

Phonon dispersion curves of bcc Ba

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Large single crystals of bcc Ba were grown and were used to study the lattice dynamics of this divalent metal by inelastic neutron scattering. The phonon dispersion curves were measured, at room temperature, along the $[\xi 00]$, $[\xi \xi 0]$, and $[\xi \xi \xi]$ symmetry directions. Along the $[\xi 00]$ symmetry direction, the frequencies of the longitudinal dispersion curve were found to be lower than those of the transverse branch, a surprising result in view of the relatively simple electronic structure of this metal. This anomalous feature of the dispersion curves was attributed to the hybridization of the free-electron-like states with the d bands, which in this metal are only slightly above the Fermi level. To provide support for this interpretation, the frequencies of the longitudinal and transverse branches along the $[\xi 00]$ direction were evaluated at the middle of the zone ($\xi = \frac{1}{2}$) with use of first-principles frozen-phonon techniques. The results of these calculations are in good agreement with the experimental data and, in addition, clearly demonstrate that the observed anomaly is sensitive to the position of the d bands relative to the Fermi level. The data were used to evaluate the elastic constants, the phonon density of states, and the lattice specific heat of Ba.

I. INTRODUCTION

The alkaline-earth metals Ca, Sr, and Ba are divalent, and exhibit quite similar physical properties. The general features of the electronic structure of these metals are intermediate between those of the simple and transition metals. In fact, band theoretical calculations¹⁻⁴ have established that, below the Fermi level E_F , the electronic bands are practically free-electron-like. The electronic wave functions at E_F contain, however, a substantial admixture of d character arising from hybridization with the d bands, which in these metals are only slightly above the Fermi level. As a result, the structure and physical properties of these metals were found⁴ to be quite sensitive to the d -occupation number.

Investigations from first principles of the lattice dynamics of these metals, in particular of how the hybridization of the free-electron-like states with the d states affects the dispersion curves, are not presently available. Because of the simplicity of their electronic structure it is reasonable to assume, however, that the general features of their dispersion curves are quite similar to those of simple metals. This motivated several studies of their phonon dispersion curves within the framework of the pseudopotential theory of metals. Clearly, comparison of these calculations with detailed measurements could provide information about the effect of the occupation of the d bands on the dispersion curves. Until recently, however, such detailed experimental data were not available. This was due to the difficulty of growing single crystals of sufficient size for a systematic study of the dispersion curves and elastic constants. Quite recently, we were able to grow large *single* crystals of Ca and Ba, which were used to study the phonon dispersion curves of these metals by inelastic neutron scattering. The experimental results for fcc Ca were reported in a previous communica-

tion.⁵ In this paper we present the results obtained in our study of the dispersion curves of Ba.

II. EXPERIMENTAL DETAILS

Polycrystalline samples of high purity Ba were encapsulated, under He, in thin-wall tantalum crucibles. The major impurity in Ba (as well as in Ca) is hydrogen. To reduce the amount of hydrogen, the encapsulated samples, kept at 950°C, were pumped for several weeks in a high vacuum system (at this temperature hydrogen diffuses readily through tantalum). From the rate of evolution of the hydrogen in the system (and the initial hydrogen concentration) it was estimated that the samples contained approximately 0.3 at. % of hydrogen or less.

The crystals were grown in a high vacuum furnace positioned on the sample goniometer of a conventional double-axis diffractometer. With this experimental arrangement, various techniques for growing the crystals can be attempted, and their success can be immediately assessed by standard neutron-diffraction techniques.

Large single crystals of Ba were grown by cooling slowly below the melting point of approximately 725°C. At high temperatures the measured full width at half maximum (FWHM) of the rocking curves was approximately 15 min of arc, and remained constant between the melting point and approximately 350°C. Below 350°C, quite independently of the cooling rate, we observed a significant increase in the FWHM of the rocking curves. This broadening of the mosaic spread may be due either to strains arising from the difference in the expansion coefficients⁶ of the Ta crucible and Ba, or the precipitation of a hydride phase formed with the hydrogen impurities. The highest quality crystals that we were able to obtain had, at room temperature, a mosaic spread of approximately 1°. Three of these crystals were used in the experiments.

Most measurements were performed using triple-axis spectrometers at the High Flux Isotope Reactor (HFIR) and the Oak Ridge Research Reactor (ORR) of the Oak Ridge National Laboratory. In addition, some data were taken using a triple-axis spectrometer at the High Flux Beam Reactor (HFBR) of the Brookhaven National Laboratory. All data were collected using the constant- Q method (where Q is the neutron scattering vector), and constant scattered (or incident) neutron energy of 3.3 or 3.6 THz. A pyrolytic graphite filter was placed in the scattered (or incident) beam to attenuate higher-order contaminations. Pyrolytic graphite or beryllium was used as monochromator and pyrolytic graphite as analyzer; both monochromator and analyzer were set to reflect from the (002) planes. The frequencies of a selected number of phonons were measured on all three crystals and were found to agree within experimental precision.

Along the $[\xi 00]$ direction the frequencies of the longitudinal branch, for ξ between approximately 0.2 and 0.8, were found to be lower than those of the transverse branch. Some typical neutron groups obtained in this direction are shown in Figs. 1 and 2. This unusual aspect of the dispersion curves was verified by measuring the $[\xi 00]$ branches on each of the three crystals used in the experiments. For each of the crystals, these branches were obtained by measurements in the $(1\bar{1}0)$ as well as the (100) scattering plane. The frequencies of both branches in the

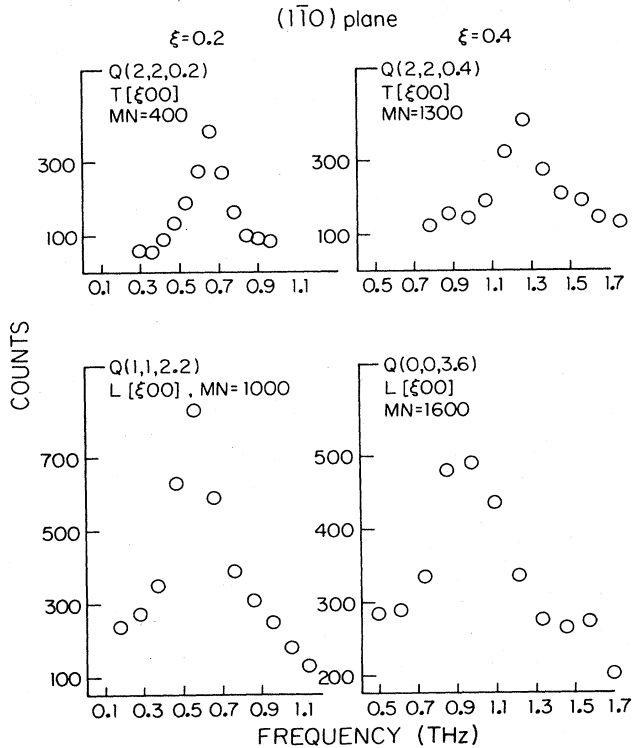


FIG. 1. Typical neutron groups obtained by scans along $[\xi 00]$. The measurements were performed in the $(1\bar{1}0)$ scattering plane. MN=1000 corresponds to a counting time per point of approximately 14 min.

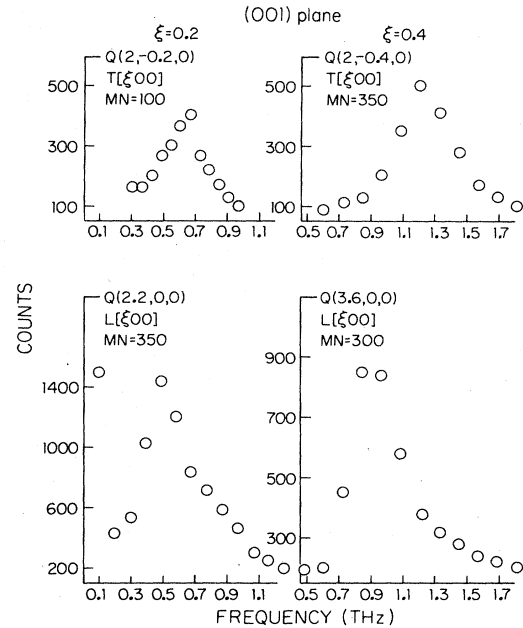


FIG. 2. Typical neutron groups obtained by scans along $[\xi 00]$. The measurements were performed in the (100) scattering plane. MN=1000 corresponds to a counting time of approximately 30 min.

region of interest ($0.2 \lesssim \xi \lesssim 0.8$) were also checked by repeating the measurements with various instrumental resolutions and experimental configurations.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

The phonon dispersion curves were measured, at room temperature, along the $[\xi 00]$, $[\xi \xi 0]$, and $[\xi \xi \xi]$ symmetry directions. The measured phonon frequencies are listed in Table I and the room-temperature dispersion curves are plotted in Fig. 3. The general features of the dispersion

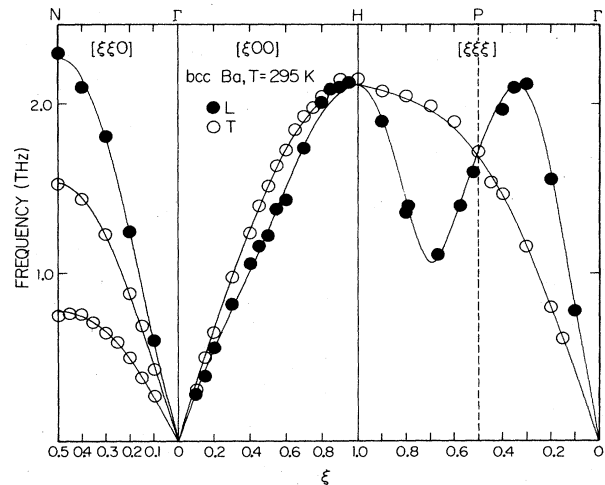


FIG. 3. Experimental dispersion curves of bcc Ba. The solid lines were obtained by fitting the data to a seven-nearest-neighbor force-constant model.

curves are in reasonable agreement with those obtained⁶ by Buchenau *et al.* from Born–von Kármán force constants, which were determined from the neutron time-of-flight spectrum of a polycrystalline sample. In these experiments,⁷ however, the longitudinal and transverse branches along the $[\xi 00]$ direction were found to be degenerate.

The frequencies of the longitudinal and transverse branches along the $[\xi 00]$ direction were determined, on each of the three crystals, using a variety of experimental configurations (see Sec. II). The frequencies obtained, for each mode, were found to agree within the precision of the measurements, and their average was adopted; the results are shown in Fig. 4. It can be seen (Fig. 4) that for ξ between approximately 0.2 and 0.8 the frequencies of the longitudinal branch are lower than those of the transverse. Measurements at 600°C showed that this unusual feature of the dispersion curves remains practically unchanged at high temperatures. Measurements⁸ at 660°C on the high-temperature bcc phase of Sr (whose d bands are higher relative to E_F than those of Ba) showed, on the other hand, that in this metal the frequencies of the $L[\xi 00]$ are slightly above those of the transverse branch. These experimental observations suggest that the anomalous behavior of the dispersion curves along the $[\xi 00]$ direction of Ba may be due to the occupation of the d states.

Several calculations^{9–11} of the dispersion curves of Ba have been performed within the framework of the pseudopotential theory of metals. The phonon frequencies calculated by Animalu⁹ and Sharma,¹⁰ using local pseudopotentials, are substantially higher than the measured values (at the point N by almost a factor of 2). Furthermore, in both of these studies^{9,10} the frequencies of the $L[\xi 00]$

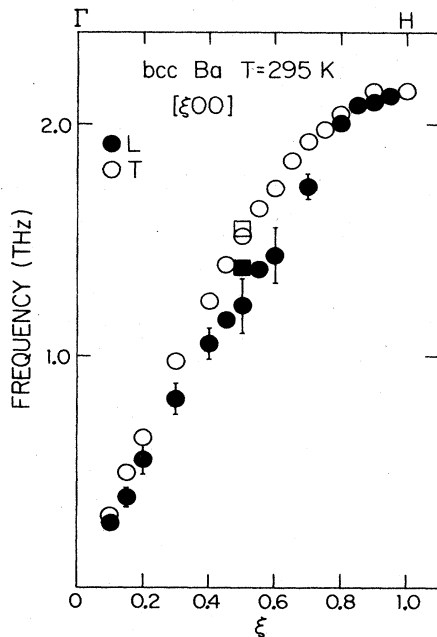


FIG. 4. Phonon dispersion curves of bcc Ba along the $[\xi 00]$ symmetry direction. The square symbols at $\xi = \frac{1}{2}$ are the frequencies obtained by first-principles frozen-phonon calculations (see text).

TABLE I. Measured phonon frequencies (THz) of bcc Ba.

ξ		ν
	L $[\xi 00]$	
0.1		0.28 ± 0.03
0.15		0.39 ± 0.05
0.2		0.56 ± 0.07
0.3		0.82 ± 0.07
0.4		1.05 ± 0.07
0.45		1.16 ± 0.05
0.5		1.22 ± 0.12
0.55		1.38 ± 0.03
0.6		1.44 ± 0.12
0.7		1.74 ± 0.05
0.8		2.01 ± 0.05
0.85		2.09 ± 0.05
0.9		2.10 ± 0.04
0.95		2.13 ± 0.05
	T $[\xi 00]$	
0.1		0.31 ± 0.02
0.15		0.50 ± 0.03
0.2		0.65 ± 0.02
0.3		0.98 ± 0.04
0.4		1.24 ± 0.03
0.45		1.40 ± 0.03
0.5		1.52 ± 0.04
0.55		1.64 ± 0.05
0.6		1.73 ± 0.03
0.65		1.85 ± 0.04
0.7		1.93 ± 0.05
0.75		1.98 ± 0.05
0.8		2.05 ± 0.05
0.9		2.15 ± 0.05
1.0		2.15 ± 0.07
	T ₁ $[\xi\xi 0]$	
0.1		0.27 ± 0.02
0.15		0.38 ± 0.02
0.2		0.5 ± 0.03
0.25		0.59 ± 0.03
0.3		0.65 ± 0.03
0.35		0.71 ± 0.03
0.4		0.76 ± 0.04
0.45		0.76 ± 0.04
0.5		0.75 ± 0.04
	T ₂ $[\xi\xi 0]$	
0.1		0.47 ± 0.02
0.15		0.69 ± 0.02
0.2		0.88 ± 0.03
0.3		1.23 ± 0.03
0.4		1.44 ± 0.03
0.5		1.53 ± 0.04
	L $[\xi\xi 0]$	
0.1		0.6 ± 0.04
0.2		1.25 ± 0.03
0.3		1.81 ± 0.04
0.4		2.10 ± 0.05
0.5		2.30 ± 0.07
	T $[\xi\xi\xi]$	
0.15		0.615 ± 0.02
0.2		0.80 ± 0.04
0.3		1.16 ± 0.03
0.4		1.47 ± 0.03
0.45		1.54 ± 0.03
0.5		1.72 ± 0.05

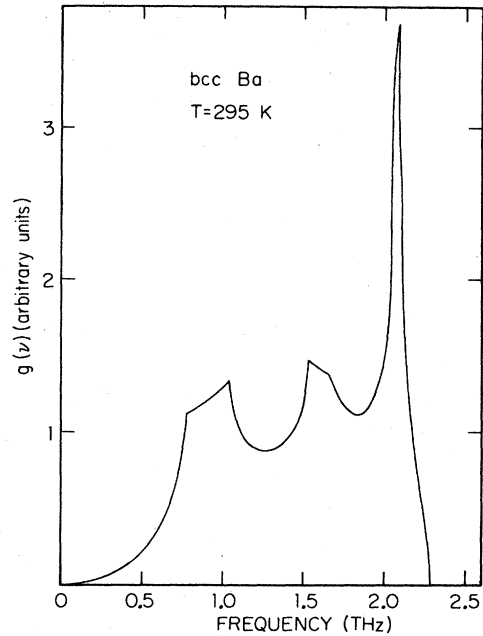
TABLE I. (Continued).

ξ	ν
0.6	1.9 ± 0.04
0.7	1.99 ± 0.03
0.8	2.05 ± 0.10
0.9	2.08 ± 0.08
$L[\xi\xi\xi]$	
0.1	0.78 ± 0.04
0.2	1.56 ± 0.05
0.3	2.12 ± 0.08
0.35	2.10 ± 0.09
0.4	1.97 ± 0.06
0.5	1.72 ± 0.03
0.52	1.6 ± 0.04
0.575	1.4 ± 0.04
0.667	1.11 ± 0.04
0.79	1.4 ± 0.05
0.8	1.36 ± 0.05
0.9	1.9 ± 0.06

dispersion curve were found to be higher than those of the transverse branch. More recently, Moriarty¹¹ calculated the zone boundary frequencies along some high-symmetry directions, using a generalized pseudopotential approach which incorporates the effect of hybridization of the free-electron-like states with the d states. The phonon frequencies calculated by Moriarty¹¹ are in relatively better agreement with the experiment than those obtained by Animalu⁹ and Sharma,¹⁰ the calculated frequencies are, however, still higher than the experimental values (with a maximum deviation of approximately 40% at the N point). We conclude that pseudopotential calculations, which were so successful for the simple metals, cannot provide, at the present time, an adequate description of the lattice dynamics of Ba.

TABLE II. Atomic force constants and elastic constants obtained by fitting the data to a seventh-nearest-neighbor model.

Atomic force constants (dyn/cm)		Elastic constants (10^{12} dyn/cm ²)	
1XX	2387.3±41.0	C_{11}	0.081 18
1XY	2623.1±74.8		
2XX	588.5±145.7	C_{44}	0.101 08
2YY	799.3±69.5		
3XX	-332.5±37.6	$\frac{1}{2}(C_{11}-C_{12})$	0.042 47
3ZZ	384.6±76.4		
3XY	0.1±70.6		
4XX	176.0±63.4		
4YY	22.3±37.1		
4YZ	-47.0±43.2		
4XZ	26.1±37.6		
5XX	-186.2±35.8		
5XY	-112.5±61.4		
6XX	133.1±131.1		
6YY	13.3±66.9		
7XX	-57.4±24.5		
7ZZ	13.2±35.5		
7YZ	-55.2±31.3		
7XY	-55.0±31.0		

FIG. 5. Room-temperature phonon density of states $g(\nu)$ of bcc Ba, evaluated using the force constants listed in Table II.

To assess whether the anomalous features of the dispersion curves of Ba are due to the occupation of the d bands, we carried out first-principles frozen-phonon calculations¹² for both modes with wave vector $\mathbf{q}=(0,0,\frac{1}{2})$. In these calculations we used norm-conserving pseudopotentials¹³ determined from atomic calculations. In a frozen-phonon calculation, the lattice is subjected to a static distortion corresponding to a particular mode and the total energy of the crystal as a function of displacement is obtained from first-principles self-consistent band-structure calculations in the local-density-functional formalism.^{14,15} The phonon frequency of the mode is then determined from the curvature of the energy-displacement curve. Our calculated values for the bulk properties of Ba (cohesive energy, lattice constant, and bulk modulus) were found to be in good agreement with those determined ex-

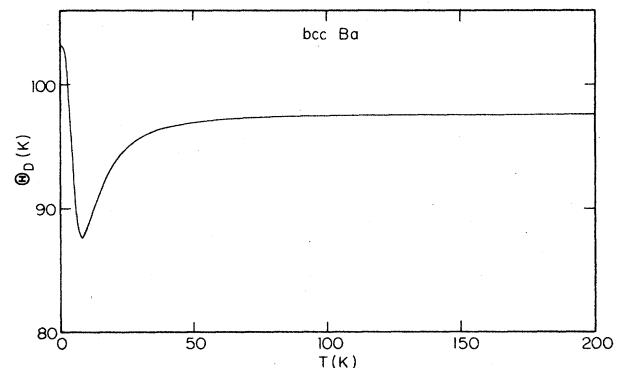


FIG. 6. Temperature dependence of the effective Debye temperature of bcc Ba, evaluated using the room-temperature phonon density of states plotted in Fig. 5.

perimentally. For the longitudinal and transverse modes with $\mathbf{q}=(0,0,\frac{1}{2})$ we obtained frequencies of 1.38 and 1.55 THz, respectively. These values are in quite good agreement with the experimental observations (Fig. 4). To assess the effects of the d electrons, the calculations were repeated with the d bands removed from the vicinity of the Fermi level; this was realized by adjusting the angular-momentum dependent pseudopotential so that it is more repulsive for the d -wave functions. With these conditions we obtained frequencies of 2.5 and 2.0 THz for the longitudinal and transverse modes, respectively. Therefore, by decreasing the occupation of the d bands both frequencies increase and the normal relative ordering of the branches is restored. In addition, the calculations show that the relative softening of the $L[\xi 00]$ dispersion curve in Ba is related to the coupling of this branch to the s - d charge fluctuations. A complete account of these calculations will be presented elsewhere.

To evaluate the elastic constants and lattice specific heat we analyzed the data by conventional Born—von Kármán force-constant models. It can be seen (Fig. 1) that, for this purpose, a seven-nearest-neighbor force-constant model is adequate. The force and elastic constants obtained by fitting the data to this model are listed in Table II. No single-crystal measurements of the elastic constants of bcc Ba are presently available for comparison

with the results of the present analysis. The values for C_{11} and C_{44} obtained in the present analysis are, however, in reasonable agreement with those obtained by measurements⁷ on polycrystalline samples; our value for $\frac{1}{2}(C_{11}-C_{12})$, on the other hand, is almost two times larger than that reported by Buchenau *et al.*⁷

Using the force constants listed in Table II, we evaluated the phonon density of states $g(\nu)$ (Fig. 5) by the method of Gilat and Raubenheimer.¹⁶ The lattice specific heat, expressed in terms of an effective Debye temperature $\Theta_D(T)$, was evaluated (Fig. 6) by assuming that the phonon density of states is independent of temperature. The 0-K Debye temperature (103.1) obtained in the present analysis is in good agreement with the value (110.5) obtained from low-temperature specific-heat measurements.¹⁷

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