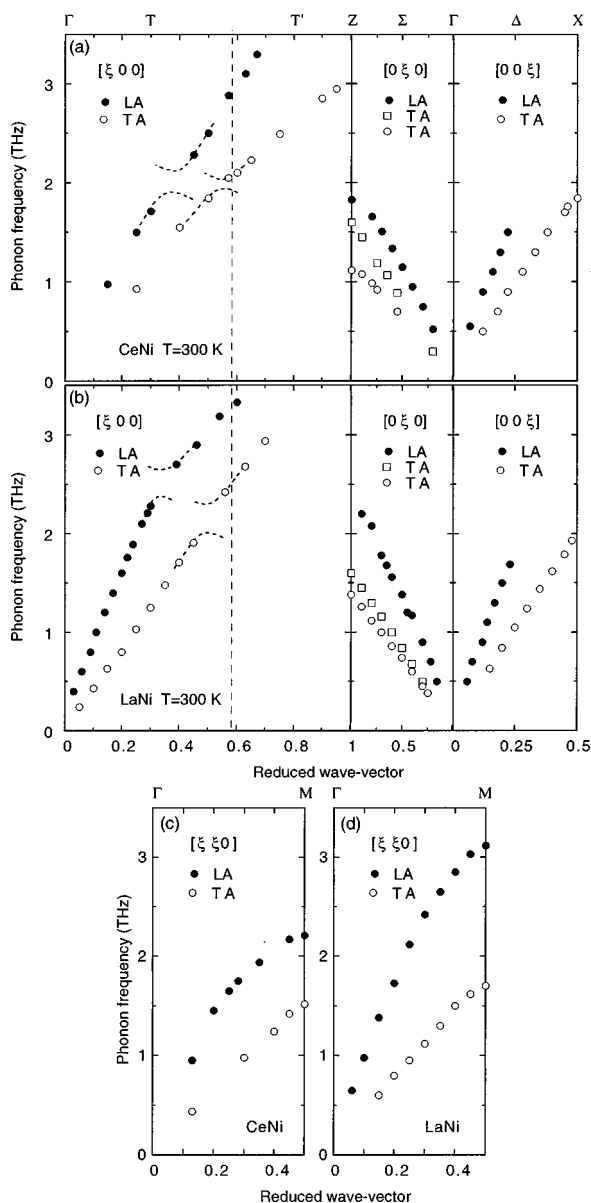


FIG. 2. Room-temperature phonon dispersions of CeNi [(a) and (c)], and LaNi [(b) and (d)] measured in the a - b and b - c scattering planes. Only branches with dominant acoustic character have been plotted. Dashed lines represent interactions with optical modes (not shown).

branch along $[100]$. Preliminary data (shown as dashed lines in Fig. 2) actually support this interpretation.

Clearly, the large overall softening observed here cannot be due to the difference in the lattice parameters since the volume of the unit cell of CeNi is 7% smaller than that of LaNi and, based on Grüneisen relations, one would rather predict an overall *increase* of the phonon frequencies by about 10%. It can be noted that, in this sense, even the $[001]$ branches, which are nearly identical in both compounds, have to be regarded as anomalous in CeNi.

We are thus led to the conclusion that the anomalies in the lattice dynamics of CeNi, are a genuine effect of the peculiar magnetic properties of $4f$ electrons in this material, as in CeNi₅ and, probably, in CePd₃. One possible mechanism is a coupling between phonons and crystal-field excitations, as reported previously for the Kondo compound CeAl₂.¹⁴ In

this system, a strong depression of optical branches occurs at low temperature, due to their coupling with crystal-field excitations leading to an apparent softening of “acoustic” modes with the same symmetry. However, such a scenario seems unlikely in the present system because the energies of the crystal-field excitations in CeNi (which cannot be observed directly owing to strong magnetic fluctuations)¹⁵ have been estimated to be approximately 14 and 25 meV,¹⁶ near the upper limit of the phonon spectrum. Possible magnetovibrational effects, if any, should thus be restricted to the higher optical branches. Furthermore, in the CeNi dispersion curves, softening is a much more general effect than in CeAl₂, not being restricted to modes of a given symmetry. Therefore, the strong softening observed in CeNi should have a different origin.

The valence instability of Ce appears to be the most plausible candidate, even though the exact mechanism through which it may affect the lattice dynamics is still an open question. One interpretation is connected with the breathing deformability of the Ce shell, as invoked in Ref. 6 for CePd₃. Alternatively, phonon softening in CeNi₅ was traced back to a coupling between lattice distortions having dipolar character with respect to the Ce atom and virtual electronic transitions between f and d states.^{8,17} It is interesting to note, in connection with the present work, that the latter model predicts the strongest softening to take place near zone center for optical modes and near zone boundary for acoustic ones. However, it would be premature to draw definite conclusions without a more detailed knowledge of the optical branches and their symmetry properties. One should also consider the possibility that phonon softening in CeNi might be related with the proximity of a crystallographic phase transition.¹⁸ Up to now, x-ray diffraction measurements performed on pure CeNi and Ce_{1-x}(La,Y)_xNi solid solutions in the temperature interval 15–300 K did not reveal any structural transition.^{12,16} On the other hand, CeNi has been reported to undergo a first-order, isostructural, electronic phase transition as a function of temperature, accompanied by a volume collapse of almost 5%, when it is subjected to a hydrostatic pressure in excess of 0.13 GPa at $T=0$ and 0.5 GPa at $T=150$ K.¹⁹ This transition was denoted “ $\gamma \rightarrow \alpha$ -like” in reference to elemental Ce, even though the ambient-pressure phase of CeNi already belongs to the IV regime. In the case of pure Ce, it was argued²⁰ that phonon anomalies observed at $P=0$ bear direct relation to this pressure-induced lattice collapse. In order to check whether this idea might apply to CeNi, it is necessary to investigate selected phonon branches at high pressure to see how they are affected by the approach to the transition.

In conclusion, CeNi provides the first example of strong phonon anomalies in a Ce-based mixed-valence compound. The comparison with LaNi clearly shows that a pronounced softening occurs at room temperature in several branches with acoustic character, especially near the zone boundary. Despite some complications arising from the interaction of these modes with low-lying optical branches, it appears most likely that the effect has an electronic origin and reflects the peculiar state of $4f$ electrons in cerium. This system thus seems very promising for a detailed study comprising a full determination of all dispersion curves, their modelization by an appropriate lattice-dynamics model, and a study of the

effects of temperature and/or pressure in connection with the electronic phase transition observed in Ref. 19.

We would like to acknowledge valuable discussions with A. S. Ivanov, A. Yu. Rumyantsev, and A. S. Mishchenko. Comments by D. Gignoux and B. Hennion on their earlier work were greatly appreciated. We are grateful to O. D.

Chistyakov and N. B. Kolchugina for the preparation of RNi materials. P.A.A. and E.S.C. wish to thank the LLB for its hospitality and support during the experiments. This research was performed with the financial support of the RFBR Grant Program (Grant No. 95-02-04734) and State Program "Neutron Investigations of Condensed Matter."

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