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To cite this version:
H. Mook, T. Penney, F. Holtzberg, M. Shafer. MAGNETIC EXCITATIONS IN THE INTERMEDIATE VALENCE SYSTEM Sm0.75 Y0.25S. Journal de Physique Colloques, 1978, 39 (C6), pp.C6-837-C6-839. 10.1051/jphyscol:19786373 . jpa-00217840

HAL Id: jpa-00217840
https://hal.archives-ouvertes.fr/jpa-00217840
Submitted on 1 Jan 1978

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MAGNETIC EXCITATIONS IN THE INTERMEDIATE VALENCE SYSTEM\textsuperscript{\dagger} \textsuperscript{\ddagger} Sm\textsubscript{0.75}Y\textsubscript{0.25}S

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Résumé.- Nous avons étudié par la diffusion inélastique de neutrons, les excitations magnétiques des composés SmS et Sm\textsubscript{0.75}Y\textsubscript{0.25}S. Pour le SmS les résultats s'expliquent facilement à l'aide d'une théorie simple du type champ-moyen. Par contre l'alliage se comporte comme un système à valence mixte. Les largeurs d'énergie d'excitation du Sm\textsubscript{0.75}Y\textsubscript{0.25}S sont de l'ordre de 15 meV ce qui correspond à une durée de vie moyenne d'environ $3 \times 10^{-15}$ s.

Abstract.— Neutron inelastic scattering measurements have been made for the magnetic excitations in SmS and Sm\textsubscript{0.75}Y\textsubscript{0.25}S. The results for SmS can be understood using a simple mean-field theory, but the Sm\textsubscript{0.75}Y\textsubscript{0.25}S measurements show a temperature dependence and linewidth that appear to result from intermediate valence effects. The energy widths of the excitations in Sm\textsubscript{0.75}Y\textsubscript{0.25}S are on the order of 15 meV corresponding to a lifetime of about $3 \times 10^{-15}$ s.

There has been wide interest recently in the samarium monochalcogenides because of their unusual physical properties /1/. In particular, SmS undergoes a pressure induced semiconductor to metal transition at about 6.5 kbar in which there is a large volume decrease but no change in the crystal structure /2/. This phase transition is thought to result from a change in the Sm ion from a Sm\textsuperscript{++} ($^7F_0$) configuration to an intermediate valence configuration which is some sort of mixture of the Sm\textsuperscript{++} and Sm\textsuperscript{+++} ($^7H_{25}$) configuration. A similar lattice collapse can be obtained by alloying YS with SmS. In this case the Sm configuration change can be studied as a function of temperature and high pressure cells are not needed/3,4/. The unusual magnetic properties associated with this lattice collapse and the absence of magnetic ordering at low temperatures lead Maple and Wohlleben to the conclusion that the collapsed phase can be described by a fluctuating state in which there are rapid fluctuations between the Sm\textsuperscript{++} and Sm\textsuperscript{+++} configurations /5/. The configurations of SmS and Sm(Y)S have been examined by both X-ray photoemission/6,8/ and Mössbauer/9/ isomer shift measurements at room temperature. These two sets of measurements show that both the Sm\textsuperscript{++} and Sm\textsuperscript{+++} valence states exist in collapsed SmS but while X-ray photoemission results show separate sets of spectra for the two configurations, the Mössbauer measurements show a single sharp line corresponding to an intermediate valence. The Mössbauer measurements show that any fluctuations between the two valence states must be faster than $10^{-9}$ s. The time scale for X-ray photoemission studies is much shorter, on the order of $10^{-16}$ s, so that it appears that the fluctuation time must be between $10^{-9}$ and $10^{-16}$ s. Neutron scattering studies usually involve energy resolutions of a few millivolts. A linewidth of this magnitude would correspond by $\Delta E\tau$ to a time of about $10^{-11}$ s, which appears to be the time scale of interest in the mixed valence problem.

Our measurements were performed on powdered samples of Sm\textsubscript{0.75}Y\textsubscript{0.25}S in which the Sm is isotopically enriched to 99 % $^{151}$Sm to avoid the high capture cross section of naturally occuring Sm. Lattice constant measurements, assuming Vegard's law, suggest that the valence state is 40 % Sm\textsuperscript{++} at room temperature when the crystals have a gold color and about 70 % Sm\textsuperscript{++} at 100 K when the material is black. The transition takes place over a temperature range of about 50 K centered at 200 K.

The $^7F_0$ state does not split in a crystalline field but transitions can be observed between the $^7F_0$ ground state and the first multiplet level $^7F_1$. This transition has been studied by Shapiro et al. /10/ for SmS which is thought to be in the pure Sm\textsuperscript{++} state at all temperatures. Their measurements demonstrated the dispersion of the $^7F_0 - ^7F_1$ transition but did not include intensity measure-
ments. We have measured the strength of the $^7F_2 - ^7F_1$ transition as a function of temperature using time-of-flight techniques. The results of the measurements are shown in figure 1.

As one warms up from $T=0$ the intensities of the peaks diminish, they narrow, and the center of gravity shifts upward in energy. The narrowing and shift is consistent with the change in dispersion which varies from about 6 meV at 15 K to 3 meV at room temperature. The width of the peak is well accounted for by dispersion and spectrometer resolution and no intrinsic broadening of the line was observed. The plot on the bottom of figure 1 shows the intensity of $^7F_2 - ^7F_1$ transition plotted against temperature using a scale such that the expected temperature behaviour of the cross section calculated from a mean-field-random-phase-approximation (MF-RPA) given in reference /10/ is set to unity. The agreement appears to be satisfactory and we feel that SmS can be understood in a straightforward manner within the (MF-RPA) approximation.

Figure 2 shows an identical set of measurements made on Sm$_{0.75}$Y$_{0.25}$S. One notices immediately that the lines are much broader and that the temperature dependence appears to be different than for SmS. The graph at the bottom of figure 2 shows a similar intensity plot as that given in Figure 1 and we see that the intensities do not fit the (MF-RPA) temperature dependence of Sm$^{+++}$.

The variation from (MF-RPA) theory can be explained by a change in the Sm valence state from Sm$^{++}$ to Sm$^{+++}$ upon warming and the dotted line shows the expected temperature dependence if the amount of Sm$^{+++}$ in the system is given by the lattice constant interpolation between Sm$^{++}$ and Sm$^{+++}$. The agreement in this case appears to be satisfactory.

The measured width of the transition is very broad, on the order of 15 meV. Raman scattering measurements on Sm$_{1-x}$Y$_x$S have shown that some broadening occurs in the $^7F_2 - ^7F_1$ transition as Y is introduced into SmS /11/. However, because of the reflectivity changes in the sample, intensity changes with temperature could not be measured accura-
Because some broadening may be due to alloy effects the most we can say from the neutron experiments is that there is an upper bound of about 15 meV in the linewidth from mixed valence effects. This tells us that the fluctuation time for the mixed valence state must be longer than $3 \times 10^{-16}$ s, a value considerably larger than the lower bound given by the photoemission measurements.

One might expect to see strong transitions from the crystal field excitations of the $\text{Sm}^{++}$ ($^4H_{15/2}$) configuration. However, the crystal field splitting should be at most about 10 meV and if the linewidths are as broad as the $^7F_3^0$-$^7F_1$ transition the $^4H_{15/2}$ configuration would not be well defined. This is in agreement with the magnetic measurements which show no indication of a large Curie component to the susceptibility.

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