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Lattice dynamics of mixed-valent SmS

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Neutron scattering techniques have been used to measure the phonon dispersion curves for SmS in both the semiconducting and the metallic mixed-valent state. Large softening of the longitudinal acoustic phonon branches was found in the mixed-valent state, particularly for the [111] direction. It is apparent there is a strong coupling between the valence fluctuations and the phonons in the mixed-valent phase of SmS.

Since it was discovered by Jayaraman *et al.*[1] that SmS undergoes a discontinuous semiconductor-to-metal transition at about 0.6 GPa, there has been a lot of interest in the nature of the collapsed phase. In the semiconducting phase that exists at standard pressures Sm appears to have a 2+ valence; however, the lattice constant of the collapsed phase suggests a valence state that is intermediate between 2+ and 3+. Mössbauer isomer shift measurements show that the collapsed phase exists in a homogeneous mixed-valent state with a Sm valence that is about 70% 3+ and 30% 2+.[2,3] Since there is such a large change in the lattice constant as a function of valence state, one might expect that the lattice dynamics of SmS in the collapsed state might have phonon anomalies that result from a coupling of the valence fluctuations to the phonons.

Unfortunately, it is difficult to measure the phonon dispersion curves in SmS in the collapsed phase, since a crystal isotopically enriched in ^{154}Sm must be placed in a pressure cell and taken through the first-order transition in which the crystal volume changes by about 15%. An easier experiment is to alloy SmS with YS, which produces a similar collapse to a mixed-valent state, and extensive phonon measurements have been made on $Sm_{0.75}Y_{0.25}S$ which changes valence with temperature.[4–6] Large phonon anomalies were found in this material which could be attributed to a coupling between phonons and valence fluctuations. A number of theoretical models have been made which give good agreement with the phonon anomalies in $Sm_{0.75}Y_{0.25}S$.[7–12] These theoretical models are based either on a microscopic picture for the $4f$ electron-phonon interaction or on a more phenomenological approach which involves deformabilities of the NaCl lattice.

Despite the successful observation of mixed-valent effects on the lattice dynamics of the alloy $Sm_{0.75}Y_{0.25}S$, it is important to make measurements on pure SmS. First of all, it is not clear what effect the Y has on the phonon anomalies. It is unlikely that alloy effects would change the dispersion curves greatly, since the YS local mode is between the acoustic- and optical-phonon branches and this would not be expected to interfere much with these branches. Nevertheless, the Y breaks the symmetry of the lattice, and it is not clear how this affects the valence fluctuations. A second advantage of SmS is that we know that it exists in only one valence state at normal pressure so that the mixed-valent state can be compared directly with a state that we know is not mixed valent. The valence state in the alloy with Y could be changed with temperature, but the material was intermediate valent at all temperatures.

A cylindrical crystal of SmS enriched in ^{154}Sm to avoid neutron absorption was grown to fit into a pressure cell made of beryllium copper. The crystal was about 0.5 cm in diameter by 2 cm long. The pressure cell was a clamp device and a fluorocarbon was used to transmit the pressure to the SmS crystal. The pressure cell was used earlier to measure the magnetic form factor of SmS and a description of the cell can be found in Ref. 13. The pressure cell was mounted on a triple-axis spectrometer at the High Flux Isotope Reactor at Oak Ridge National Laboratory. Pyrolytic graphite was used as a monochromator, filter, and analyzer. All measurements were taken at room temperature. Phonon measurements were made at zero pressure and dispersion curves established for the semiconducting black phase. Dispersion curves had previously been established for SmS in this phase by Birgeneau and Shaprio[14] and good agreement was obtained between the two sets of results. The measured lattice constant at zero pres-

sure was 5.97 Å.

The pressure cell was removed from the spectrometer and force applied to the crystal to produce a pressure of about 0.2 GPa. The cell was then replaced on the spectrometer and measurements were resumed. The lattice constant did not change greatly (about 5.96 Å), and the crystal still had a fairly high degree of perfection (a mosaic spread of 0.5°). LA phonons were measured for the [111] direction since these phonons were greatly affected by intermediate-valence effects in $Sm_{0.75}Y_{0.25}S$. No changes were observable in the phonon dispersion relations within the accuracy of the experiment (about 0.1 THz). Increasing the pressure to about 0.4 GPa still had no observable effect on the phonons.

After increasing the pressure to about 0.6 GPa it was found that all but a small fraction of the crystal was converted to the collapsed phase with a lattice constant of 5.66 Å. The untransformed part was at the very bottom of the crystal and increasing the pressure to about 0.7 GPa transformed this into the collapsed or gold phase as well. The crystal now had a well-defined lattice constant of 5.66 Å, but the mosaic spread of the crystal had increased to about 4°. It was perhaps fortunate that the crystal held together so well after undergoing a sudden volume collapse of around 15%.

Resolution calculations that correctly took into account the mosaic spread of the sample were made for the triple-axis spectrometer. It was found that longitudinal phonons could be measured with a fairly small linewidth if the region near the zone center was avoided. Transverse phonons were calculated to be strongly broadened by the large mosaic spread and not well defined. This was confirmed when phonon measurements were started on the triple-axis spectrometer. Figure 1 shows phonon dispersion curves established for SmS both in the semiconducting black phase and in the metallic intermediate-valent gold phase. Only the acoustic phonons are shown, since neutron background from the pressure cell precluded measurements of the optical modes which have only weak-scattering intensity because of the small-scattering amplitude of S. In the high-pressure gold phase large shifts were found in the longitudinal acoustic phonons, particularly for the [111] direction.

The theoretical calculations for the effect of valence fluctuations on the phonon dispersion curves are helpful in telling what part of the dispersion curves should be affected by the valence fluctuations. The calculations show that the valence fluctuations do not affect the zone-boundary phonons but have the largest effect about halfway between the zone center and zone boundary. The expected energy shifts are smallest for the [100] direction and largest for the [111] direction. Examination of the dispersion curves shows that this indeed is the case. For the [100] direction the dispersion curve for the gold phase lies above that for the black phase as would be expected for a material whose volume is 15% smaller. For the [110] direction the LA acoustic branch is nearly identical for both phases despite the fact that the gold phase has a much smaller lattice constant. The LA [111] phonon branch for the gold phase is very anomalous, lying below the branch for the black phase except near the zone boundary.

Figure 2 shows an expanded view of the [111] LA branches for the two phases. We see a remarkable softening of the phonon branch for the collapsed phase in the region about halfway to the zone boundary. Symmetry considerations tell us that the LA zone-boundary phonon should not be affected much by valence fluctuations so that this point shows where a standard dispersion curve should end in the absence of mixed-valence effects.

Similar though smaller shifts were found for the $Sm_{0.75}Y_{0.25}S$ alloy system. The SmS sample shows very large effects since we can compare the

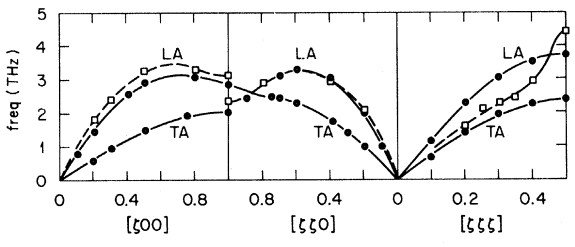

FIG. 1. Phonon dispersion curves for SmS. The solid points show measurements made at standard pressure. The open points show measurements made at 0.7 GPa.

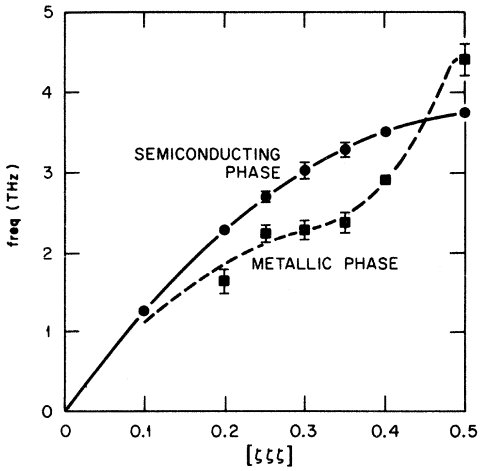

FIG. 2. LA phonon dispersion curves for the [111] direction for metallic and semiconducting SmS.

intermediate-valent state directly with the 2+ state. One noticeable difference between SmS in the mixed-valent state and $Sm_{0.75}Y_{0.25}S$ is that the phonon widths were larger for the alloy. The large mosaic spread hampers width measurements for the SmS sample; however, some information can be obtained. After the phonon measurements were completed in the high-pressure phase the pressure was removed from the sample. The entire sample returned to the semiconducting phase with a lattice constant of 5.97 Å. The sample mosaic spread remained about the same (4°) despite the sudden increase in sample volume in returning through the transition. The LA [111] dispersion curve was then remeasured to confirm that the large mosaic spread did not greatly affect the LA phonon measurements. Excellent agreement was obtained with the earlier measurements made before the sample was taken through the transition. Figure 3 shows phonon measurements for the the [111] direction taken while the sample was in the metallic phase, and in the semiconducting phase after the pressure was removed. A flat background has been subtracted from the data. The softening and broadening of the phonons in the metallic phase is easily observable. With the pressure removed measured phonon widths between 0.2 to 0.3 of the [111] zone boundary were about 0.35 ±0.08 THz in good agreement with our resolution calculations. The value for the width was obtained by least-squares analysis of the phonon measurements. Phonon widths were larger for the mixed-valent phase averaging about 0.50 ±0.1. The errors are such that we cannot give an accurate estimate for phonon broadening in the mixed-valent phase for SmS, but it appears that the phonons are not as broad as those measured for $Sm_{0.75}Y_{0.25}S$ which have a width of about 0.75 THz for the same position in the zone. Apparently the Y in the alloy causes extra phonon broadening not observed in pure SmS.

We see that valence fluctuations have a dramatic effect on the phonon dipsersion curves in the mixed-valent phase of SmS. It is apparent that any theoretical model used to understand the mixed-valent nature of SmS must consider the large coupling between the valence fluctuations and the phonons.

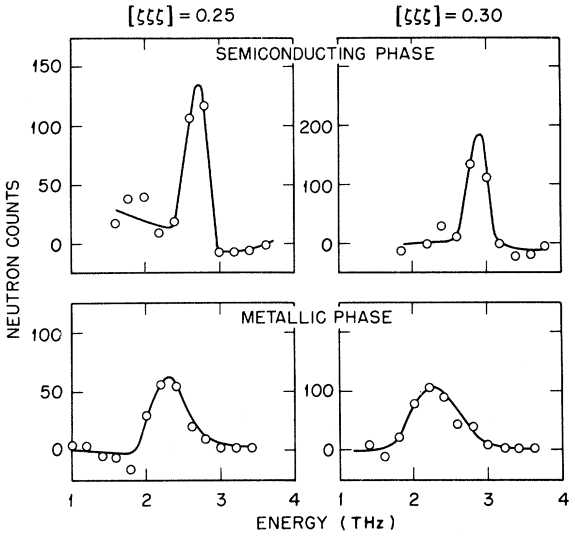

FIG. 3. Phonon measurements for the [111] direction of SmS. Measurements are shown for the metallic phase and for the semiconducting phase after the pressure was removed from the sample.

ACKNOWLEDGMENTS

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[1]A. Jayaraman, V. Narayamanurti, E. Bucher, and R. G. Maines, Phys. Rev. Lett. 25, 1430 (1970).

[2]J. M. Coey, S. K. Ghatak, and F. Holtzberg, in *Magnetism and Magnetic Materials–1974,* edited by C. D. Graham, G. H. Lander, and J. J. Rhyne, AIP Conf. Proc. No. 24 (AIP, New York, 1974), p. 38.

[3]J. M. D. Coey, S. K. Ghatak, M. Avingnon, and F. Holtzberg, Phys. Rev. B 14, 3744 (1976).

[4]H. A. Mook, R. M. Nicklow, T. Penny, F. Holtzberg, and M. W. Shafer, Phys. Rev. B 18, 2925 (1978).

[5]H. A. Mook and R. M. Nicklow, Phys. Rev. B 20, 1656 (1979).

[6]H. A. Mook and F. Holtzberg, in *Valence Fluctuations in Solids,* edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 113.

[7]P. Entel, N. Grewe, M. Sietz, and K. Kowalski, Phys. Rev. Lett. 43, 2002 (1979).

[8]H. Bilz, G. Guntherodt, W. Kleppmann, and W. Kress, Phys. Rev. Lett. 43, 1998 (1979).

[9]K. H. Bennemann and M. Avignon, Solid State Commun. 31, 645 (1979).

[10]T. Matsuura, R. Kittler, and K. H. Bennemann, Phys. Rev. B 21, 3467 (1980).

[11]N. Wakabayashi, Phys. Rev. B 22, 5833 (1980).

[12]P. Entel and M. Sietz, Solid State Commun. 39, 249 (1981).

[13]R. M. Moon, W. C. Koehler, D. B. McWhan, and F. Holtzberg, J. Appl. Phys. 49, 2107 (1978).

[14]R. J. Birgeneau and S. M. Shapiro, in *Valence Instabilities and Related Narrow Band Phenomena,* edited by R. D. Parks, (Plenum, New York, 1977), p. 54.