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# Addendum to the lattice dynamics of $\gamma$-Ce

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Inelastic neutron scattering techniques have been used to study the temperature dependence of the dispersion curves of $\gamma$-Ce. We find that the frequencies of all but the $T[111]$ branches exhibit normal temperature dependence. Close to the zone boundary the frequencies of the $T[111]$ branch, on the other hand, decrease with decreasing temperature, and at room temperature this branch exhibits a dip at the zone boundary. This anomalous behavior may be related to the fcc→dhcp phase transition.

## I. INTRODUCTION

The properties of cerium metal have been the subject of many experimental and theoretical investigations.[1] Of particular interest are the physical properties of the fcc phase ($\gamma$) which is stable at room temperature and atmospheric pressure. The $\gamma$ phase of cerium transforms under moderate pressure ($\sim 8$ kbar at 300 K) or upon cooling to low temperatures ($\lesssim 100$ K at 1 atm) to the fcc $\alpha$ phase in which the cerium ions are in a mixed-valence state. Furthermore, $\gamma$-Ce transforms to the dhcp phase below approximately 260 K at 1 atm.

In a previous paper[2] (hereafter referred to as I), published previously in this journal, we have reported the results of an inelastic neutron scattering study of the phonon dispersion curves of $\gamma$-Ce along the [100], [110], [111], and $[0\xi1]$ symmetry directions. Comparison of the measured dispersion curves with those of Th has indicated that the $\gamma$-Ce phonon frequencies are lower than one would expect, this relative softening being more pronounced for the $T[111]$ branch. We therefore felt that a study of the temperature dependence of the phonon frequencies of $\gamma$-Ce may provide additional information regarding the lattice dynamics of this phase and in this paper we present the results of these experiments.

## II. EXPERIMENTAL DETAILS

In the present experiment a single crystal of $\gamma$-Ce grown at the Ames Laboratory (for details see I and Ref. 3) was mounted in a high-temperature vacuum furnace positioned on the sample goniometer of a triple-axis neutron spectrometer. At 875 K the temperature was controlled to within a few degrees and the vacuum was approximately $10^{-5}$ Torr.

The measurements were performed using a triple-axis spectrometer at the 100-MW high flux isotope reactor of the Oak Ridge National Laboratory. All data were collected using the constant $Q$ (where $Q$ is the neutron scattering vector) mode of operation and a fixed scattered-neutron energy of 3.6 THz. Pyrolytic graphite [reflecting from the (002) planes] was used as both monochromator and analyzer, and a pyrolytic graphite filter was placed in the scattered beam to attenuate higher-order contaminations. The collimation of the neutron beam before and after the sample was 40′ of arc.

## III. EXPERIMENTAL RESULTS AND DISCUSSION

The $T[111]$ branch of $\gamma$-Ce has been studied in considerable detail at room temperature and 875 K. The frequencies of a selected number of phonons of the $L[111]$, $L[110]$, $L[100]$, $T[100]$, and $T_2[110]$ branches were also determined both at room temperature and 875 K. In all cases the room- and high-temperature data were collected under identical experimental conditions. The measured phonon frequencies are listed in Table I and the temperature dependence of the $T[111]$ disper-

TABLE I. Measured frequencies (THz) at 295 and 875 K of $\gamma$-Ce.

| Branch | $\xi$ | $\nu$ (295) | $\nu$ (875) | Branch | $\xi$ | $\nu$ (295) | $\nu$ (875) |
|---|---|---|---|---|---|---|---|
| $T[111]$ | 0.1 | 0.46±0.02 | 0.41±0.02 | $T[110]$ | 0.15 | 0.70±0.02 | 0.67±0.02 |
| | 0.15 | 0.63±0.02 | 0.60±0.02 | | 0.4 | 1.80±0.03 | 1.65±0.03 |
| | 0.2 | 0.80±0.03 | 0.70±0.03 | | 0.8 | 2.83±0.04 | 2.70±0.04 |
| | 0.25 | 0.94±0.03 | 0.84±0.03 | $L[110]$ | 0.3 | 1.80±0.06 | 1.80±0.06 |
| | 0.3 | 1.05±0.04 | 0.90±0.03 | | 0.8 | 2.19±0.05 | 2.17±0.06 |
| | 0.35 | 1.01±0.04 | 0.96±0.03 | $T[100]$ | 0.4 | 1.27±0.03 | 1.17±0.03 |
| | 0.4 | 0.92±0.04 | 0.97±0.04 | | 0.8 | 2.10±0.04 | 1.94±0.04 |
| | 0.45 | 0.86±0.04 | 0.98±0.03 | | 1.0 | 2.10±0.05 | 2.00±0.06 |
| | 0.5 | 0.82±0.04 | 0.94±0.03 | $L[100]$ | 0.4 | 1.50±0.06 | 1.44±0.06 |
| $L[111]$ | 0.1 | 0.95±0.05 | 0.90±0.07 | | 0.8 | 2.73±0.08 | 2.65±0.07 |
| | 0.3 | 2.40±0.05 | 2.40±0.08 | | 1.0 | 3.20±0.08 | 3.03±0.08 |
| | 0.5 | 2.86±0.05 | 2.80±0.06 | | | | |

sion curve is shown in Fig. 1. The room-temperature data are in good agreement[4] with the measurements reported in I.

It can be seen (see Table I) that the frequencies of all but the $T[111]$ branch of $\gamma$-Ce decrease with increasing temperature. This behavior is what one would normally expect from the effect on the vibrational frequencies of the thermal expansion of the lattice. The temperature dependence of the frequencies of the $T[111]$ branch of $\gamma$-Ce is, on the other hand, anomalous (see Fig. 1). Close to the zone boundary the frequencies of this branch decrease with decreasing temperature and at room temperature the $T[111]$ branch exhibits a dip at the zone boundary.

It is unlikely that the anomalous dispersion and temperature dependence of the frequencies of the $T[111]$ branch of $\gamma$-Ce are related to the mixed-valence transition to the $\alpha$ phase. In fact, the $T[111]$ branch of fcc La, which does not undergo a transition to a mixed-valence state, was found[5] to also exhibit similar dispersion (see Fig. 1) and temperature dependence as the corresponding branch of $\gamma$-Ce. This is not surprising since La and Ce have comparable masses and similar ($5d\,6s^2$) outer electronic configurations (of course La, unlike Ce, does not have any $4f$ electrons); actually one would expect nearly identical dispersion curves for these two metals in the absence of any mixed-valence effects on the dispersion curves of Ce or pronounced electron-phonon effects on those of superconducting La. Thus the anomalous dispersion and temperature dependence exhibited by the $T[111]$ branch must be related to the common electronic structure of these metals.

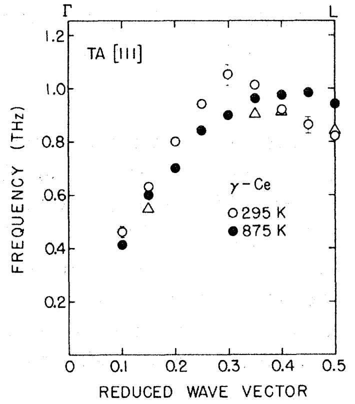

FIG. 1. Temperature dependence of the TA[111] branch of $\gamma$-Ce. Some phonon frequencies (Ref. 5) for fcc La at 660 K are also shown (triangles).

It is important to recall at this point that fcc Ce and fcc La both undergo a transformation to the dhcp phase ($\gamma$-Ce at ~260 K and $\beta$-La at ~583 K); actually below the transformation temperature the fcc and dhcp phases coexist in these metals. The fcc→dhcp phase transformation involves four transverse waves propagating along the [111] direction with reduced wave vectors $\vec{q}$ of $\frac{1}{4}$, $\frac{1}{3}$, and $\frac{1}{2}$. It is natural therefore to assume that the anomalous dispersion and temperature dependence of the $T[111]$ branch of $\gamma$-Ce (and $\beta$-La) is related to the fcc→dhcp phase transformation in this metal. A similar conclusion has been reached by Pickett, Freeman, and Koelling in their detailed theoretical study[6] of the electronic band structure of $\gamma$-Ce and $\beta$-La. In particular, Pickett, Freeman, and Koelling found that the calculated generalized susceptibility $\chi(q)$ of La is remarkably large along the [111] symmetry direction and exhibits peaks near the wave vectors which are involved in the fcc dhcp phase transformation. A more fundamental understanding of the relationship between the anomalous dispersion and temperature dependence of the $T[111]$ branch of $\gamma$-Ce, the electronic structure and the fcc→dhcp phase transformation can only be obtained within the framework of the microscopic theories[7] of lattice dynamics. Only recently, calculations at finite temperatures using these theories have been attempted.[8]

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[1] For a comprehensive review of the properties of Ce, see D. C. Koskenmaki and K. A. Gschneidner, Jr., in *Handbook on the Physics and Chemistry of Rare Earths,* edited by K. A. Gschneidner, Jr. and L. Eyring (North-Holland, Amsterdam, 1978), Vol. 1, Chap. 4.

[2] C. Stassis, T. Gould, O. D. McMasters, K. A. Gschneidner, Jr., and R. M. Nicklow, Phys. Rev. B 19, 5746 (1979).

[3] D. C. Koskinmaki, K. A. Gschneidner, Jr., and N. J. Panousis, J. Cryst. Growth 22, 225 (1974).

[4] The frequencies determined in the present experiment were found to be slightly higher than those reported in I. This was expected, since most of the frequencies reported in I were obtained with better instrumental resolution (using a Be crystal as monochromator). For further details see Sec. II of I.

[5] C. Stassis, J. Zarestky, C.-K. Loong, and O. D. McMasters (unpublished).

[6] W. E. Pickett, A. J. Freeman, and D. D. Koelling, Phys. Rev. B 23, 1266 (1981); 22, 2695 (1980).

[7] C. M. Varma and W. Weber, Phys. Rev. B 19, 6142 (1979), and references therein.

[8] K. Motizuki, N. Suzuki, Y. Yoshida, and Y. Takaoka (unpublished).