Magnetic Excitations in Semiconducting SmS

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Inelastic neutron scattering measurements of the Sm^{2+}, ${}^7F_0\rightarrow{}^7F_1$ singlet-triplet exciton dispersion in semiconducting SmS at 77, 197, and 273°K are reported. The results are in good agreement with current theory predicting the temperature dependence of the singlet-triplet excitations. The ${}^7F_0$-${}^7F_1$ separation is found to be (420 ± 2)°K, in agreement with the free-ion value of 422°K, while the exchange interactions are characteristic of a magnetic semiconductor. The implications for the Sm-ion eigenstate are discussed.

SmS has recently been the subject of a number of optical,[1] microwave,[2] and photoemission[3] spectroscopic investigations. This work has been motivated by the unusual electronic properties of SmS and, in particular, the pressure-induced semiconductor-metal transition[1] at 7 kbar. This transition is thought to arise from a $4f^6\rightarrow4f^5 5d^1$ Sm-ion configurational change, where the valence of the Sm ion changes from Sm^{2+} to Sm^{3+}. Indeed, there has been considerable controversy[3-5] concerning the nature of the Sm wave function in the semiconducting and metallic states. In this Letter we report an inelastic magnetic neutron scattering study of the dispersion relation of the S_m^{2+} $(4f^6)$ ${}^7F_0\rightarrow{}^7F_1$ electronic excitation in SmS at atmospheric pressure and at temperatures of 77, 197, and 273°K. This gives detailed information about the Sm eigenstate and Sm-Sm interactions in the crystal. Furthermore, as we shall show, the ${}^7F_0$-${}^7F_1$ excitation serves as a model paramagnetic singlet-triplet system[6] and, as such, allows a detailed test of the mean-field–random-phase-approximation (MF-RPA) theory[7] for the temperature-dependent dynamics of the idealized singlet-triplet model.

From previous measurements[1-4] it is known that at atmospheric pressure the Sm-ion wave function is predominantly $\mathrm{Sm}^{2+}(4f^6)$ in character although it has been proposed[4] that there may be up to 15% $\mathrm{Sm}^{3+}(4f^5 5d^1)$ admixture. We consider first the theory for the excitations and the concomitant neutron scattering in the limit that the wave function is pure $4f^6$. We shall discuss the significance of this assumption later in this note.

For an assemblage of $\mathrm{Sm}^{2+}(4f^6)$ ${}^7F$ ions the Hamiltonian may be written

$$\mathcal{H}=\Delta\sum_i\vec{\mathrm{L}}_i\cdot\vec{\mathrm{S}}_i+\sum_i\mathcal{H}_{\mathrm{CEF},i}-2\sum_{i>j}J_{ij}\vec{\mathrm{S}}_i\cdot\vec{\mathrm{S}}_j, \qquad (1)$$

where Δ is the spin-orbit coupling constant, $\mathcal{H}_{\mathrm{CEF}}$ is the SmS cubic-crystal-field Hamiltonian, and J_{ij} is the isotropic exchange coupling between the Sm^{2+} *spins* i and j. In this case, Eq. (1) is best treated by diagonalizing each term in succession. Diagonalization of the spin-orbit coupling term yields the ${}^7F_0$ atomic manifold lowest, ${}^7F_1$ at energy Δ, ${}^7F_2$ at energy 3Δ, etc. In the free ion[8] $\Delta=422$°K so that for measurements below room temperature we need only consider the ${}^7F_0$ and ${}^7F_1$ J manifolds. In SmS, because of the O_h symmetry, the crystal-field term $\mathcal{H}_{\mathrm{CEF}}$ will couple the ${}^7F_0$ and ${}^7F_1$ manifolds to the higher-J multiplets but it will not lift the ${}^7F_1$ triple degeneracy. The change in $E({}^7F_1)-E({}^7F_0)$ due to $\mathcal{H}_{\mathrm{CEF}}$ in SmS is almost certainly less than 10°K.

The exchange term $J_{ij}\vec{\mathrm{S}}_i\cdot\vec{\mathrm{S}}_j$ serves to couple the ${}^7F_0\rightarrow{}^7F_1$ ionic excitations on sites i and j. Thus, the single-ion transition becomes a propagating excitation in the crystal. Indeed, it corresponds almost exactly to the idealized singlet-triplet model which has been discussed extensively in the literature.[6,7] Using the value $\langle{}^7F_1|S|{}^7F_0\rangle=2$, the ${}^7F_0$-${}^7F_1$ singlet-triplet dispersion relation within the MF-RPA approximation is given by[6]

$$\hbar\omega(\vec{\mathrm{k}})=\Delta[1-16R(T)J(\vec{\mathrm{q}})/\Delta]^{1/2}\,. \qquad (2)$$

where

$$J(\vec{\mathrm{q}})=\sum{}_j J_{ij}\exp[i\vec{\mathrm{q}}\cdot(\vec{\mathrm{r}}_i-\vec{\mathrm{r}}_j)]$$

and

$$R(T)=\frac{1-\exp(-\Delta/k_{\rm B}T)}{1+3\exp(-\Delta/k_{\rm B}T)}.$$

For a paramagnet this mode is triply degenerate. This result for the temperature renormalization factor $R(T)$ has not yet been tested experimentally. The ${}^7F_0$-${}^7F_1$ excitation may be studied directly throughout the Brillouin zone using magnetic inelastic neutron scattering. In the dipole approximation the neutron scattering cross section for excitation creation is given approximately by[6]

$$\frac{\partial^2\sigma}{\partial\Omega_f\partial\omega_f}=N\left(\frac{1.91e^2}{2mc^2}\right)^2\frac{k_f}{k_i}F^2(\vec{k})\frac{8\Delta}{\hbar\omega(\vec{k})}\delta(\omega(\vec{k})-\omega)\,\delta(\vec{k}_i-\vec{k}_f-\vec{k})\frac{1}{1+3\exp(-\Delta/k_{\rm B}T)},\tag{3}$$

where the symbols have their usual definitions.[9] In (3) we have used the cubic symmetry and the fact that $\langle{}^7F_1|L+2S|{}^7F_0\rangle=2$. We now consider the experimental technique and results.

The experiments were performed on a triple-axis spectrometer at the Brookhaven National Laboratory high-flux beam reactor on a single crystal of SmS made with the Sm^{154} isotope (the normal Sm^{156} has too large an absorption cross section for thermal neutrons). The sample, which was cylindrical in shape with a 5 mm diam and 15 mm length, was prepared by conventional techniques.[1] The mosaic distribution was approximately 1.5° full width at half-maximum. The crystal was mounted in a Cryogenics Associates CT-14 temperature-control cryostat with a [100] axis vertical. Constant-Q energy scans in the range 25–45 meV were performed with a fixed analyzer energy of 14.8 meV and a varying incident energy. Pyrolytic graphite crystals were used as monochromator, analyzer, and filter to eliminate higher-order contamination. 20-min horizontal collimation was used before the monochromator and 40-min collimation in the remainder of the spectrometer.

Measurements along several symmetry directions were performed at three different temperatures, 77, 197, and 273°K. The low-temperature data were taken along $[0,0,\zeta]$, $[\zeta,\zeta,0]$, and $[0,\zeta,1]$ ($\vec{\zeta}=a\vec{k}/2\pi$), while the high-temperature data were taken only along $[0,0,\zeta]$ and $[\zeta,\zeta,0]$. In all cases a single sharp peak was observed with energy varying between 31 and ~37 meV (1 meV = 11.6°K). This excitation could be identified as the singlet-triplet transition[10] rather than phonon scattering from the characteristic temperature and k dependence of the intensity as predicted by Eq. (3). Resolution calculations show that at 77°K the measured widths are accounted for by instrumental effects alone; thus these are long-lived elementary excitations. The experimentally measured dispersion curves are shown in Fig. 1. At $T=77$°K, $R(77)=0.983$; these data thence may be fitted by least squares with the theoretical dispersion relation, Eq. (2), to obtain precise values for Δ and the successive near-neighbor exchange constants J_1, J_2, and J_3. The theoretical dispersion curve so obtained is shown as the solid line in Fig. 1; as expected, the agreement is quite satisfactory. The values of the best-fit Δ and exchange constants are given in Table I. We shall discuss the significance of these interaction constants below. We consider first the higher-temperature data. As discussed above, in the MF-RPA approximation the temperature renormalization is determined simply by the factor $R(T)$ in Eq. (2). Thus using the values tabulated in Table I, the 197 and 273°K dispersion curves may be calculated without any adjustable parameters. The agreement with experiment is seen to be quite satisfactory, especially at 273°K where $R(T)=0.48$. This work thence represents the first proper test of the MF-RPA theory for the idealized *paramagnetic*

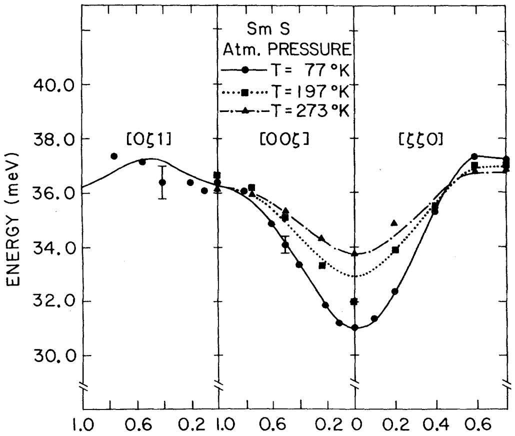

FIG. 1. Dispersion relations of the $\mathrm{Sm}^{2+}(4f^6)$ ${}^7F_0$-${}^7F_1$ singlet-triplet excitons at 77, 197, and 273°K. The lines are theoretical curves as described in the text.

TABLE I. Parameters for Sm^{2+} obtained from fit of Eq. (2) to the exciton dispersion at 77°K together with the corresponding values in EuO.

	Δ (meV)	J_1 (meV)	J_2 (meV)	J_3 (meV)	$J(0)= 12J_1+6J_2+24J_3$ (meV)
SmS	36.2 ± 0.2	0.043 ± 0.003	0.025 ± 0.007	-0.003 ± 0.001	0.60
EuO [a]	…	0.052 ± 0.001	0.013 ± 0.001	…	0.70

[a] L. Passell, O. W. Dietrich, and J. Als-Nielsen, in *Magnetism and Magnetic Materials—1971,* AIP Conference Proceedings No. 5, edited by C. D. Graham, Jr., and J. J. Rhyne (American Institute of Physics, New York, 1972), p. 1251.

singlet-triplet system. As discussed extensively elsewhere,[5,6,11] however, the *ferromagnetic* singlet-triplet model is more complicated and the various theories for it remain untested.

We now consider the implications of these results for the microscopic electronic states in semiconducting SmS. Firstly we note that the splitting factor, $\Delta=36.2\pm0.2$ meV $=(420\pm2)$°K, coincides to within the error with the free-ion $Sm^{2+}(4f^6)$ spin-orbit coupling value $\Delta=422$°K. Thus, in spite of the incipient metallic nature of SmS, the $4f^6$ electrons retain an almost purely atomiclike character. We may use the values tabulated in Table I to calculate the Van Vleck susceptibility at $T=0$ assuming pure $4f^6$ states. Within the mean-field approximation[2]

$$\chi_{\mathrm{VV}}(0)=8N\mu_{\mathrm{B}}^2/[\Delta-16J(0)] \\ =9.8\pm0.2\ \mathrm{cm}^3/\mathrm{mole}. \tag{4}$$

This may be compared with the experimental value[2,12] of 9.2 ± 0.3 cm^3/mole. Considering the combination of theoretical and experimental uncertainties, the agreement is most satisfactory. At the mimimum, it precludes any large (>10%) $Sm^{3+}(4f^5 5d^1)$ admixture, in agreement with the results of Campagna *et al.*[3]

The exchange interactions in SmS have already been extensively discussed by Birgeneau *et al.*[2] and our results are in close accord with their analysis although, of course, our experimental results are much more detailed since we obtain J_1, J_2, and J_3 separately. The exchange interactions are short-range, basically nearest and next-nearest neighbors alone, as expected in a magnetic semiconductor. Indeed there is close quantitative agreement between J_1 and J_2 in SmS and EuO as shown in Table I. This again argues for a relatively simple form for the Sm $4f$ wave function. We might also note that if the Sm ion in semiconducting SmS were in a mixed-valence state exhibiting interconfigurational fluctuations then the fact that we observe resolution-limited $^7F_0$-$^7F_1$ excitations would require that the fluctuation lifetime be longer than 10^{-11} sec, a bound 10^3 longer than that given by the photoemission measurements.[3,4]

Clearly it is desirable to extend these measurements to higher pressures into the metallic phase; this should give us detailed microscopic information about the variation of the Sm wave function and magnetism through the semiconductor-metal transition. Efforts to effect this are now underway.

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Low-Temperature Specific Heat of a One-Dimensional System: $K_2Pt(CN)_4Br_{0.3}\cdot 3(H_2O)$

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Measurements of the specific heat of $K_2Pt(CN)_4Br_{0.3}\cdot 3(H_2O)$ between 0.059 and 40 K reveal three unexpected features: (1) a contribution linear in temperature above ~0.15 K, (2) a sharp decrease in this linear contribution below ~0.15 K, and (3) a marked dependence upon the state of hydration of the sample above 6 K.

The continuing extensive interest[1] in the properties of one-dimensional (1D) systems stems in part from the unique properties inherent in 1D materials but also from the possibility that some of these materials may be a key to high-temperature superconductivity. Any successful description of these materials will have to account for not only the transport properties but also the thermodynamic properties such as the specific heat. In this Letter we report the specific heat C_p of the "mixed-valence" square planar compound[2] $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$ (KCP) between 0.059 and 40 K. Our results are summarized as follows: There is a contribution to C_p which varies linearly with temperature T for $T > 0.15$ K but below that temperature the linear contribution sharply decreases. Our observation of a linear contribution is contrary to the measurements on $K_2Pt(CN)_4Cl_{0.3}\cdot n(H_2O)$ [3] and tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ),[4] where the absence of a linear term was reported. We also measure a marked dependence of C_p upon the degree of hydration of the sample for $T > 6$ K.

The measurements were made in the temperature range 0.059 to 1.2 K using a thermal-relaxation method.[5] Five single crystals (0.210 g total) with the typical rodlike crystal habit (approximately 2 mm × 2 mm × 5 mm each) grown by the diffusion method[6] were selected, one end sanded flat, and mounted with Apiezon-*N* grease end-on to a sapphire substrate. To prevent loss of water from the sample, the calorimeter was flushed with dry N_2 gas and cooled in 15 min to 273 K and in 3 h to 77 K. After the gas was removed, the sample was cooled to 59 mK using a dilution refrigerator. The measurements between 1.2 and 40 K were made on three sets of samples (0.653, 0.735, and 0.680 g total) using a standard pulse calorimeter.[7] Seven of the rodlike crystals were flattened at one end and attached with Ge-7031 varnish to a Si holder. The samples were cooled quickly (in 10 min) to 77 K in air (to minimize the loss of water), the air was removed from the sample chamber, and the samples were then cooled to 1.2 K for measurement.

Figures 1 and 2 show our data for the temperature ranges 0.059–1.4 K and 1.2–3.7 K, respectively, plotted as C_p/T versus T^2. The sample numbers mean the crystals were selected from the same growth batch. If we analyze our data in a conventional manner and fit by the equation

$$C_p/T = \gamma + \beta T^2 + \delta T^4 \qquad (1)$$

we obtain $\gamma = 1.1 \pm 0.2$ mJ/K^2 mole, a Debye temperature $\Theta_D = 255 \pm 5$ K (from β assuming 20 atoms per molecule), and $\delta = (4 \pm 1)\times 10^{-4}$ mJ/K^6 mole.[8]