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Soft-Mode Behavior in the Phonon Dispersion of YS

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We have measured the phonon dispersion of the superconducting transition-metal chalcogenide YS by inelastic neutron scattering. The longitudinal branches exhibit well-defined soft-mode regions that closely resemble those found in the structural and electronic analogs NbC and TiN. In contrast, no softening is observed in the transverse-acoustic branches. The experimental dispersion curves are well reproduced by calculations based on a double-shell model.

The discovery[1] of anomalies in the phonon dispersion of superconducting transition-metal (TM) carbides of group Vb has instigated both intensive theoretical efforts[2-4] to elucidate their origin and a search for the occurrence of similar anomalies in related compounds. The correlation between soft-mode behavior and high-temperature superconductivity in NbC and TaC has been investigated[3,4] by theories aiming at a microscopic description of the electron-phonon exchange interaction. Recently, soft-mode regions have been observed[5] in the acoustic branches of the phonon dispersion of TiN. This finding indicates that the rigid-band picture is appropriate for the electronic band structure of TM carbides and nitrides with nine valence electrons per molecule.

The monochalcogenides of the TM's of group IIIb are related in many of their physical properties to the IVb nitrides and Vb carbides. Just like these, they crystallize in the rock-salt structure and possess 9 valence electrons per molecule. They are also superconducting; however, their transition temperatures are generally lower than those of the carbides and nitrides.

In view of the established correlation between superconductivity and phonon anomalies in these compounds, the question arose whether the phonon spectra of the IIIb chalcogenides should exhibit soft-mode regions—as suggested by the rigid-band model—or whether the decrease of their T_c's should be associated with the disappearance of the phonon anomalies.

In this Letter we report on measurements of the phonon dispersion relations of YS. We have found that phonon anomalies exist in the longitudinal acoustic branches, similar to those observed in the IVb nitrides and Vb carbides, whereas they are completely absent in the transverse acoustic branches. Thus our results provide a sensitive test for the validity both of model theories developed for the lattice dynamics of TM's and their compounds, and of microscopic theories aiming specifically at an explanation of the electronic origin of the phonon anomalies in this class of materials.

YS crystallizes in the rock-salt structure. The lattice constant of our samples was determined as $a_0 = 5.496 \pm 0.001$ Å. Sample preparation techniques have been described by Jayaraman, Dernier, and Longinotti.[6] The sample had a volume of ~ 0.6 cm^3 and contained two slightly misoriented single-crystalline regions; the resulting "mosiac spread" was ~ 1.3°. The nonmetal-to-metal ratio x was investigated by electron microprobe techniques; it varied from 0.94 to 1.01 across the surface of the sample. The superconducting transition of a sample grown under identical conditions had been observed around 2.8 K.[7]

Neutron-scattering measurements were performed at the Karlsruhe FR2 reactor on the triple-axis spectrometer TAS1. Figure 1 shows the experimentally determined phonon dispersion relations of YS in the three main symmetry directions. The slopes of the dispersion curves at $q = 0$ as given in Fig. 1 are calculated from measured elastic constants.[8] They agree very well with our data. A striking feature in the phonon dispersion relations of YS is the softening of the LA phonons in certain parts of the Brillouin zone. In the [110] and [111] directions, the dispersion curves for LA phonons closely resemble those observed, e.g., in NbC and TiN, whereas in the [001] direction the dip seems to be masked by the overall depression of the branch towards the zone boundary. In contrast to NbC and TiN none of the TA branches of YS exhibit a soft-mode region. The optic branches are quite different from those of the isoelectronic carbides and nitrides. They resemble more those of UC[1] and indicate that the ionicity of YS is quite small.

For an analysis of the data we have fitted the double-shell model (DSM) of Weber[2] to the experimental data. Data for the elastic constants were not included in the fit. The curves in Fig. 1 were obtained from an eleven-parameter fit, with five parameters for the normal shell model and six parameters for the supershell. The model calculations give a good overall description of the data and, in particular, satisfactorily reproduce the behavior of the phonon branches in the soft-mode regions. The model parameters are listed in Table I. Central forces were assumed for the short-range interactions Y-S and Y-Y; the corresponding parameters are $A(12)$, $B(12)$ and $A(22)$, $B(22)$, respectively. k_2 is the shell-core coupling constant of the Y ion. All charges in the simple shell model were put equal to zero and a rigid coupling between shell and core of the sulfur atom was assumed. The parameters, A_1', B_1', C_1' and A_2', B_2' determine the nearest-neighbor and second-nearest-neighbor interaction, respectively, between the supershells of Y.

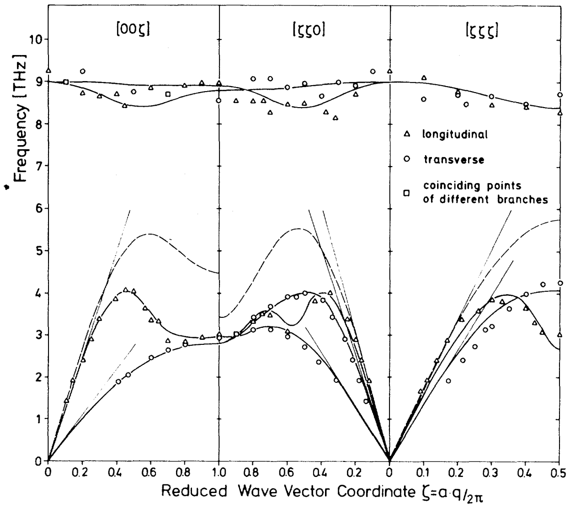

FIG. 1. Phonon dispersion curves of YS in the main symmetry directions. Full curves are the result of a fit using an eleven-parameter DSM. Broken curves represent the LA branches if the supershell interactions are omitted.

TABLE I. DSM parameters for YS obtained from the fit to experimental phonon data. For comparison the parameters of NbC are also given. Force constants are in units of $2e^2/a_0^3$, charges in units of the elementary charge e; k_f and k_s are normalized to $2\pi/a_0$. The parameters are defined as in Ref. 3.

Shell model parameters			Supershell parameters		
	YS	NbC		YS	NbC
$A(12)$	23.61	19.62	A_1'	−1.085	−0.713
$B(12)$	1.55	3.96	B_1'	−0.453	−0.484
$A(22)$	4.62	9.02	C_1'	−0.152	0
$B(22)$	0.41	−0.7	A_2'	−1.424	−0.943
$C(22)$	0.41	−0.7	B_2'	0.063	−0.136
Z	0	−0.696	k'	9	6
Y_1	0	0			
Y_2	0	−1.6			
k_1	10^6	726			
k_2	141.7	145			
k_f	···	0.4			
k_s	···	0.4			

The supershell-shell coupling constant k' is determined by the width of the dips in the dispersion curves. We note that without inclusion of C_1' the dip in the [110] direction could not be fitted satisfactorily.

The large anisotropy of the elastic constants is a consequence of the strongly dominating nearest-neighbor Y-S interaction. The total Y-Y interaction turns out to be quite small since the contributions from the simple-shell-model part are largely compensated by the supershell interactions. The dashed curves in Fig. 1 represent the LA branches if the supershell interactions are omitted in the model. It is seen that part of the softening close to the X point is already accounted for by contributions from the simple shell model. A comparison with the full curves shows that the supershell interactions lower the phonon frequencies over a wide range of q values. In NbC and TiN the resonances in the dispersion curves are more sharply defined; this results in smaller values for k' in the model (9 for YS, 6 for NbC, and 1.9 for TiN, all in units of $2e^2/a_0^3$).

In the DSM, two resonancelike interactions have been incorporated. The interaction between supershells of second-nearest TM neighbors accounts for well-defined soft-mode regions at reduced wave vectors $q = 0.5$ in all directions. According to a microscopic theory by Hanke, Hofner, and Bilz,[3] this interaction is mediated by hybridized orbitals of TM d and nonmetal p electrons. The interaction between the supershells of nearest TM neighbors lowers the phonon frequencies in the vicinity of the X point, thereby shifting the anomaly in the [001] and [110] directions toward the X point, and enhances the dips at the L point. We note that the values for the longitudinal force constants A_1' and A_2' of NbC and YS agree within a few percent when scaled with the shell-supershell coupling constants k'. This points to a closely related mechanism responsible for the soft-mode behavior observed in their LA branches. On the other hand, the transverse force constants B_1' and B_2' differ considerably: the value of B_1' for YS is smaller than for NbC by a factor of 2, and B_2' for YS even shows a positive sign. This reflects the absence of anomalies in the TA branches of YS. We conclude that any generally valid theory dealing with the phonon anomalies in superconducting 9-valence-electron transition-metal compounds should invoke one and the same origin for their occurrence in each of these compounds while at the same time accounting for the disappearance of the TA anomalies when going from the carbides to the sulfides.

In conclusion, we want to comment on the correlation between phonon spectra and superconductivity in the TM compounds with 9 valence electrons. In order to arrive at a trend analysis we have calculated frequency moments of the amplitude-weighted phonon density of states for both the TM and nonmetal components of YS and NbC which are relevant within the framework of McMillan's formalism.[9] They are given in Table II, together with empirical values for the electron-phonon coupling parameter λ and the electronic density of states at the Fermi energy $N(E_F)$ obtained from measurements[7,10] of T_c and the electronic specific heat, respectively. The differently defined frequency averages correspond to different choices for the electron-phonon spectral function $\alpha^2(\omega)F(\omega)$. In the first, $\alpha^2(\omega)F(\omega) \sim F(\omega)$, which is commonly assumed in the absence of tunneling data, whereas in the second, $\alpha^2(\omega)F(\omega) \sim F(\omega)/\omega$, which probably represents a more realistic approximation for this class of materials.[11] For this case, the quantities in the

TABLE II. Empirical values for YS and $NbC_{0.98}$ used in McMillan's analysis.

	T_c (°K)	λ	$N(E_F)$ (states/eV)	$M\langle\omega\rangle/\langle\omega^{-1}\rangle$ (eV/Å^2)	$M\langle\omega^{-2}\rangle^{-2}$ (eV/Å^2)	$\frac{\lambda}{N(E_F)} \times M\langle\omega^{-2}\rangle^{-2}$
YS	2.8	0.56	0.41			
Y				5.24	3.84	5.2
S				7.08	4.28	
$NbC_{0.98}$	10	0.74	0.34			
Nb				12.61	10.26	22.3
C				11.86	10.86	

last row of Table II may be identified with the average of the square of the electron-ion interaction $\langle I^2 \rangle$.

Part of the decrease of T_c may be due to the much larger atomic volume of YS ($V_{\rm YS} = 1.9 V_{\rm NbC}$) which reduces both the prefactor $\langle \omega \rangle$ and λ in McMillan's[9] T_c formula. In the free-electron model λ is proportional to $V^{-1/3}$. A similar trend may be expected also for the TM's. This conjecture is supported by a recent work of Butler's[12] which showed that for the 4-d TM's $\langle I^2 \rangle$ is proportional to V^{-2} within the rigid-muffin-tin approximation. A similar dependence is observed in our values for $\langle I^2 \rangle$.

Another reason for the lowering of λ may be found in the characteristic differences in the soft-mode behavior of YS and NbC. Hanke, Hofner, and Bilz[3] have concluded that the hybridization of the Fermi energy is responsible both for the occurrence of anomalies in the TA branches and for an enhancement of the electron-phonon interaction. Calculations of the electronic band structure by Appelbaum and Hamann[13] have shown that these hybridized p-d bands are shifted well below $E_{\rm F}$ in YS. This result may explain the absence of TA soft modes and, in consequence, part of the observed decrease in T_c.

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