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Vibrational Spectra and Structural Order in the Lithium–Rare Earth Sulfides*

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Raman spectra have been measured on a series of sulfide compounds $LiLnS_2$, where Ln is one of the rare earths between Pr and Yb. Compounds of the smaller rare earths have the ordered α-$NaFeO_2$ structure and give two-band Raman spectra in agreement with group theoretical calculations. Compounds of the larger rare earths have a disordered NaCl structure which, contrary to the NaCl selection rules, give an intense broad Raman band spanning the wavenumber region between the bands of the ordered structure. The broad band is interpreted as a density of states function with contributions of phonons from throughout the Brillouin zone. The massive breakdown of the k = 0 selection rule occurs because of the charge mismatch between monovalent and trivalent ions distributed over the crystallographically equivalent sites of the NaCl structure.

INTRODUCTION

The alkali–rare earth disulfides, $ALnS_2$, crystallize in one of two structure types (1–5). In compounds of the larger rare earths and smaller alkali ions, the two cations are randomly distributed and the resulting structure is that of NaCl. Introduction of the larger alkali ions and the smaller rare earth ions causes the cations to order, forming compounds with the α-$NaFeO_2$ ($NaHF_2$) type structure. This structure is an ordered and trigonally distorted variant of the NaCl structure with space group $R\bar{3}m$ with one formula unit in the primative unit cell. High-temperature order–disorder phase transitions have been described in the Dy, Ho, Er, and Y compounds (5). The systematics of the crystal chemistry drawn from the structural data compiled in Wyckoff (6) are illustrated in Fig. 1 where the structure field map has been drawn using Shannon–Prewitt (7) crystal radii. Although sulfide radii are now available (8), they did not seem to improve the structure field map.

The alkali–rare earth disulfides are insulating compounds with band gaps in the range of 2–3 eV judging from their colors. There is some interest in these compounds as optical ceramics (9, 10) and thus it is of interest to know something of their vibrational spectra. Powder infrared measurements have been made on oxide analogs of many of the $NaHF_2$ structure compounds (11–13) and both infrared and Raman data have been collected for some of the ordered sulfides (13).

The present investigation presents spectra of the lithium compounds, $LiLnS_2$, for both ordered and disordered structures. The objective is to examine the effect of structural order on the spectra and to use the spectra as a means of examining the order–disorder phase transition.

EXPERIMENTAL METHODS

The lithium–rare earth sulfides were synthesized by the reaction

$$Li_2CO_3 + Ln_2O_3 + 4H_2S \rightarrow 2LiLnS_2 + CO_2 + 4H_2O.$$

The rare earth oxides were mixed with an excess of lithium carbonate. Both a 5% excess as recommended by Ballestracci (2) and a 20% excess as recommended by Tromme (3) were investigated. The powders were mixed in a Teflon container and then tumbled in a ball mill (without balls) for ½ to 2 hr. Approximately half-gram samples were placed in graphite boats and reacted in a furnace in an atmosphere of flowing H_2S. The furnace was first purged with argon for 1.5 hr, then flushed with H_2S for 1.5 hr. The furnace was then brought slowly to temperature with a continuous flow of H_2S. After the prescribed run time, the furnace was shut off and allowed to cool with the H_2S continuously flowing. After cooling, the furnace was purged with argon and opened. The samples, originally powders, were now small hard pellets. The samples prepared with the 20% excess of Li_2CO_3 were much more homogenous in color

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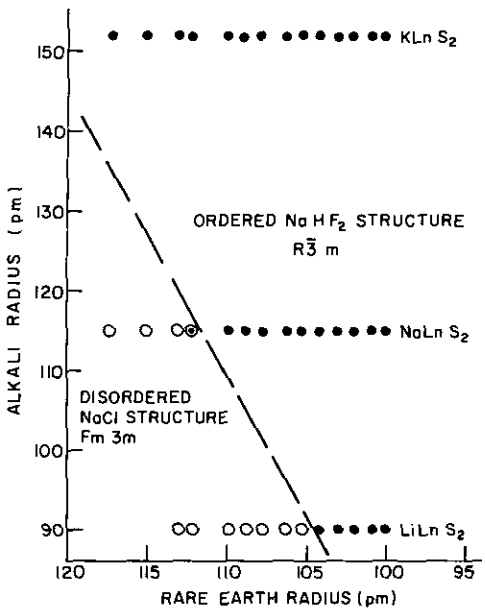

FIG. 1. Crystal chemistry of $LiLnS_2$ compounds. Structural data drawn from Wyckoff (6). Radii are Shannon–Prewitt crystal radii for sixfold coordination (7).

and texture than those prepared with only a 5% excess Li_2CO_3. As a final treatment, the samples were ground in an agate mortar, washed in 50–150 ml of deionized water to remove any traces of lithium sulfides, and then dried with acetone.

All preparations were characterized by X-ray powder diffraction using a Scintag diffractometer with CuK_α radiation. Except as noted, all preparations were phase pure to the detection limits of X-ray powder diffraction. The powder patterns of the synthesized compounds were in good agreement with the JCPDS powder diffraction file. A clean distinction was found between powder patterns of the ordered $NaHF_2$-type structures and the disordered NaCl-type structures. The diffraction lines were sharp for both ordered and disordered structures, indicating good crystallinity.

Raman spectra were measured using an Instruments SA Ramanor U-1000 instrument with a 15-mW He–Ne laser as an excitation source. Resonance enhancement allowed sufficient Raman intensity with this source. Attempts to measure spectra with either green or blue line of an argon ion laser simply caused the decomposition of the sulfide compound. Spectral slit widths were 2–3 cm^{-1}.

SPECTRA

Raman spectra for a selection of the disordered NaCl-structure compounds are shown in Fig. 2. There is a single broad band in the range of 230 to 260 cm^{-1} with a shoulder on the low wavenumber side. The band narrows somewhat and the shoulder becomes more pronounced as the ionic radius of the rare earth decreases. Reaction times and temperatures are shown on the spectra. The bands at 450 cm^{-1} in the Pr and Nd spectra are due to unreacted rare earth oxide (14).

The Raman spectra of the ordered compounds consist mainly of two moderately sharp bands observed at 210 and 285 cm^{-1} in $LiYbS_2$ (Fig. 3). The bands appear at similar wavenumbers in the other ordered compounds. Extra bands, such as those appearing in the spectrum of $LiErS_2$, are shown to be due to rare earth fluorescence. The test for fluorescence is to measure the spectra with several laser wavelengths. Because Raman spectrometers are set up to display the wavenumber shift with the laser line set at zero, Raman lines appear at the same wavenumber but fluorescence lines appear to shift by an amount equal to the wavenumber difference between the laser lines.

Spectral line shapes are dependent on the firing times and temperatures used during synthesis. In $LiDyS_2$ (Fig. 4), firing at 800°C for 5 days produced the characteristic NaCl spectrum. Raising the firing temperature to 930°C caused a narrowing of the band combined with a resolution of the shoulder almost into an independent band. A different result was obtained with $LiHoS_2$ (Fig. 5) where a 5-day firing at 800°C produced a compound that gave

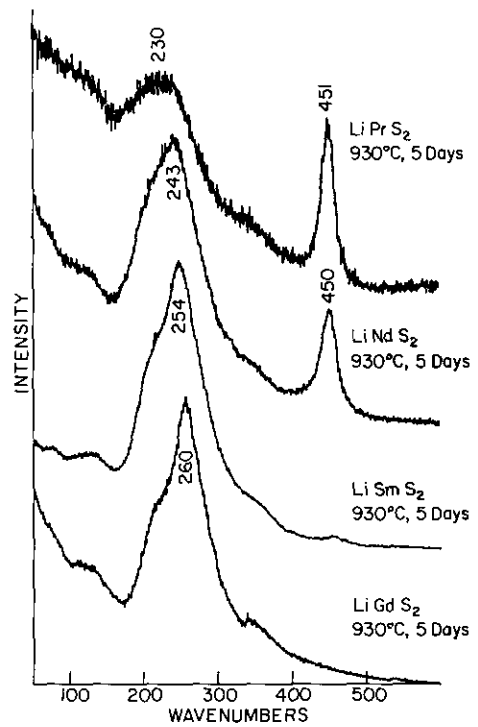

FIG. 2. Raman spectra for $LiLnS_2$ compounds with disordered NaCl structure.

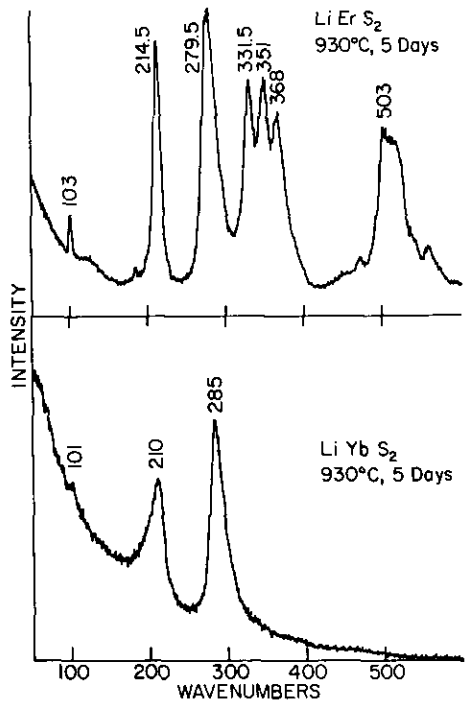

FIG. 3. Raman spectra for $LiLnS_2$ compounds with ordered α-$NaFeO_2$ ($NaHF_2$) structure.

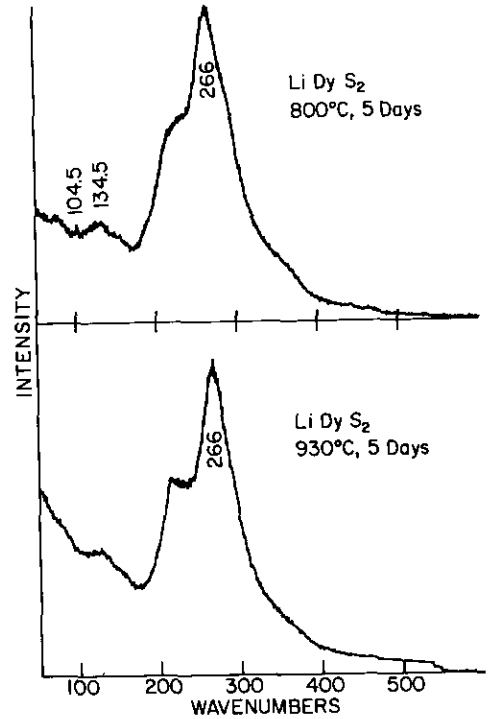

FIG. 4. Raman spectra of $LiDyS_2$. Firing temperature and time are given in the figure.

the NaCl pattern but a 5-day firing at 930°C produced material with the spectrum of the ordered structure. In this case, at least, the effect appears to be one of kinetics rather than equilibrium. Material prepared by a 1-day firing at 930°C also produced the NaCl pattern. Reaction of the component lithium carbonate and rare earth oxide to form the $LiLnS_2$ compounds appears to take place rather quickly but with a random distribution of cations. Cation ordering to form the α-$NaFeO_2$ structure requires longer times or higher temperatures.

INTERPRETATION

The classification and selection rules for the normal modes of the α-$NaFeO_2$ structure under the D_{3d} factor group are given in Table 1. The calculation predicts two Raman-active modes, one of A_{1g} and one of E_g symmetry. Consideration of the degrees of freedom contributed by the individual sublattices shows that both Raman bands are motions of only the anion sublattice. The cations are stationary during the execution of these vibrations as Tarte *et al.* (13) deduced. The two observed Raman bands are in exact agreement with this prediction. The nondegenerate A_{1g} mode corresponds to anion displacements along the c axis while the corresponding E_g modes produce vibrations perpendicular to the c axis. Because the Ln–S and Li–S bonds are parallel to the crystallographic axes (see Ohtani *et al.* (5) for an illustration of the struc-

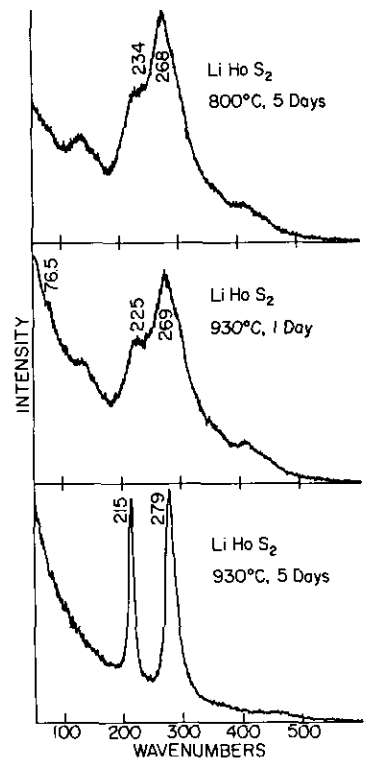

FIG. 5. Raman spectra of $LiHoS_2$. Firing temperature and time are given in the figure.

TABLE 1
Factor Group Classification of the Normal Modes of Ordered $LiLnS_2$ Compounds (Space Group $R\bar{3}m$; Factor Group D_{3d})

	Degrees of freedom					
D_{3d}	Li site	*Ln* site	S site	Lattice modes	Acoustic modes	Selection rules
A_{1g}	—	—	1	1	—	Raman
A_{2g}	—	—	—	—	—	—
E_g	—	—	1	1	—	Raman
A_{1u}	—	—	—	—	—	—
A_{2u}	1	1	1	2	z	IR, $E \parallel c$
E_u	1	1	1	2	(x, y)	IR, $E \perp c$

ture), these bands are an approximate measure of the metal–sulfur symmetric stretching modes. The 215-cm^{-1} band is distinctly sharper, especially in the $LiErS_2$ and $LiHoS_2$ spectra, suggesting that this may be the A_1g mode.

The wavenumbers of both bands decrease linearly with increasing ionic radius of the trivalent ion as Tarte *et al.* (13) reported. Unfortunately, the α-$NaFeO_2$ crystal structure contains an adjustable parameter for the anion position so that the metal–anion distances cannot be calculated from the lattice parameters alone so that one cannot further explore the vibrational wavenumber–bond length relationships without specific data on the individual crystal structures. Tarte *et al.* (13) also note that the band wavenumbers are essentially independent of the alkali ion radii.

The primitive cell of the NaCl structure is diatomic. There is only one vibrational mode with T_{1u} symmetry in the O_h factor group. The T_{1u} mode is infrared but not Raman active. Compounds with the NaCl structure should have no first-order Raman spectra. This is indeed the case for *AX* compounds with the rocksalt structure such as NaF, NaCl, and MgO. However, a single broad band with full intensity appears in the spectra of the disordered $LiLnS_2$ compounds with the NaCl structure.

The broadening of Raman bands in disordered compounds is generally taken to be the result of the relaxation of the $\mathbf{k} = 0$ momentum conservation selection rule. Considering the Raman band of the disordered NaCl-structure compounds, the disorder has the effect of relaxing the selection rule of the tensor coupling operator. The broad band should then be a map of the density of states in the disordered structure.

Some evidence for this hypothesis is obtained from the second-order Raman spectra of NaCl-structure compounds (15). The second-order spectra of NaF and NaCl consist of a broad band centered at roughly twice the transverse mode wavenumber. This broad band has sharper bands as shoulders on both wings of the main band. The shoulders seen on compounds of the smaller rare earths may be part of the intrinsic dynamics of the system or it may indicate a partial ordering on an atomic scale. Calculations of density-of-states functions for NaCl and NaF show many sharp maxima which do not appear in either the second-order Raman spectra of the diatomic crystals or in the first-order spectra of the disordered $LiLnS_2$ compounds.

SUMMARY AND CONCLUSIONS

The series of compounds $LiLnS2$ (*Ln* = Pr to Yb) crystallize in either the disordered NaCl-type structure with a random distribution of Li and *Ln* on the cation sites or in the α-$NaFeO_2$-type structure which is a trigonally distorted ordered arrangement based on alternating monovalent and trivalent cation layers in the NaCl-type structure. The ordered structure produces two-band Raman spectra with band wavenumbers decreasing linearly with increasing rare earth ionic radii. The disordered structure produces an intense broad Raman band in violation of selection rules for the NaCl structure. The broad band is interpreted as a map of the density of states in the NaCl-type disordered structure made Raman active by breakdown of the $\mathbf{k} = 0$ selection rule.

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