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Effect of Configuration Crossover on the Electronic Raman Scattering by 4f Multiplets

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The effect of configuration crossover on excited $4f^6(^7F_J)$ levels has been investigated by electronic Raman scattering in $\mathrm{Sm}_{1-x}\mathrm{Y}_x\mathrm{Se}$ and $\mathrm{Sm}_{1-x}\mathrm{Y}_x\mathrm{S}$. The multiplet levels are wiped out when they merge with the conduction band, or when interacting with phonons. Polarized Raman-scattering data on $\mathrm{Sm}_{1-x}\mathrm{Y}_x\mathrm{S}$ for $x > 0.15$ show that the contribution from J-multiplet levels is unobservable and that the peak near 250 cm^{-1} arises from optic phonons and not from $J = 0 \rightarrow J = 1$ excitations.

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The anomalous features of the intermediate valence state of rare earth ions in solids arise from the degeneracy of nominally two $4f$ configurations. From previous Raman[1] and neutron studies[2] on SmS and $\mathrm{Sm}_{1-x}\mathrm{Y}_x\mathrm{S}$ it is believed that the ionic character of the original $4f$ configuration is still preserved at configuration crossover (CC) and beyond, and that a Hund's rule description is still valid. On this basis the lifetime broadening of excited $4f$-multiplet levels due to mixing with conduction-electron states has been predicted theoretically.[3]

In this Letter we show for the first time and convincingly by means of Raman scattering that the $4f$-multiplet structure is strongly affected near CC and becomes unobservable by Raman scattering beyond CC. The Raman feature observed[1] near 250 cm^{-1} in $\mathrm{Sm}_{1-x}\mathrm{Y}_x\mathrm{S}$ for $x > 0.15$ (beyond CC), exhibiting a clear-cut polarization characteristic opposite to that associated with the electronic $J=0 \rightarrow J=1$ excitation of Sm^{2+}, is due to optical phonons. In this connection we have carried out Raman-scattering experiments on $\mathrm{Sm}_{1-x}\mathrm{Y}_x\mathrm{Se}$, $\mathrm{Sm}_{1-x}\mathrm{Y}_x\mathrm{S}$, and $\mathrm{Sm}_{1-x}\mathrm{Gd}_x\mathrm{S}$ near, at, and beyond CC. We first establish the polarization selection rules for the electronic Raman scattering arising from the J multiplets by studying pure SmSe and SmS, and then show how these multiplet levels are affected by the Y substitution.

Single crystals of $Sm_{1-x}Y_xSe$, $Sm_{1-x}Y_xS$, and $Sm_{1-x}Gd_xS$ with NaCl structure were prepared by techniques that have been described before.[4] Polarized Raman spectra, with use of the 5145 Å Ar laser line, were obtained from freshly cleaved (100) faces, with the crystal kept under vacuum. The following geometries were used in backscattering from the (100) face: $\bar{x}(yy)x(\Gamma_1{}^+ + 4\Gamma_{12}{}^+)$, $\bar{x}(zy)x(\Gamma_{25}{}^+ + \Gamma_{15}{}^+)$, $\bar{x}(\bar{z}y, \bar{z}y)x(\Gamma_1{}^+ + \Gamma_{12}{}^+ + \Gamma_{25}{}^+)$, and $\bar{x}(zy, \bar{z}y)x(3\Gamma_{12}{}^+ + \Gamma_{15}{}^+)$. Here the antisymmetric $\Gamma_{15}{}^+$ Raman tensor component has been included in order to account for the electronic ($J = 0 \rightarrow J = 1, 3, 5$) Raman scattering. The first two geometries are those denoted in Figs. 1–3 by $\vec{E}_i \parallel \vec{E}_s$ and $\vec{E}_i \perp \vec{E}_s$, indicating the directions of the incident and scattered electric field vectors.

In Fig. 1 we show the electronic Raman scattering by the $Sm^{2+}4f^6({}^7F_J)$ configuration of SmSe at 80 K. The peaks correspond to excitations from the $J = 0$ ground state into the different $J \neq 0$ excited multiplet levels. The peak width is simply resolution limited. The peaks in Fig. 1 exhibit a clear-cut polarization dependence, alternating between $\vec{E}_i \perp \vec{E}_s$ and $\vec{E}_i \parallel \vec{E}_s$ for odd and even J values, respectively. The alternating residual weak scattering intensity for each J value in the opposite scattering configuration arises from nonideal geometric conditions. However, the weak additional peaks near 832 cm^{-1} and 2339 cm^{-1} in the $\vec{E}_i \perp \vec{E}_s$ geometry are real. The scattering intensity for odd as well as even J values exhibits a monotonic decrease with increasing J. The $J = 6$ level at 4010 cm^{-1} coincides with the $4f-5d$ excitation gap of SmSe.[5]

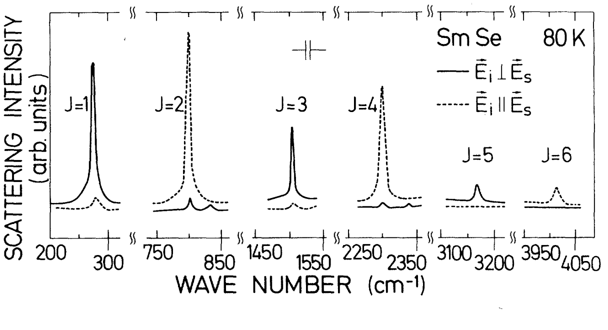

FIG. 1. Electronic Raman scattering from the $Sm^{2+}4f^6({}^7F_J)$ configuration in SmSe at 80 K under 5145 Å laser excitation with use of the backscattering from a (100) face (see text); $\vec{E}_i \parallel \vec{E}_s$ $(\Gamma_1{}^+ + 4\Gamma_{12}{}^+)$, $\vec{E}_i \perp \vec{E}_s$ $(\Gamma_{25}{}^+ + \Gamma_{15}{}^+)$, where $\vec{E}_{i(s)}$ denotes the direction of the electric-field vector of the incident (scattered) photon.

In Fig. 2 we present polarized Raman spectra of $Sm_{1-x}Y_xSe$ at 80 K for $x = 0$, 0.25, 0.50, 0.75, and 1.0. We have included one La-substituted sample with $x = 0.05$ to bridge the gap between $x = 0$ and $x = 0.25$. In this sample we observe be-

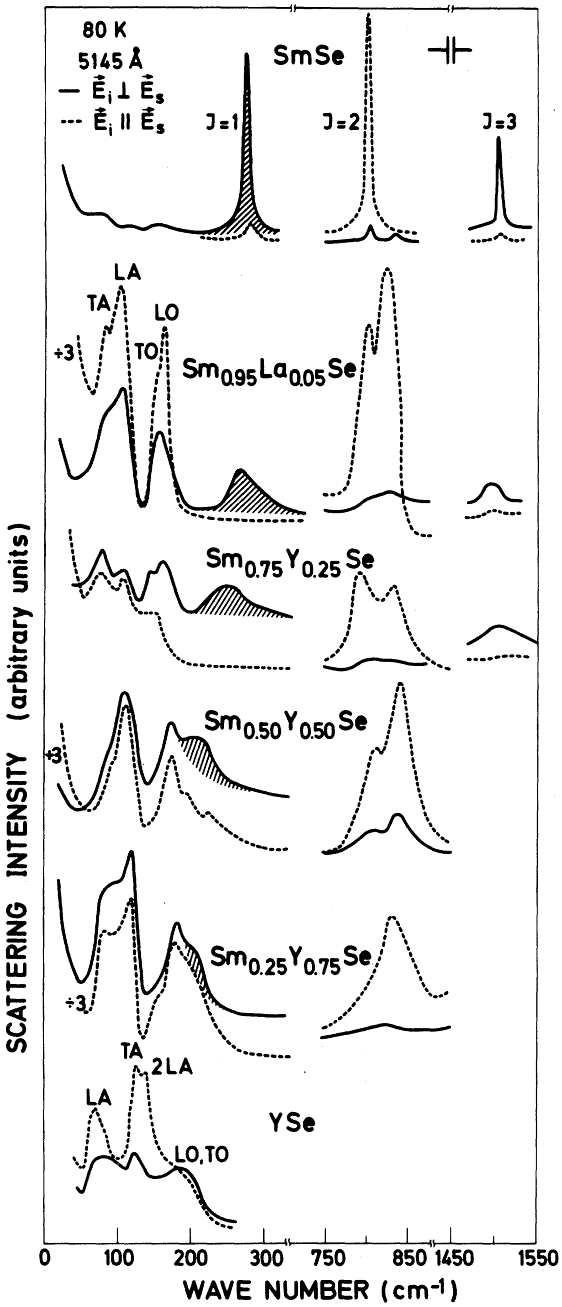

FIG. 2. Electronic and phonon Raman scattering of $Sm_{1-x}Y_xSe$ at 80 K for different values of $0 \leq x \leq 1.0$; the scattering geometries are the same as in Fig. 1. Data for one La substitution with $x = 0.05$ are included.

low 200 cm^{-1} first-order defect-induced Raman scattering from acoustic and optic phonons which is absent in pure SmSe. The $J=1$ peak for $x=0.05$ La substitution has drastically broadened compared to that of pure SmSe (275 cm^{-1}) and has shifted to 266 cm^{-1}. The $J=2$ peak is unshifted, but reduced in intensity by about 20% with respect to that of pure SmSe. A stronger satellite peak appears near 823 cm^{-1}. The $J=3$ peak is unshifted, but is strongly reduced in intensity and broadened, compared to that of SmSe. All J levels higher than $J=3$ are unobservable.

With increasing x the peak corresponding to the $J=1$ level progressively broadens and merges with the phonons for $x=0.50$ Y. It is barely seen for $x=0.75$ Y. The $J=2$ peak changes in intensity as well as shape, but does not disappear even at $x=0.75$ Y. On the contrary, the $J=3$ peak is not observed for $x>0.25$ Y. The phonon assignment given in Fig. 2 for $x=0.05$ La and YSe follows from that of $Sm_{1-x}Y_xS$ for $x=0$ and 1.0.[6,7]

As Y is substituted for Sm in SmSe, the lattice parameter shrinks, and in analogy with the behavior of SmSe under pressure we may expect the bottom of the 5d conduction band to approach the 4f level. With the progressive closing of the 4f−5d gap, the higher lying 4f-multiplet levels will overlap one by one with the conduction band. When this happens, we believe, the latter get broadened so much as to loose their distinct character and are progressively wiped out. This is the reason for the progressive disappearance of the electronic Raman peaks corresponding to the higher-lying J-multiplet levels, with increasing Y concentration. The fact that one is able to see a Raman peak corresponding to the $J=2$ level even in $Sm_{0.25}Y_{0.75}Se$ must mean that the 4f−5d gap is still present and should at least be 0.1 eV. This is consistent with the fact that $Sm_{1-x}Y_xSe$ does not undergo a transition into a homogeneously mixed-valent phase for all values of x as concluded from lattice constant and magnetic susceptibility data.[8]

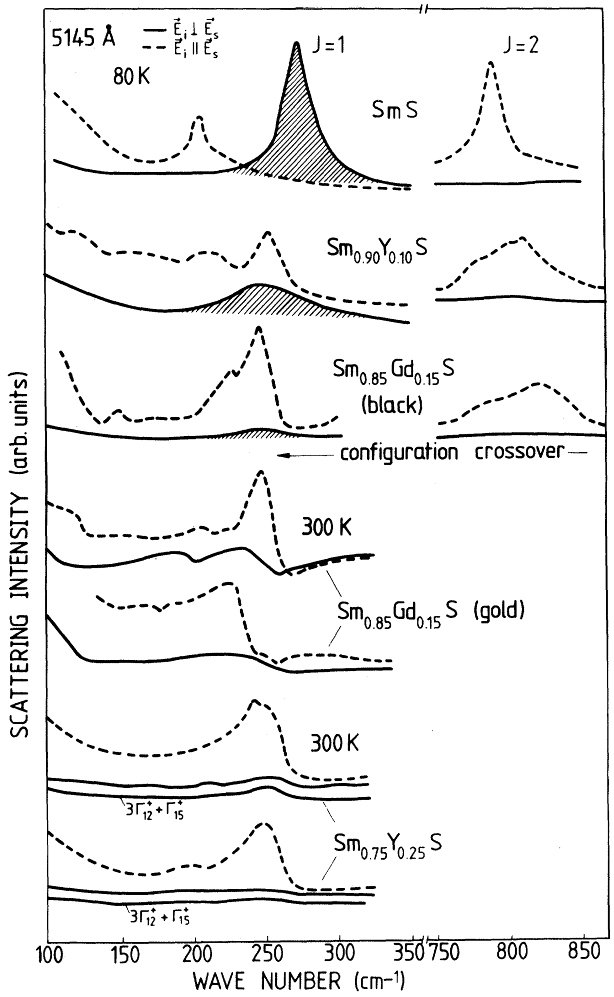

FIG. 3. Polarized Raman spectra of $Sm_{1-x}Y_xS$ ($x=0.0$, 0.10, 0.25) and of $Sm_{0.85}Gd_{0.15}S$ (black) and $Sm_{0.85}Gd_{0.15}S$ (gold, pressure transformed at $p>4$ kbar) at 80 K. Scattering geometries as in Fig. 1, including $3\Gamma_{12}^{+}+\Gamma_{15}^{+}$ for $Sm_{0.75}Y_{0.25}S$. The spectra for $x\gtrsim 0.15$ are also shown at 300 K.

To clarify the phonon versus electronic (magnetic) contributions in $Sm_{1-x}Y_xS$ we have measured polarized Raman spectra for $x=0.0$, 0.10, 0.25, 0.30, and 0.35 at 300 K and 80 K. For SmS it has been shown that the $J=1$ peak, and consequently (see Fig. 1) the $J=3, 5$ peaks, appears only in the antisymmetric Γ_{15}^{+} component ($\vec{E}_i \perp \vec{E}_s$).[9] In Fig. 3 we show polarized Raman spectra for $x=0.0$, 0.10, and 0.25 at 80 K. The "crucial" case of $Sm_{0.85}Gd_{0.15}S$ in its black phase (near CC) and its pressure-transformed ($p>4$ kbar) gold phase (beyond CC) has been included. The spectra for $x\gtrsim 0.15$ are also shown at 300 K. In addition we show for $Sm_{0.75}Y_{0.25}S$ the $3\Gamma_{12}^{+}+\Gamma_{15}^{+}$ spectra.

Contrary to the case of $Sm_{1-x}Y_xSe$, the separation between phonons (near 205 cm^{-1}) and the $J=1$ peak (near 275 cm^{-1}) in SmS has already disappeared for small Y substitutions, as seen for $Sm_{0.90}Y_{0.10}S$. Consequently, the $J=1$ peak is seen to shift towards lower energy with respect to its position in SmS and is subject to strong broadening. It is hardly observable near CC in $Sm_{0.85}Gd_{0.15}S$ (black). The strong broadening of the $J=1$ level upon approaching CC ($0<x\leq 0.15$), which

cannot be observed as clearly in unpolarized spectra,[1] arises most likely from the strong electron-phonon interaction.[6,7] The latter acts apart from the effect of the conduction electrons on the higher-lying J levels in $Sm_{1-x}Y_xSe$ and $Sm_{1-x}Y_xS$ (see below).

The Raman spectra of the intermediate valence phase ($x \gtrsim 0.15$) in Fig. 3 are dominated by the broad band near 250 cm^{-1}, which appears only in the Γ_1^+ component ($\vec{E}_i \parallel \vec{E}_s$). Any residual scattering intensity in the $\vec{E}_i \perp \vec{E}_s$ spectra at room temperature is due to second-order Raman scattering from acoustic phonons and is strongly quenched at 80 K. Evidently, any contribution from the $J=0 \rightarrow J=1$ excitation is absent near 250 cm^{-1}. Thus our polarized Raman spectra of $Sm_{0.85}Gd_{0.15}S$ (gold, beyond CC) and of $Sm_{1-x}Y_xS$ ($x > 0.15$) show that the peak near 250 cm^{-1}, which appears only in the Γ_1^+ component and coincides for $Sm_{0.75}Y_{0.25}S$ with the optic phonons,[10] is due to defect-induced first-order Raman scattering from optic phonons and not due to the $J=0 \rightarrow J=1$ excitation, as was concluded from previous unpolarized Raman data.[1] A detailed analysis of the Γ_1^+-only scattering intensity of $Sm_{0.75}Y_{0.25}S$ in terms of a lattice-dynamical model will be given elsewhere.[7]

The behavior of the $J=2$ level for $0 \leq x \leq 0.15$ in Fig. 3 is in agreement with the observations by Tsang.[1] However, we disagree on the point that in our measurements the $J=2$ peak is unobservable for $x \gtrsim 0.15$ (beyond CC) at 300 K as well as at 80 K. In no spectrum in Fig. 3 did we observe any $J \geq 3$ levels.

In neutron scattering measurements on powdered $Sm_{0.75}Y_{0.25}S$ an inelastic peak near 31 meV (250 cm^{-1}) is seen.[2] From its temperature dependence and comparison with SmS it was concluded that the peak is due to magnetic $J=0 \rightarrow J=1$ excitations. However, in the neutron scattering studies on metallic SmS under pressure reported by McWhan *et al.*[11] no evidence for either a (Sm^{2+}) $J=0 \rightarrow J=1$ excitation or a (Sm^{3+}) $\Gamma_7 \rightarrow \Gamma_8$ crystal field excitation was found. The latter study is consistent with our findings above. On the other hand the broad peak (~120 cm^{-1} wide) centered around 31 meV seen in neutron scattering on $Sm_{0.75}Y_{0.25}S$[2] appears to result from magnetic scattering. It is possible that a broad peak, especially weak in intensity would be difficult to observe in Raman-scattering studies. Perhaps the neutron and Raman peaks have different origins. We believe that a neutron study of a single crystal of $Sm_{0.75}Y_{0.25}S$ would provide some clues to this very important question.

Hirst[3] has predicted the mixing-decay widths of the excited $4f$-multiplet levels for SmS near and beyond CC. For a particular case near CC, which might be realized by our $Sm_{0.25}Y_{0.75}Se$ and $Sm_{0.90}Y_{0.10}S$ samples, sharp levels are expected for $J=0, 1, 2, 5$, and 6, whereas for $J=3, 4$ some finite broadening is indicated. However in our Raman-scattering experiments on the above two samples the $J \geq 3$ multiplet levels are not seen. It is not improbable that they are broadened to such an extent (> 300 cm^{-1}) they have become unobservable. Our results do reflect that the $J = 1, 2$ levels are subject to strong broadening.

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