PHYSICAL REVIEW B VOLUME 59, NUMBER 9 1 MARCH 1999-I

Raman spectroscopy investigation of lanthanide-filled and unfilled skutterudites

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(Received 2 October 1998)

Raman-scattering spectra at room temperature and 10 K are studied for binary ''unfilled'' and lanthanide-filled skutterudite antimonides. In the binary skutterudites $IrSb_3$ and $RhSb_3$ all eight Raman-active vibrational modes have been identified while seven of the eight modes have been identified in $CoSb_3$. In the case of the filled skutterudites these vibrational modes are sensitive to the lanthanide ''filler'' ions which produce a shift and large broadening of the vibrational modes. Polarization measurements on these polycrystalline samples were used to identify the A_g modes. The experimental data are compared to theoretical predictions. [S0163-1829(99)04309-X]

INTRODUCTION

In recent years attention has been focused on the skutterudite family of compounds for thermoelectric applications because of their interesting crystal structure and transport properties.[1] The interest in this material system arises from the high mobility and Seebeck coefficient of the binary skutterudites and the marked reduction in lattice thermal conductivity upon interstitially filling the voids of the crystal structure with lanthanide ions. The ''rattling'' motion of these atomic inclusions act as excellent phonon scatterers. It is now apparent that in-depth investigations are necessary in order to more fully understand the effect of the ''void-fillers'' on the lattice dynamics of this material system.[1]

The binary skutterudites (indicated by AX_3 where A represents a metal atom and X is a pnictide atom) form with the $Im3\,(T_h^5)$ space group. There are eight formula units per cubic unit cell. The skutterudite structure consists of nearly square planar X_4 rings, the centers of which are located at the centers of cubes formed by the A atoms. There are six mutually orthogonal X_4 rings per cubic unit cell thereby resulting in two relatively large voids per unit cell. The centers of these voids are 12 coordinated by the pnictide atoms. The void radii of the nine binary semiconducting skutterudite compounds have been estimated from x-ray crystallographic data and range in radii from 1.763 for CoP_3 to 2.040 for $IrSb_3$.[2] Filled skutterudites have been formed with lanthanide, actinide, and alkaline-earth ions interstitially occupying the voids. Large x-ray thermal parameters have been reported for these ions indicating that these ions move or ''rattle'' about in the voids of this crystal structure.[3] Nolas *et al.*[2] have shown that this ''rattling'' has a marked effect on the lattice thermal conductivity κ_g of these compounds. The smaller and more massive the ion the larger the reduction in κ_g. A decrease of greater than an order-of-magnitude in κ_g was observed as compared to the ''unfilled'' skutterudites.[2] These x-ray and thermal conductivity results, along with initial Raman spectroscopy[4] and neutron-scattering[5] studies indicate that the interstitial ions interact with the lattice phonons. In addition, frozen-phonon calculations indicate that the ''caged'' lanthanide ions produce low-energy soft phonon modes.[6] These studies have resulted in a renewed interest in the investigation of the optical modes of filled skutterudite compounds. The measured infrared-active modes of the binary skutterudite antimonides have been tabulated by Slack and Tsoukala.[7] Most recently an investigation into the Raman modes of lanthanide filled skutterudite-phosphides has been published.[8] In the present article we investigate the Raman-active vibrational modes of filled skutterudites with trivalent lanthanum La^{3+}, samarium Sm^{3+}, and neodymium Nd^{3+}, in the voids of this structure. In addition three binary skutterudite antimonides ($IrSb_3$, $RhSb_3$, and $CoSb_3$) are also studied in order to compare with that of the lanthanide-filled skutterudites. We employ low-temperature (10 K) Stokes and anti-Stokes spectra along with polarization and excitation wavelength dependence measurements in order to elucidate the effect of these caged lanthanide ions on the lattice phonons in this crystal structure. The experimental results are compared to theoretical predictions.

EXPERIMENTAL ARRANGEMENT AND SAMPLE SYNTHESIS

Polarized Raman-scattering measurements were carried out using the 514.5 and 488.0 nm excitations of an Ar^+-ion laser and the 647.1 and 676.4 nm excitation of a Kr^+-ion laser. The incident beam was backscattered off the sample at roughly 45 degrees to avoid the direct reflection impinging on the collection lens. The collected light was analyzed with a Dilor 500 mm triple-grating spectrometer and counted with a liquid-nitrogen-cooled CCD array. The low thermal conductivity of the polycrystalline filled-skutterudite samples limited the incident power which could be used below the damage threshold to roughly 75 mW with a 100 μm spot diameter. Typical collection times for the filled skutterudite samples ranged from 5 to 10 min and several scans were averaged to increase the signal/noise ratio. The spectral resolution was set to 3 cm^{-1} for the 514.5 nm excitation and 2 cm^{-1} for the 647.1 nm line. The low-temperature measure-

TABLE I. Structural data for the six skutterudite compounds studied for this report.

Compound	Lattice parameter (Å)	x-ray density (g/cm^3)	Bulk density (g/cm^3)
$CoSb_3$	9.035	7.639	7.486
$RhSb_3$	9.230	7.908	7.750
$IrSb_3$	9.250	9.355	9.168
$Ir_4LaGe_3Sb_9$	9.104	9.737	7.790
$Ir_4NdGe_3Sb_9$	9.113	9.732	7.008
$Ir_4SmGe_3Sb_9$	9.159	9.612	8.170

ments were made in flowing He vapor to minimize the effects of laser heating.

The synthesis approach and techniques used to structurally and chemically characterize the six phase-pure samples studied in the present work have been extensively reported elsewhere.[2,4] The results showed single-phase samples with the appropriate stoichiometries. In addition, Hall measurements on these samples indicated all were P-type with the filled skutterudites being heavily doped ($>10^{20}\,\mathrm{cm}^{-3}$). The faces of the samples where polished down to a final polish with 0.3 μm alumina paste for the Raman experiments. Table I summarizes the structural data of the six skutterudite samples. In the case of the filled skutterudite compounds Ge was used in an attempt to charge compensate for the trivalent lanthanide ions; three Ge atoms for each lanthanide atom. The Ge atoms are smaller and have a smaller mass than the Sb atoms. Their average concentration is one Ge for every Sb_4 ring. It is assumed that the Ge atoms are randomly distributed in the crystal lattice.

RESULTS AND DISCUSSION

The first-order Raman-active modes can readily be determined by group theory to be $2A_g+2E_g+4T_g$ where the A_g modes are singly degenerate, E_g are doubly degenerate, and T_g are triply degenerate. Room-temperature Stokes Raman spectra of the three ''unfilled'' binary skutterudite samples from 50 to 250 cm^{-1} using the 514.5 nm Ar$^+$-laser line are shown in Fig. 1. The spectra consist of many sharp peaks. There were no other sharp features observed above 250 cm^{-1}. The peak positions and linewidths (full width at half-maximum, FWHM) along with the experimentally determined A_g modes and results from theoretical analyses are shown in Table II. The theoretical analyses are based on a fit of six central bond-stretching force constants to the experimental infrared data of $CoSb_3$, [Lutz and Kliche (LK)] and using the local orbital extension of the general potential linearized augmented plane-wave method [Feldman and Singh (FS)].[9,10] The positions and linewidths of the experimentally observed Raman lines were obtained from a Lorentzian fit to the data.

In order to identify the A_g modes of these compounds we employed polarization measurements as follows. We define the depolarization ratio P as[11]

$$P=\frac{I_r}{I_p}, \tag{1}$$

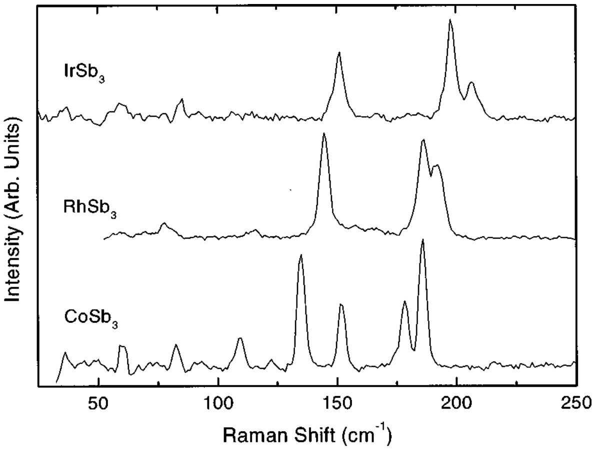

FIG. 1. Stokes Raman-scattering spectra of the phonon modes of the three binary skutterudite antimonide at room temperature using 514.5 nm excitation with the scattered light polarized parallel to the laser line.

where I_p is the Raman scattered intensity polarized parallel to the laser line and I_r is the intensity polarized perpendicular to the laser line. In the case of randomly oriented scattering centers, e.g., polycrystalline materials, with a cubic crystal structure $P=0$ for A_g modes and is nonzero for all other symmetries. This is due to the fact that the scattered light may be averaged over a large number of scattering centers in a polycrystalline sample.[11] The degree of depolarization can therefore distinguish the A_g symmetry modes from the other vibrational symmetries. Figure 2 illustrates this approach with the Raman spectra of $RhSb_3$ taken with the scattered light polarized parallel (VV) and perpendicular (HV) to that of the 514.5 nm Ar$^+$-laser line at room temperature. We have used this technique to identify the two A_g modes in the binary skutterudites. This technique however cannot unambiguously identify the other vibrational symmetries.

The A_g modes of these skutterudites are the ''symmetric breathing modes'' of the Sb_4 rings. Two such modes arise due to the fact that the Sb_4 rings are not exactly square. If y

TABLE II. Peak positions, FWHM, and A_g mode assignments of the experimentally observed Raman-active phonon modes of the three binary skutterudites. The $IrSb_3$ and $RhSb_3$ spectra are similar, however quite different than that of $CoSb_3$. The data are therefore listed in ascending Raman shift, in cm^{-1}, with only the A_g modes assigned. The theoretical predictions are also shown.

$IrSb_3$		$RhSb_3$		$CoSb_3$			FS	LK
ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$		ν	$\Delta\nu$
60	5.4	61	Broad	60	3.0			71
85	3.1	78	6.6	82	3.0			103
117	3.0	114	6.2	109	3.2			140
151	4.1	145	4.3					162
160	3.0	150	Shoulder	135	3.1	A_g	150	162
				152	3.0			
183	3.7	166	5.8	178	3.2			
198	4.0	186	5.0	186	3.1	A_g	178	183
207	4.4	192	5.1					188
								194

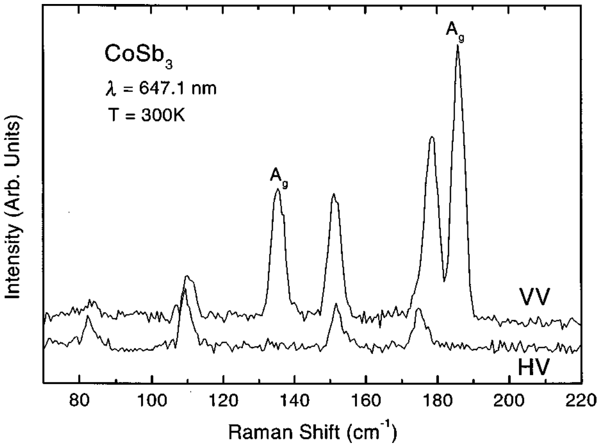

FIG. 2. Stokes Raman-scattering spectrum of $CoSb_3$ taken with the scattered light polarized parallel (*VV*) and perpendicular (*HV*) to that of the 647.1 nm excitation at room temperature.

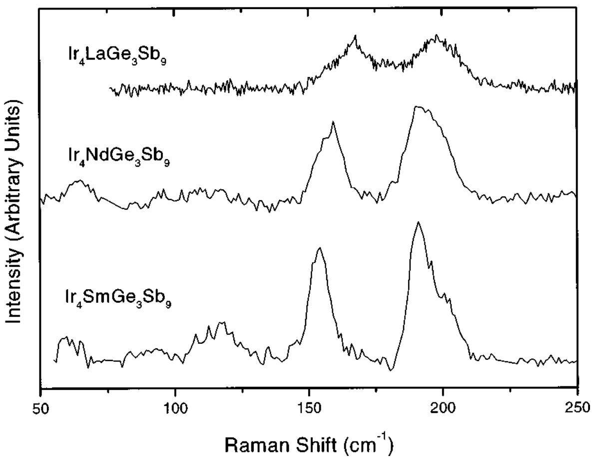

FIG. 3. Stokes Raman spectrum of the La, Nd, and Sm-filled skutterudites at at room temperature using 514.5 nm excitation with parallel polarization.

and z are the reduced coordinate positions of the Sb atoms in this structure the two Sb-Sb bond lengths are $2za_0$ and $(1-2y)a_0$, their difference being $[1-2(y+z)]a_0$ where a_0 is the lattice parameter. If $y+z=0.5$ the two modes would be degenerate. This is not the case in skutterudite compounds.[12] The higher energy mode is presumably due to the stretching of the shorter Sb-Sb bond and the lower-energy one is the stretching of the longer Sb-Sb bond.

From the data of Table II we note that we have confirmed the majority of the Raman data of the previous study[4] while detecting all but one of the Raman-active modes (in $CoSb_3$) of the three binary skutterudite antimonides. In the previous study theoretical results were used in assigning the experimental data. From Table II, however, we see that there is some discrepancy between experimentally observed Raman lines of $CoSb_3$ and the theoretically predicted results of LK and FS. In addition, from Fig. 1 we see that the $IrSb_3$ and $RhSb_3$ spectra are somewhat similar but different from that of $CoSb_3$. The Raman-active modes in the skutterudite structure do not involve any motion of the metal sublattice atoms but are all relative motions of the Sb atoms with respect to one-another in such a way that the center of mass of the Sb in the unit cell remains unchanged.[13] Since the Sb-to-Sb distances are similar in $IrSb_3$ and $RhSb_3$ ($y=0.340$ Å and $z=0.153$ Å for $IrSb_3$ and $y=0.342$ Å and $z=0.151$ Å for $RhSb_3$ with $y+z=0.493$ Å for both compounds[12]), the Raman mode energies should be somewhat independent of the mass of the metal atom. The mass difference between Ir and Rh would therefore not have a great affect on the Raman-active vibrational modes. However, in the case of $CoSb_3$, Co being smaller in radius than Ir or Rh,[14] $y=0.335$ Å and $z=0.160$ Å with $y+z=0.495$ Å.[12] There is therefore a difference in the size and shape of the $CoSb_3$ Sb_4 rings, as compared to that of the other two compounds, which results in the difference in the phonon mode energies. The infrared-active vibrational modes involve the metal atoms.[4,13]

The Stokes Raman spectrum of the three filled skutterudites from 50 to 250 cm^{-1} using the 514.5 nm Ar^+-laser line at room temperature is shown in Fig. 3. The spectra is much sharper and the vibrational modes have been well resolved as compared to that of the previous work.[4] The Sm-filled skutterudite sample was the most dense of the filled skutterudite samples. The other two filled skutterudites showed a similar spectrum although not as well structured due to the background from the specular reflection (stray light) of the incident laser line caused by the porosity of these two samples. In addition, there was a large electronic Raman signal for the filled skutterudites which appears as a frequency-independent background extending upward for at least several thousand cm^{-1}, the highest energy shifts measured. The electronic signal was distinguished from photoluminescence by virtue of its independence of incident wavelength and by comparing the Stokes and anti-Stokes spectra. When the samples were cooled below room temperature, both the phonon and the electronic background anti-Stokes intensities decreased according to the thermal Bose factor $\exp(-\hbar\nu/k_BT)$. This provides a strong indication that both are coupled to electronic excitations near the Fermi surface and can therefore be treated as Raman signal. Such electronic Raman scattering is not surprising given the large number of carriers in the filled skutterudites. Qualitatively similar phenomena are observed in doped semiconductors[15] and metals.[16] For the purposes of the present investigation however, the electronic background and any upturn at low energies due to stray light have been fit with a smooth function and subtracted from the spectra to emphasize the phonon features, as seen in Fig. 3. The Raman data of the three filled skutterudite compounds are tabulated in Table III. As in the case of the binary skutterudites, polarization measurements were used to assign the high-energy A_g mode in these com-

TABLE III. Peak positions and FWHM for the three filled skutterudites.

$Ir_4LaGe_3Sb_9$		$Ir_4NdGe_3Sb_9$		$Ir_4SmGe_3Sb_9$		
ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	
		65	9.8	60	7.7	
				91	10.1	
		119	Broad	116	13.1	
161	16.2	156	8.3	154	7.6	
192	18.2	194	14.1	191	6.7	A_g
198	Shoulder	200	Shoulder	200	10.4	

pounds. The theoretically predicted A_g modes were at 137 and 157 cm^{-1}.[17] A relatively sharp Raman line at 52 cm^{-1} for the Sm-filled skutterudite sample may be an electronic Raman transition from the ground state to the first excited state of the $^6H_{5/2}$ manifold in the $4f$ ground-state configuration of Sm^{3+}. This is similar in energy to that observed for Sm^{3+} substituted for yttrium in $\mathrm{Y_3Ga_5O_{12}}$.[18]

In all spectra the energies of the Raman lines upshift slightly at 10 K as compared to that at room temperature, as is typical for lattice contraction upon cooling. In addition most of the modes are narrower as compared to those observed at room temperature indicating that phonon-phonon interaction is a major line broadening mechanism. In the case of the filled skutterudites, another broadening mechanism may be due to the disorder-induced broadening caused by the (assumed) random distribution of Ge substituted for Sb in the filled-skutterudite samples. This may break down the Γ-point phonon ($q\sim 0$) selection rule that only zero wave-vector phonons participate in first-order scattering. Other phonons with small, nonzero q vectors and slightly different frequencies may also exist thereby inducing line broadening. However, careful x-ray-diffraction analysis of the three filled skutterudites did not reveal such an effect. We speculate that the line broadening in these compounds is due to the lanthanide ions. As discussed above these ions have large x-ray thermal parameters due to the fact that they are entrapped in oversized cages formed by Sb atoms in this structure. The ''rattling'' motion of these ions may therefore result in fluctuating bonding with the Sb atoms that define these voids. This would cause a broadening of the vibrational energies of the $\mathrm{Sb_4}$ ring vibrational modes.

We have failed to detect the vibrational mode(s) of the ''rattling'' lanthanide ions in the spectra of the three filled skutterudites. The lanthanide-Sb vibrations are expected to be at low energies.[6] It is expected that the large lanthanide vibrational amplitudes may broaden these transitions a great deal thereby making it difficult to resolve these lines, even at 10 K. It may also be that these vibrational modes are infrared-active since they would involve the displacement of trivalent lanthanide ions. A low-temperature investigation of the infrared absorption spectra of these compounds is currently under consideration.

CONCLUSIONS

We have identified all eight Raman-active modes of the antimony-based binary skutterudites $\mathrm{IrSb_3}$ and $\mathrm{RhSb_3}$, and seven of the eight modes in $\mathrm{CoSb_3}$. We have also identified many of the modes in the filled skutterudites. In addition we employed polarization measurements to identify the A_g modes. The lanthanide ions broaden as well as shift the vibrational modes as compared to $\mathrm{IrSb_3}$. The ''rattling'' of these lanthanide ions in the skutterudite cages, formed by Sb, interact with the lattice phonons. This is in corroboration with the low thermal conductivity[2] and large x-ray thermal parameter[3] measured for these compounds. The discrepancy between the experimental results and the predicted Raman-active modes demonstrates the difficulty in simulating the vibrational spectra of this crystal system.

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[1] See for example, *Thermoelectric Materials—New Directions and Approaches*, edited by T. M. Tritt, M. G. Kanatzidis, H. B. Lyon, Jr., and G. D. Mahan, MRS Symposia Proceedings No. 478 (Materials Research Society, Pittsburgh, 1997), and references therein.

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