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Lattice dynamics of fcc Yb

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The lattice dynamics of fcc Yb at room temperature and atmospheric pressure has been studied by coherent inelastic scattering of neutrons. The phonon dispersion curves were determined along the $[\xi 00]$, $[\xi\xi 0]$, $[\xi\xi\xi]$, and $[0\xi 1]$ symmetry directions. The dispersion curves of this divalent element bear a striking resemblance to those of γ-Ce. In particular, the shear moduli c_{44} and $\frac{1}{2}(c_{11}-c_{12})$ differ by approximately a factor of 4 which implies that fcc Yb (like γ-Ce) is very anisotropic regarding the propagation of elastic waves. The frequencies of the $T_1[\xi\xi 0]$ branch for ξ between approximately 0.5 and 0.7 are slightly above the velocity-of-sound line determined from the low-frequency measurements, an anomaly which may be related to the electronic structure of this divalent element. The data were used to evaluate the elastic constants, the phonon density of states, and the lattice specific heat.

I. INTRODUCTION

Of all the rare-earth metals only Yb and Eu have a $4f$ occupation ($4f^{14}$ for Yb and $4f^{7}$ for Eu) such that only two electrons per atom are available for the conduction bands. As a result, the physical properties of these divalent elements are quite different from those of the trivalent rare-earth metals. In fact, the electronic structure and physical properties of these metals bear a striking resemblance to those of the divalent alkaline-earth metals.

One would have expected the electronic structure of these divalent metals (Ca, Sr, Ba, Yb, Eu) to be relatively simple and almost free-electron-like. Below the Fermi level, indeed, this has been substantiated by a large number[1–4] of theoretical calculations of the electronic band structure of these elements. These calculations,[1–4] however, also have demonstrated that the electronic wave functions at the Fermi level contain a significant admixture of d character. Actually, it is generally believed that the position of the d bands relative to the Fermi level, and hence the amount of hybridization, plays a predominant role in determining the physical properties of these elements.

Of these divalent elements, Yb exhibits the most unusual physical properties. It exists[5] in three different crystallographic modifications: bcc, fcc, and hcp. At atmospheric pressure, the high-temperature bcc phase transforms below approximately 935 K to the fcc phase. The fcc phase is stable at room temperature, but upon cooling, it starts transforming[6–9] to the hcp phase at approximately 260 K. Of particular interest are the phase transformations of fcc Yb under relatively moderate pressures. At approximately 40 kbar the fcc phase transforms[10–12] to the bcc phase. Furthermore, resistivity measurements[13,14] suggest that at approximately 13 kbar, fcc Yb undergoes a metal-to-semiconductor transition. Both these transitions have been attributed[1] to the broadening of the d bands with increasing pressure, and hence the increased d hybridization with the s-p bands. Clearly, studies of the lattice dynamics of fcc Yb under pressure could provide important information regarding these phase transformations. The lattice dynamics of fcc Yb, however, has not been studied, even under normal conditions of temperature and pressure, probably because of the difficulty of growing large single crystals of this element. Recently we have obtained a few single crystals of fcc Yb of sufficient size for inelastic neutron scattering experiments. In this paper we report measurements of the dispersion curves of fcc Yb at room temperature and atmospheric pressure.

II. EXPERIMENTAL DETAILS

From a large number of samples of Yb prepared at the Ames Laboratory, we separated several relatively small single crystals of fcc Yb. The largest of these (~ 0.1 cm^3) and a composite crystal (~ 0.2 cm^3) assembled from two other crystals were used to measure the dispersion curves. The measured phonon frequencies obtained using these two single-crystal specimens were found to agree to within experimental precision.

The measurements were performed using a triple-axis spectrometer at the 100-MW High-Flux Isotope Reactor (HFIR) of the Oak Ridge National Laboratory. All data were collected using the constant $\vec{Q}$ (where $\vec{Q}$ 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.

The frequencies of the $T_1[\xi\xi 0]$ branch for ξ between approximately 0.5 and 0.7 were found, for both samples, to be slightly above the values expected from measurements at low frequencies. To verify this point we systematically have studied this branch, using three crystal specimens, the two crystals used for the determination of the dispersion curves, and a third small crystal. These studies have been performed on a different spectrometer operating at a constant incident energy of 3.6 THz (with a pyrolytic graphite filter placed after the monochromator). The monochromator and analyzer were pyrolytic graphite and Be, respectively, both reflecting from the (002) planes. The collimation of the neutron beam before and after the sample was 20′ and 40′ of arc, respectively. The frequencies of the $T_1[\xi\xi 0]$ measured with these three crystals were found to agree to within experimental precision.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The phonon dispersion curves were determined, at room temperature and atmospheric pressure, along the $[00\xi]$, $[\xi\xi 0]$, $[\xi\xi\xi]$, and $[0\xi 1]$ symmetry directions. The measured phonon frequencies are listed in Table I and the dispersion curves are plotted in Fig. 1.

It would have been interesting to compare the measured dispersion curves with those of divalent fcc Sr, since it is generally believed that the latter element has nearly the same electronic structure as fcc Yb. Unfortunately, the dispersion curves of fcc Sr have not yet been measured. Some interesting features of the measured dispersion curves can be revealed, however, by comparing them with those of other fcc metals. The measured dispersion curves of Yb bear a striking resemblance to those[15] of fcc γ-Ce, except for the $T[\xi\xi\xi]$ branch which, in Ce, was found to exhibit anomalous dispersion close to the zone boundary. Actually, the measured phonon frequencies of Yb (except those of the $T[\xi\xi\xi]$ branch close to the zone boundary) agree quite well with those obtained from the γ-Ce frequencies, when the differences in masses, interatomic spacings, and melting temperatures of these elements are taken into account. In particular, notice (Fig. 1) the large difference in the slopes of the $T_1[\xi\xi 0]$ and $T_2[\xi\xi 0]$ branches, which implies that fcc Yb (like γ-Ce) is very anisotropic with regard to the propagation of elastic waves. These strong similarities between the dispersion curves of these two metals are quite surprising since γ-Ce is practically trivalent (at room temperature and atmospheric pressure) and its electronic structure is expected to be quite different from that of Yb.

The following feature of the dispersion curves of fcc Yb should also be mentioned. The frequencies of the $T_1[\xi\xi 0]$ branch for ξ between approximately 0.5 and 0.7 are slightly above the velocity of sound line determined from the low-ξ measurements (positive dispersion). This positive dispersion of the $T_1[\xi\xi 0]$ branch was verified by systematic measurements on all three crystals used in the experiments. A similar but much more pronounced effect

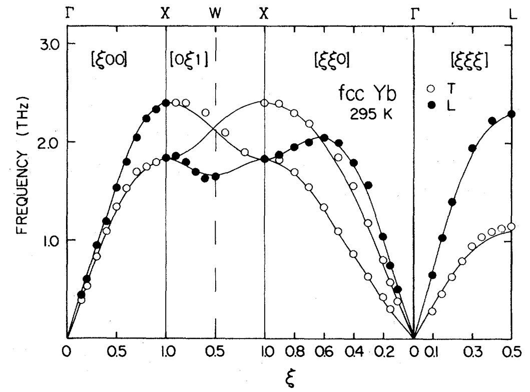

FIG. 1. Experimental dispersion curves of fcc Yb. Solid lines were obtained by fitting the data to a two-nearest-neighbor force-constant model.

TABLE I. Measured phonon frequencies (THz) of fcc Yb.

ξ	ν	ξ	ν	ξ	ν
	$[00\xi]L$		$[00\xi]T$		$[\xi\xi\xi]L$
				0.1	0.65±0.04
0.15	0.44 ±0.04	0.15	0.385±0.02	0.15	1.04±0.05
0.2	0.60 ±0.03	0.2	0.535±0.02	0.2	1.40±0.05
0.3	0.95 ±0.03	0.3	0.835±0.02	0.3	1.95±0.04
0.4	1.20 ±0.04	0.4	1.10 ±0.04	0.4	2.23±0.06
0.5	1.55 ±0.04	0.5	1.35 ±0.04	0.5	2.30±0.04
0.6	1.80 ±0.04	0.6	1.54 ±0.04		
0.7	2.05 ±0.04	0.7	1.70 ±0.06		
0.8	2.24 ±0.12	0.8	1.75 ±0.04		
0.9	2.33 ±0.05	0.9	1.80 ±0.05		
1.0	2.40 ±0.06	1.0	1.85 ±0.05		
	$[\xi\xi\xi]T$		$[0\xi\xi]L$		$[0\xi\xi]T_2$
0.1	0.28 ±0.03	0.1	0.50 ±0.03	0.1	0.38±0.02
0.15	0.45 ±0.03	0.15	0.75 ±0.03	0.15	0.58±0.02
0.2	0.63 ±0.03	0.2	1.05 ±0.03	0.2	0.80±0.03
0.25	0.80 ±0.04	0.3	1.57 ±0.04	0.3	1.18±0.04
0.3	0.95 ±0.05	0.4	1.80 ±0.04	0.4	1.56±0.04
0.35	1.05 ±0.04	0.5	2.00 ±0.04	0.5	1.85±0.04
0.4	1.10 ±0.04	0.6	2.05 ±0.04	0.6	2.05±0.04
0.45	1.14 ±0.04	0.7	2.00 ±0.05	0.7	2.20±0.05
0.5	1.16 ±0.04	0.8	1.95 ±0.05	0.8	2.30±0.04
		0.9	1.88 ±0.06	0.9	2.40±0.06
		1.0	1.85 ±0.04	1.0	2.40±0.05
	$[0\xi\xi]T_1$		$[0\xi 1]\Lambda$		$[0\xi 1]\Pi$
0.15	0.30 ±0.03	0.1	1.86 ±0.04	0.1	2.40±0.06
0.2	0.425±0.02	0.2	1.80 ±0.05	0.2	2.38±0.05
0.3	0.64 ±0.03	0.3	1.70 ±0.07	0.4	2.30±0.05
0.4	0.86 ±0.03	0.4	1.63 ±0.06	0.6	2.10±0.03
0.5	1.10 ±0.04	0.5	1.65 ±0.05	0.8	1.90±0.07
0.6	1.35 ±0.03				
0.7	1.55 ±0.04				
0.8	1.70 ±0.05				
0.9	1.83 ±0.05				
1.0	1.85 ±0.07				

has been observed[16] in Au by Lynn, Smith, and Nicklow. More interesting, however, is the fact that a similar effect has been observed[17] recently in fcc Ca. In the case of Ca the anomalous dispersion of the $T_1[\xi\xi 0]$ branch has been related to the electronic structure through band-theoretical calculations[17] of the generalized susceptibility of this metal. Since the electronic structure of Yb is quite similar to that of Ca (although the d bands of Ca are slightly higher than those of Yb) it is natural to assume that electronic effects are also responsible for the anomalous dispersion of the $T_1[\xi\xi 0]$ branch of fcc Yb.

To obtain information about the elastic constants of fcc Yb (which have not yet been measured) and to evaluate the lattice specific heat, we analyzed the data with the use of conventional Born—von Kármán force-constant models. Various models with up to eighth-nearest-neighbor atomic force constants were used in the analysis of the experimental results. We have found (see Fig. 1) that an adequate fit to the experimental data can be obtained by including only second-nearest-neighbor atomic forces; the force constants obtained by fitting the data to the two-nearest-neighbor model, and the elastic constants evaluated using this model, are listed in Table II. Notice the small difference between c_{11} and c_{44} which reflects, as we have men-

TABLE II. Atomic force constants obtained by fitting the data to a two-nearest-neighbor model. The notation is that of Ref. 25.

Atomic force constants (dynes/cm)		Elastic constants (10^{12} dynes/cm^2)	
1*XX*	4167±55	c_{11}	0.1862±0.0083
1*ZZ*	650±81		
1*XY*	3849±73	c_{44}	0.1772±0.0055
2*XX*	−1615±101		
2*YY*	20±58	c_{12}	0.1036±0.0077

tioned already, the strong anisotropy in the propagation of elastic waves in fcc Yb; in fact, the shear moduli c_{44} and $\frac{1}{2}(c_{11}-c_{12})$ differ by approximately a factor of 4 (see Table II). No data on the elastic constants of fcc Yb are available to be compared with the results of the present analysis. A comparison with bulk elastic moduli obtained by measurements on polycrystalline samples is not very meaningful for two reasons. Firstly, polycrystalline elastic moduli cannot be accurately evaluated from single-crystal elastic constants unless the crystal is nearly isotropic,[18] a condition certainly not fulfilled for fcc Yb. Secondly, since the bulk moduli were measured between 4.2 and 230 K, the polycrystalline samples may have contained an appreciable amount of the hcp phase. Nevertheless, the polycrystalline elastic moduli, evaluated using the elastic constants listed in Table II, were found to be consistent with the experimentally[19] determined values.

With the use of the force constants listed in Table II, we evaluated the phonon density of states $g(\nu)$ (see Fig. 2) by the method[20] of Gilat and Raubenheimer. The lattice specific heat as a function of temperature was calculated, using the phonon density of states plotted in Fig. 2, and the results expressed in terms of an effective Debye temperature Θ_D are plotted in Fig. 3. Since fcc Yb transforms below room temperature to the hcp phase, no data concerning the temperature dependence of the specific heat are available for comparison with the results of the present analysis. It should be pointed out, however, that the 0-K value of Θ_D ($\sim$110 K) obtained in the present analysis is in good agreement with the values obtained by ultrasonic[19] and specific-heat measurements[21–23] for the low-temperature hcp phase.

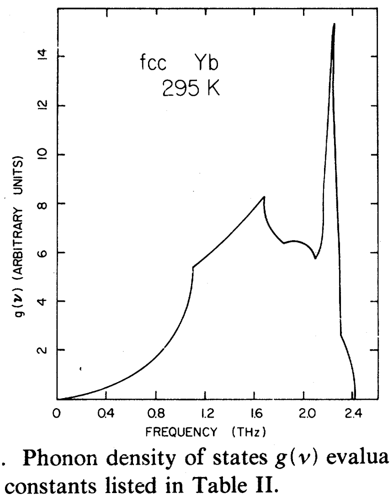

FIG. 2. Phonon density of states $g(\nu)$ evaluated using the force constants listed in Table II.

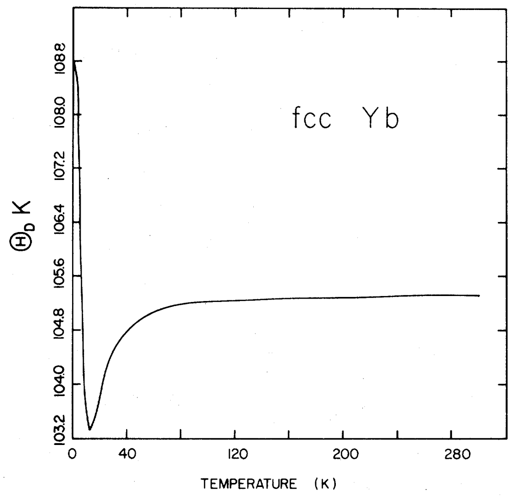

FIG. 3. Temperature dependence of the effective Debye temperature of fcc Yb, evaluated using the phonon density of states plotted in Fig. 2.

Although fcc Yb transforms to the hcp phase below room temperature, some comments should be made regarding the low-temperature behavior of the Debye temperature (Fig. 3). It is well known[24] that the calculated specific heat, especially when expressed in terms of Θ_D, depends somewhat on the details of the particular force-constant model used in deriving the phonon density of states. For fcc Yb these effects can be quite important, since Θ_D varies only by approximately 5% between 0 and 300 K (see Fig. 3). The temperature variation of Θ_D obtained using, for instance, a fourth-nearest-neighbor force-constant model differs from that plotted in Fig. 3, and it is actually quite similar to the temperature dependence obtained by Lynn *et al.*[16] for Au. It is interesting to point out that Lynn *et al.*[16] attributed the rather unusual temperature dependence of Θ_D in Au to the positive dispersion of the $T_1[\xi\xi0]$ branch. In fcc Yb, however, the deviations from normal dispersion of the $T_1[\xi\xi0]$ branch and their effects on the temperature dependence of Θ_D

are so small that, within the precision of the present experiments, no definitive statement can be made.

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