PHYSICAL REVIEW B VOLUME 30, NUMBER 6 15 SEPTEMBER 1984

Brief Reports

Lattice dynamics of strontium and barium

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(Received 13 March 1984)

The phonon dispersion curves of fcc Sr and bcc Ba at room temperature and at 100 K have been determined. Neutron time-of-flight spectra of polycrystalline samples over a wide range of Q and ω have been measured. The spectra were analyzed in terms of Born–von Kármán models. In addition, the elastic constants were obtained from the low-frequency part of the spectra.

I. INTRODUCTION

The alkaline-earth metals exhibit a number of interesting properties. The most striking one is the variety of crystal structures. At room temperature and normal pressure the stable structure is hcp for Be and Mg, fcc for Ca and Sr, and bcc for Ba. In both Ca and Sr transitions to bcc structures have been observed at higher temperatures.[1] Phase transitions can also be induced by pressure. At the same time these elements are electronically fairly simple, *s-p* bonded, and therefore the pseudopotential theory should be applicable. For the heavier elements of this group, Ca, Sr, and Ba, the situation is somewhat complicated by the presence of an empty *d* band just above the Fermi level. Therefore, one can study the effect of weak hybridizations of the *s-p* orbital and *d* band perturbatively on these elements. For quantitative tests of theoretical calculations, the lattice dynamics is useful since it contains detailed information and can be calculated fairly easily by pseudopotential methods. These methods with various grades of sophistication have been employed extensively.[2] Until recently, however, only the lattice dynamics of the light elements Be and Mg could be measured.

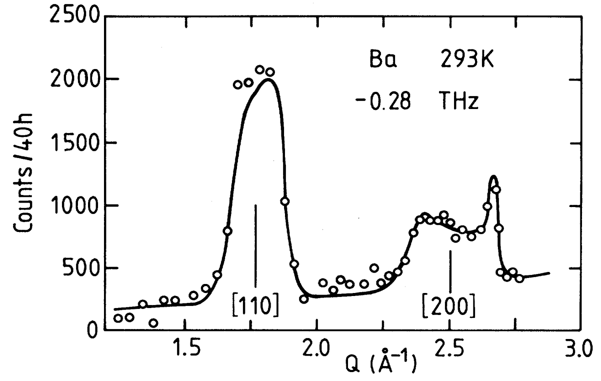

FIG. 1. Inelastic intensities obtained from polycrystalline Ba between 0.24 and 0.32 THz (energy gain of the neutrons) at 293 K.

For the other elements the standard method of triple-axis neutron spectroscopy was hindered by the difficulty of growing sufficiently large single crystals. Only recently Stassis *et al.*[3] succeeded in measuring the dispersion curves of Ca by this method. In this Brief Report for the first time experimentally determined phonon dispersion curves of fcc Sr and bcc Ba are presented. We employed a method recently developed by us using inelastic neutron scattering from polycrystalline samples.[4] We parametrize the dynamical matrix in terms of Born–von Kármán models. The parameters of these models are determined by a fit to the inelastic time-of-flight spectra over the entire ω range and in a Q range covering the first six to seven inequivalent Brillouin zones. The elastic constants are obtained by a separate fit to the region of low-energy transfer near the Debye-Scherrer rings.[5] We employed these methods earlier for Ca (Ref. 6) where our results agreed within 6% with the later

TABLE I. Elastic constants of Sr and Ba.

Substance	Temperature (K)	$c'=\frac{1}{2}(c_{11}-c_{12})$	c_{44} (GPa)	c_{11} (neutrons)	c_{11} (calc)
Sr	100	2.7 ± 0.2	12.1 ± 0.9	$\cdots$	15.6
	293	2.48 ± 0.1	9.9 ± 0.3	17 ± 8	15.3
Ba	100	2.7 ± 0.2	11.8 ± 1	$\cdots$	13.0
	293	2.29 ± 0.1	9.5 ± 0.5	10 ± 3	12.6

TABLE II. Born–von Kármán constants of fcc Sr.

	Force constants	(N/m)
Neighbor and indices	100 K	293 K
1*xx*	3.68	3.74
1*zz*	0.34	0.45
1*xy*	3.34	3.29
2*xx*	−1.14	−0.89
2*yy*	0.01	−0.17
3*xx*	−0.03	−0.10
3*yy*	−0.03	−0.06
3*yz*	0.00	−0.01
3*xz*	0.00	−0.02

TABLE III. Born–von Kármán constants of bcc Ba.

	Force constants	(N/m)
Neighbor and indices	100 K	293 K
1*xx*	2.70	2.43
1*xy*	2.93	2.81
2*xx*	1.53	2.31
2*xy*	0.73	0.92
3*xx*	−0.24	−0.40
3*zz*	0.01	−0.09
3*xy*	−0.25	−0.31

results of Stassis *et al.*[3] We expect a comparable accuracy of our results on the similar metals Sr and Ba reported here. Since our method is not restricted to the phonons in the main crystallographic symmetry directions as triple-axis measurements often are, we expect equal accuracies for symmetry and off-symmetry phonons.

II. EXPERIMENTAL DETAILS

It is well known that commercially available alkaline-earth metals strontium and barium can contain considerable amounts of nonmetallic impurities, especially hydrogen. Therefore we decided to purify these metals by ultrahigh vacuum distillation. More experimental details are given elsewhere.[7]

Starting materials for the distillation were alkaline-earth metals produced by Koch-Light Laboratories, England (strontium lumps, purity with respect to metallic impurities, ⩾99%; barium rods, 99%). These metals were distilled in a molybdenum crucible with a column of molybdenum foil at $T=760\,^{\circ}\mathrm{C}$ for strontium and $T=880\,^{\circ}\mathrm{C}$ for barium. The applied vacuum was in the order of 10^{-8} mbar at the end of the distillation at hot conditions. Without contamination by air and moisture the distillation tube was transferred into an argon box where the distilled metals were cut from the Mo foil. For samples of ~70 g strontium or ~90 g barium this procedure lasts several hours.

Since Sr and Ba are highly reactive metals, care had to be taken to avoid contaminations. The samples were sealed into the thin-walled aluminum containers in an argon box. Nevertheless a small hydrogen contamination of the order of 1 at.% (~0.01 wt.%) could not be avoided. In the Sr case the hydrogen does not enter the lattice but forms $\mathrm{SrH_2}$ at the surface.[8] Therefore the phonons should not be influenced markedly. In the Ba case where the hydrogen enters the bulk[8] we repeated the room-temperature measurements with a second sample containing less than 0.2 at.% of hydrogen. The determined phonon frequencies agreed within 3% with the previous ones. Therefore we did not repeat the low-temperature measurements.

The experiment was done on the time-of-flight spectrometer SV5 at the cold source of the DIDO reactor at Jülich (wave vector of incoming neutrons 1.314 Å^{-1}, range of scattering angles 20°–160°). During all measurements, the samples were rotated slowly around an axis perpendicular to the scattering plane in order to ensure a good orientational average.

III. RESULTS

The elastic constants were fitted to the low-frequency spectra near Debye-Scherrer reflections both in energy gain and energy loss of the neutrons. Figure 1 shows the data and the fit results for barium at 293 K in the energy-gain region between 0.24 and 0.32 THz. The resulting elastic

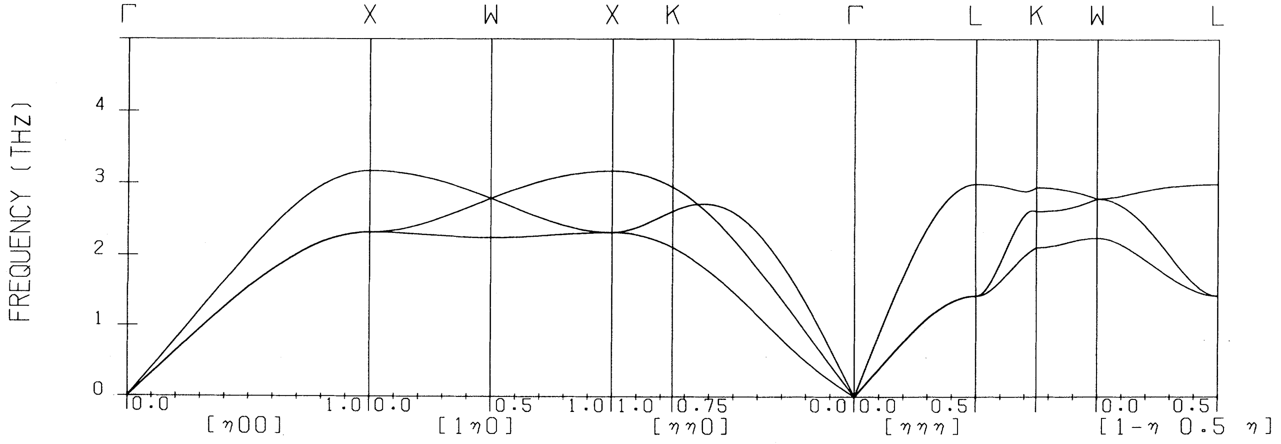

FIG. 2. Phonon dispersion curves of Sr at 293 K. Third neighbor axially symmetric Born–von Kármán fit to polycrystalline neutron time-of-flight spectra.

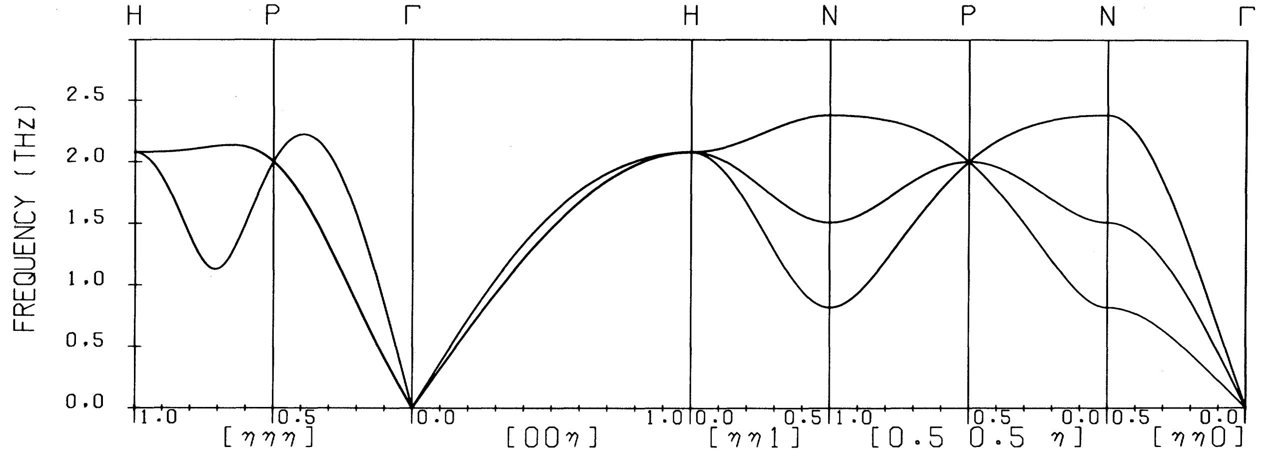

FIG. 3. Phonon dispersion curves of Ba at 293 K. Third neighbor axially symmetric Born–von Kármán fit to polycrystalline neutron time-of-flight spectra.

constants for both substances at 100 and 293 K are compiled in Table I. Note that c_{11} is very poorly determined. Therefore we chose to determine c_{11} separately from the known bulk modulus[9,10] and our well-determined values of $c' = \frac{1}{2}(c_{11} - c_{12})$ according to the formula $B = c_{11} - \frac{4}{3}c'$ (B is the bulk modulus). These values are shown in Table I under the entry c_{11}(calc).

For the determination of the phonon dispersion the measured data were corrected for multiple scattering and for multiphonon contributions as described in Ref. 4. A variety of Born–von Kármán models was fitted to the experimental data. We found axially symmetric models to the third neighbors sufficient. Inclusion of further neighbors did not improve the fit markedly. The optimal Born–von Kármán parameters for both temperatures of 100 and 239 K are given in Tables II and III for Sr and Ba, respectively. The elastic constants of Table I were used as constraints in the parameter fit. A fit of the Born–von Kármán parameters without those constraints resulted in deviations from the elastic constants of Table I of less than 10%. The only exception was a 25% higher value of c_{11} in the case of Sr at 100 K. The nominal error of the Born–von Kármán constants given by the fitting routine is of the order of 1% of the first-neighbor values. However, the error in the phonon frequencies themselves is estimated to be somewhat larger (about 2–3% on the average) due to systematic errors and shortcomings of the employed model.

The dispersion curves in the main crystallographic directions for both metals at 293 K are shown in Figs. 2 and 3, the corresponding frequency spectra at 100 and 293 K are shown in Figs. 4 and 5. The phonon spectrum at 100 K is only slightly harder than at room temperature. We could not identify any anomalous frequency changes with temperature.

The dispersion curves of Sr are similar to the ones observed in Ca (Ref. 3) and show the same anomalous positive dispersion of the (110) T_1 branch. The phonons are generally softer than predicted by simple pseudopotential theories. According to Moriarty[11] this is due to the neglect of electronic d-state hybridization in these theories. Including these effects his theoretical results agree within about 15% with our experimental ones. The dispersion curves of bcc Ba show the same degeneracy of the longitudinal and transversal (100) branches as is observed in the alkali metals. Whether the two branches cross as in Li could not be established with certainty.

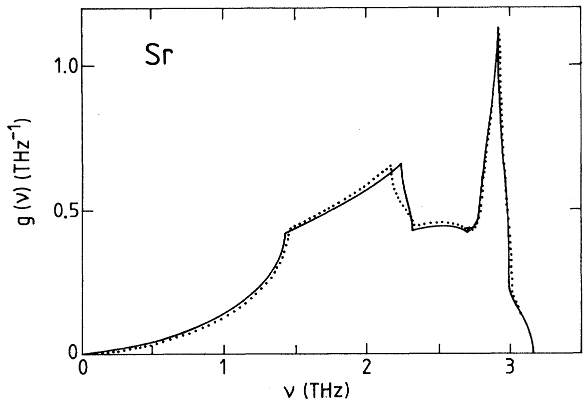

FIG. 4. Phonon spectrum of Sr calculated with the Born–von Kármán parameters of Table II (continuous line $t = 293$ K, dotted line $T = 100$ K).

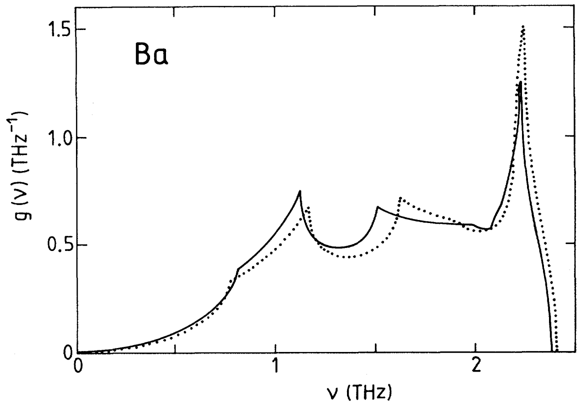

FIG. 5. Phonon spectrum of Ba calculated with the Born–von Kármán parameters of Table III (continuous line $T = 293$ K, dotted line $T = 100$ K).

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