ting burnthrough measurements on thin foils, intensity of the hard-x-ray spectra and the fraction of energy loss to fast-ion blowoff the role of lateral energy loss as described above must be considered. Detailed two-dimensional particle simulations are necessary to self-consistently determine the microscopic trajectories of hot electrons and their role in energy transport and fast-particle generation.

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Phonon Anomalies and Electron-Lattice Coupling in Intermediate-Valence $Sm_{0.25}Y_{0.75}S$

H. Bilz, G. Güntherodt, W. Kleppmann, and W. Kress
Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, Federal Republic of Germany
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The electronic structure and the phonon dispersion curves of EuS, SmS, $Sm_{0.75}Y_{0.25}S$, and YS are analyzed. A five-parameter model is deduced which describes the phonon dispersion of $Sm_{0.75}Y_{0.25}S$ quite well. Two nearest-neighbor Sm-S forces and three deformabilities are introduced, two of which are attributed to virtual f-d transitions with dipolar- and "breathing"-type symmetry while the third is a quadrupolar-type sulfur deformability. The model suggests a strongly localized form of the microscopic theory.

Recently Mook *et al.*[1] have measured strong anomalies in the phonon dispersion curves of $Sm_{0.75}Y_{0.25}S$ which may be most likely related to the intermediate-valence state of $Sm_{1-x}Y_xS$ ($x > 0.15$).[2,3]

In this Letter we show that these anomalies can be described by a simple model which exhibits a clear radiation to excitations of Sm $4f$ electrons into d states of Sm, S, and Y. For this purpose we compare the electronic and vibrational properties of EuS, SmS, $Sm_{0.75}Y_{0.25}S$, and YS. The comparison suggests a five-parameter phonon model for $Sm_{0.75}Y_{0.25}S$. Two of these parameters may be interpreted as phonon self-energies due to virtual f-d transitions. The results suggest a specific form of the microscopic theory.

In Fig. 1 the essential properties of electrons and phonons of the aforementioned crystals are shown. While the upper part represents schematic diagrams of the valence and conduction bands,[4-6] the middle and lower parts of the figure show the calculated phonon dispersion curves in the (100) and (111) directions, respectively, except for $Sm_{0.75}Y_{0.25}S$ where guide-to-the-eye lines from experimental data[1] are shown. The calculations for EuS,[7] SmS,[8] and YS[9] reproduce the experimental data nearly within the limits of experimental error.[9,10]

In EuS the $4f$ states are in the lower part of the band gap of 2.3 eV and do not lead to any significant anomalies in the phonon dispersion curves, which are typical for an ionic semiconductor.[11]

As we proceed to SmS, the $4f$ level is shifted to the bottom of the conduction band and to the Fermi level E_F. In the optic branches a drastic lowering of the LO-TO splitting at Γ reflects the increase of the dielectric constant from $\epsilon_\infty = 4.7$ in EuS (Ref. 12) to $\epsilon_\infty \simeq 6.0$ in SmS,[13] although the band gap increases to 3 eV. This is caused by an enhanced Sm polarizability due to the lowered $4f$-$5d$ promotion energy, which corresponds to an increased dipolar phonon self-energy at Γ. An effect of similar magnitude occurs at the L point ("breathing" self-energy) which also reduces the bulk modulus by about 15%.[14] Thus, there is a clear indication of an incipient effect due to intermediate valence on the phonon dispersion of SmS.

The semiconductor-metal transition produces a drastic change in the phonon spectra as we go

from SmS to $Sm_{0.75}Y_{0.25}S$ and, finally, to YS. Let us first discuss superconducting YS. The phonon spectra are strongly influenced by metallic screening due to conduction electrons in the d band. In the (111) direction the transverse and longitudinal modes are nearly degenerate (except for a strong anomaly in the LA branch near the L point). This indicates that long-range Coulomb forces are screened and that only nearest-neighbor (nn) overlap forces are important; therefore a neutral nn approach is a good starting point for the description of the phonons in YS and in $Sm_{0.75}Y_{0.25}S$.

In order to understand the anomalies of these two compounds we consider specific short-range electron-lattice interactions ("deformabilities") to the phonon self-energy.[15,16] Assuming only radial couplings between nearest neighbors in an adiabatic multipole model there are only three possible deformabilities for each ion of breathing- (Γ_1^+), quadrupole- (Γ_{12}^+), and dipole- (Γ_{15}^-) type symmetry in cubic crystals. The dynamical matrix then becomes the sum of a rigid-ion part, D^{RI}, and a deformability part, $D(\Gamma_1^+)+D(\Gamma_{12}^+)+D(\Gamma_{15}^-)$. In a nn approximation, D^{RI} contains only two Born-Mayer overlap parameters.

In Table I we have listed the various possible deformabilities of Sm and of S ions in the different compounds together with their occurrence in the experimental spectra (Y does not seem to show any local deformability). The LA(L) anomaly in YS exhibits a breathing deformability of the S ion . YS has not only Y $4d_{xy}$ states but in addition S $3d_{xy}$ states near E_F.[6] The LA anomaly may be caused by resonantlike S valence d_{xy} → conduction d_{xy}^* excitations near E_F.[17]

When going from Ys to $Sm_{0.75}Y_{0.25}S$, the frequencies in the (100) direction are lowered systematically because of the heavier mass of Sm as compared to Y. The localized modes between the optic and acoustic brances (Fig. 1) have a frequency which is consistent with Y ions moving relative to the Sm ions.[1] Therefore, the Y ions will be neglected in the further discussion. Most interesting effects are seen in the (111) direction of $Sm_{0.75}Y_{0.25}S$. Here the LA(L) anomaly of YS has disappeared probably because E_F has decreased relative to the band edge and an essential part of the S d_{xy} states may have become depopulated. A new anomaly TA(L) seems to appear because in the nn approximation TA(L) and LA(L) are degenerate. This quadrupolar deformability at the S site (Table I) is consistent with local S $3d \rightarrow 4s$ or equivalent intersite transitions.[18] Of particular interest are the strong anomalies in the LO branch near the L point and at small q values in the LA branch, which both result from a breathing deformability of the Sm ion (Table I). In addition to the splitting of TO and LO phonons at L we observe a lowering of the optic modes at Γ with respect to the optic (111) modes in YS (Ref. 19) consistent with a dipolar deformability of the Sm ion (Table I). In SmS and $Sm_{0.75}Y_{0.25}S$, these phonon self-energies are caused by the hybridization of the Sm $4f$ level with d states of S, Sm, and, in $Sm_xY_{1-x}S$, of Y. In the latter case

TABLE I. Effect of deformabilities on phonon-dispersion curves in $Sm_{1-x}Y_xS$ ($0 \leq x \leq 1$).

Symmetry of deformability	Location of main effect	Observed $x=0$	$x=0.25$	$x=1$
Γ_1^+ (Sm)	LO(L) LA(ξ,ξ,ξ)	+	+	...
Γ_{15}^- (Sm)	LO(Γ)	+	+	...
Γ_{12}^+ (Sm)	TO(L)	...	...	...
Γ_1^+ (S)	LA(L)	...	...	+
Γ_{15}^- (S)	LO(Γ)	...	...	...
Γ_{12}^+ (S)	TA(L)	?	+	...

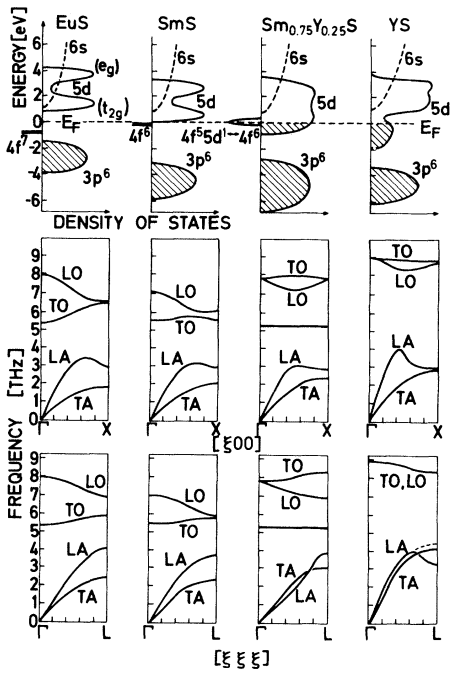

Fig. 1. Electronic densities-of-states and phonon dispersion curves of EuS, SmS, $Sm_{0.75}Y_{0.25}S$, and YS. The density of states for $Sm_{0.75}Y_{0.25}S$ represents an approximate interpolation between those of SmS and YS.

the anomalies are enhanced because of the degeneracy of f and d states near E_F and on-site Sm f-d hybridization because of inversion-symmetry breaking. The most striking effect of this is that the bulk modulus of $Sm_{0.75}Y_{0.25}S$ is less than $\frac{1}{6}$ of that in semiconducting SmS.[20]

While the breathing deformability of Sm seems to be clearly related to the isostructural phase transition in SmS under pressure or in $Sm_{1-x}Y_xS$ at $x = 0.15$, it is new to correlate the valence change of the Sm ion with a dipolar moment in the distorted electronic charge density around the Sm ion. There is a simple qualitative argument which shows that a *dipolar* deformability of the same order as the *breathing* deformability is consistent with a strong localization of all charge distortions in real space. The problem is visualized in Fig. 2, where the effect of a single displaced S ion on a neighboring Sm ion is demonstrated. The (near) equality of breathing contraction and dipolar repulsion leads to a cancellation of charge distortions between the Sm ion and the undisplaced S ion on the opposite side.

In Fig. 3 the results of our calculation are shown with only two nn force constants, a breathing and a dipolar Sm deformability, which are assumed to be equal, and a quadrupolar S deformability. In view of the simplicity of the model, the agreement with the experimental data seems to be quite satisfactory. In conclusion we emphasize a few points:

(a) The fit in Fig. 3 can obviously be somewhat improved by adding four second-nearest-neighbor force constants and four more parameters related to screened Coulomb interactions and ionic polarizabilities. Such a description with a thirteen-parameter model (except for its merits in fitting the experimental data slightly better) does not give any new physical insight, but spoils the clear description of the situation by our five-parameter model.

(b) The "intermediate valence" of Sm in $Sm_{1-x}Y_{1x}S$ manifests itself by the appearance of a breathing and a dipolar deformability of the Sm ion which arises from virtual Sm $4f \rightarrow d$ state excitations. Here, the d states of neighboring S ions may play an essential role[6,21] in addition to the usually assumed Sm $4f$-$5d$ hybridization. Our analysis supports the strongly localized character of the electron-lattice coupling.[22]

(c) Anomalous temperature dependence of the LA(111) branch has been observed.[1] In our model this behavior originates from a corresponding temperature dependence of the Sm breathing deformability which leads to a phase transition[23] at 200 K.[1]

(d) An interesting point is the transition from superconducting YS to (probably) nonsuperconducting $Sm_{0.75}Y_{0.25}S$. Valence mixing may be considered as a pair-breaking effect due to the coupling of itinerant d electrons to localized f electrons. The degree of localization of f electrons may be important for the role of electron-phonon coupling in intermediate-valence materials.

In conclusion, we have shown that the phonon anomalies in $Sm_{0.75}Y_{0.25}S$ and in SmS and YS can be understood in terms of localized phonon self-energies (deformabilities), clearly related to the electronic band structure. This model suggests

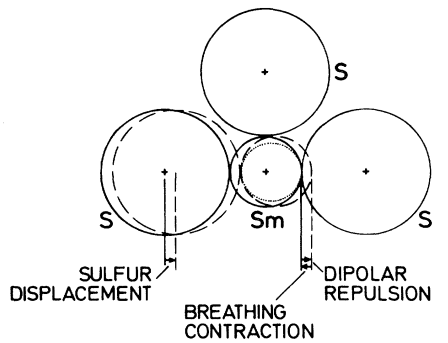

FIG. 2. Charge-density deformation of a Sm ion by a radial displacement of a neighboring S ion.

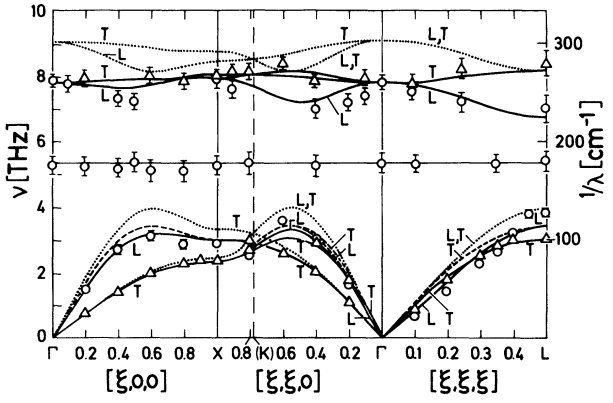

FIG. 3. Phonon dispersion curves of $Sm_{0.75}Y_{0.25}S$. Experimental points are from Ref. 1. Dotted lines, two-parameter nn model; dashed lines, four-parameter model (including Γ_1^+ and Γ_{15}^- deformabilities); solid lines, five-parameter model (including Γ_1^+, Γ_{15}^-, and Γ_{12}^+ deformabilities). Parameters (e^2/v_a) (see Ref. 18) are as follows: $A_{12} = 21.2$, $B_{12} = 3.5$, $k(\Gamma_1^+) = k(\Gamma_{15}^-) = 81.1$, and $s(\Gamma_{12}^+) = 1.5$.

a detailed microscoptic appraoch to intermediate valence, emphasizing the electron-lattice coupling and the localized f-d hybridization. Attempts in a similar direction have recently been undertaken by A. Martin[24] for the surface of SmS and by Grewe and Entel[25] and Bennemann and Avignon[26] for $Sm_{1-x}Y_xS$.

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Note added.—Very recently H. A. Mook and R. M. Nicklow [Phys. Rev. B 20, 1556 (1979)] have published a paper on phonons in $Sm_{0.75}Y_{0.25}S$. They used a ten-parameter screened rigid-ion model which reproduces roughly the general shape of the dispersion curves but fails to account for the detailed shape of the phonon anomalies.

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