

Observation of intermultiplet transitions in $\text{SmFe}_{11}\text{Ti}$ by inelastic magnetic neutron scattering

O. Moze*

*Istituto Materiali Speciali per Elettronica e Magnetismo del Consiglio Nazionale delle Ricerche, via Chiavari 18/a,
I-43100 Parma, Italy*

R. Caciuffo

*Dipartimento di Scienze dei Materiali e della Terra, Università di Ancona, via Breccie Bianche, I-60131 Ancona, Italy
and Neutron Science Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, United Kingdom*

Hong-Shuo Li, Bo-Ping Hu, and J. M. D. Coey

Department of Pure and Applied Physics, Trinity College, University of Dublin, Dublin 2, Ireland

R. Osborn and A. D. Taylor

Neutron Science Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, United Kingdom

(Received 22 November 1989)

Magnetic neutron spectroscopy of $\text{SmFe}_{11}\text{Ti}$ reveals a dispersionless electronic excitation corresponding to transitions between levels of the exchange-split ground- and first-excited-state multiplets of the Sm^{3+} ion. The observed excitation energy of 175.5 meV at $T = 20$ K may be accounted for in the framework of an exchange and crystal-field model by assuming a bare spin-orbit splitting of 129 meV for the $J = \frac{5}{2}$ and $\frac{7}{2}$ multiplets. The neutron spectroscopy data are explained with the same parameters used to fit the experimental magnetization curves of single-crystal $\text{SmFe}_{11}\text{Ti}$.

I. INTRODUCTION

The application of inelastic magnetic neutron scattering to the investigation of spin-orbit and Coulomb transitions between different multiplets in f -electron systems has been one of the major successes of neutron spectrometers at advanced spallation sources. Experiments on metallic Pr (Ref. 1) have shown that the energy separation between Russell-Saunders terms with different values of the orbital angular momentum is sensitive, in a metallic environment, to the screening by the conduction electrons of the intra- f Coulomb potential. Intermultiplet splittings are also sensitive to the degree of hybridization of f -states with band electrons and are then of particular interest for actinides and heavy-fermion systems where the hybridization is expected to be strong. This has been demonstrated in recent measurements on CeAl_3 (Ref. 2) and $\text{U}(\text{Pd}_{1-x}\text{Pt}_x)_3$.³ Microscopic information on the exchange and crystal fields may also be obtained if these are strong enough to produce observable splittings of the J multiplets. A similar insight may also be expected in systems where the magnetic properties are dominated by the indirect $3d$ - $4f$ interaction.

This paper reports the results of high-energy-transfer ($\hbar\omega > 100$ meV) neutron spectroscopy measurements performed on polycrystalline $\text{SmFe}_{11}\text{Ti}$. This compound has recently aroused considerable interest as the ferromagnetic Curie temperature of 584 K is comparable to that of $\text{Nd}_2\text{Fe}_{14}\text{B}$. The very large uniaxial magnetocrystalline anisotropy (arising from the interaction of the Sm^{3+} $4f$ electronic cloud with the surrounding charges) as well as the high-Fe content make this compound attractive as a

potential permanent magnet material. It crystallizes in the body-centered tetragonal ThMn_{12} structure^{4,5} (space group $I4/mmm$) with the Sm at the $2a$ Th site (point symmetry $4/mmm$) and the transition elements distributed nonrandomly over the three Mn sites, $8f$, $8i$, and $8j$.⁶ The average magnetic moment at 20 K on the Fe sites, as deduced from the sublattice magnetization of YFe_{11}Ti , is about $19\mu_B$ /formula unit.⁷ Neutron-diffraction measurements, however, show that the Fe magnetic moments are dependent on their local environment with Fe moments of 1.7, 1.5, and $1.2\mu_B$ at the $8i$, $8f$, and $8j$ sites, respectively, at 4.2 K.⁸ The spontaneous magnetization at room temperature is slightly larger than that of the iron sublattice, suggesting a parallel coupling of the Fe and Sm moments as is usually the case for light rare earths.

The Sm ions are trivalent with a $4f^5$ ($L = 5$, $S = \frac{5}{2}$) electronic configuration and ${}^6H_{5/2}$ Russell-Saunders ground-state multiplet. However, with the $J = \frac{7}{2}$ ${}^6H_{7/2}$ multiplet at only 129 meV above the ground state,⁹ a substantial mixing of states with different J by the very large exchange field due to the iron sublattice may be anticipated. Such J -mixing effects have, in fact, been proposed for $\text{SmFe}_{11}\text{Ti}$ in order to account for the large anisotropy field at room temperature and the occurrence of a type-II first-order magnetization process (FOMP) below 150 K when a magnetic field of 9 T is applied perpendicular to the crystallographic c axis.¹⁰ Intermultiplet mixing by exchange and crystal field has also been proposed to explain the magnetocrystalline anisotropy in Sm intermetallics such as SmCo_5 (Ref. 11) and SmFe_2 .¹²

The aim of the present measurements was to provide spectroscopic data on the electronic state of Sm in this

compound which could substantiate such a hypothesis. This should, in principle, lead to an accurate determination of the $4f$ -electron J -mixing eigenfunctions and the effects of the Sm^{3+} crystal field and the Sm-Fe exchange interactions on the J -multiplet level scheme.

II. EXPERIMENTAL DETAILS AND RESULTS

The experiment was performed on the high-energy transfer spectrometer (HET) at the U. K. spallation neutron source ISIS of the Rutherford Appleton Laboratory. HET is a direct-geometry chopper spectrometer¹³ equipped with three ^3He detector banks, one lying at 4 m from the sample and covering a full scattering angle range $\Phi=3^\circ-7^\circ$, the other at 2.5 m from the sample and spanning an angular range between 10° and 30° , the last one providing data at a large angle, $\Phi=136^\circ$. Incident energies from 30 to 2000 meV may be selected at the sample position by phasing a Fermi chopper spinning at 400–600 Hz to the source proton pulse. This gives a wide choice of experimental configurations with high-energy resolution and small scattering vector Q . The scattering function $S(Q, \omega)$ is obtained by sorting the signals from the detectors according to the scattering angle and the neutron time of flight.

The sample consisted of 72 g of polycrystalline $\text{SmFe}_{11}\text{Ti}$ mounted in an aluminum can onto the cold plate of a closed-cycle refrigerator. Measurements were performed at temperatures of 20 and 290 K with incident energies of 400 and 500 meV. Since the specimen was prepared using Sm with natural isotopic composition, complications arise due to the presence of the strong Sm^{149} neutron absorption resonances at about 98 and 873 meV. However, with the chosen incident energies, both incident and down-scattered neutrons have an absorption cross section sufficiently small to make possible the obser-

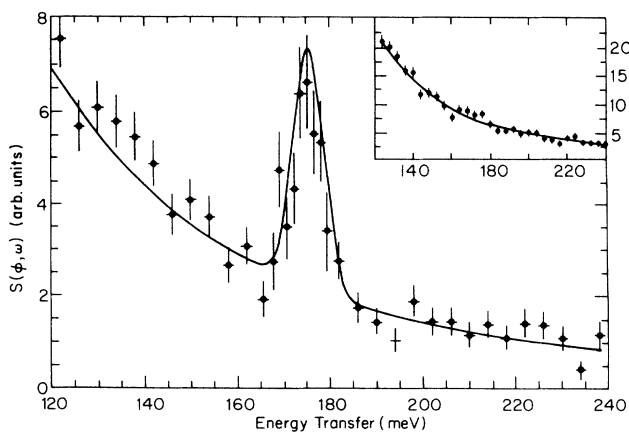


FIG. 1. Inelastic neutron-scattering cross section of $\text{SmFe}_{11}\text{Ti}$ at 20 K, measured with an incident-beam energy of 400 meV at an angle of 5° . The spectrometer energy transfer resolution at 176 meV is about 8 meV. The smooth line is the fit to a Gaussian line shape, a sloping background, and a Gaussian multiple scattering. The inset shows the data obtained in the same configuration for YFe_{11}Ti .

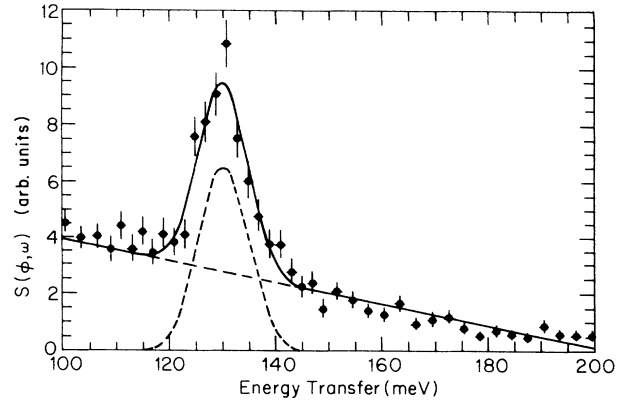


FIG. 2. Inelastic neutron-scattering cross section of SmMn_4Al_8 at 25 K, measured with an incident-beam energy of 400 meV at an angle of 5° . The smooth line is the fit to a Gaussian line shape and a sloping background.

vation of magnetic excitations up to 250 meV. An 80-g sample of the isostructural compound YFe_{11}Ti (encapsulated in an identical container) was also measured in order to identify contributions to the neutron spectra arising from magnetic modes of the Fe sublattice. A 30-g sample of the isostructural compound SmMn_4Al_8 was also used in order to measure the bare spin-orbit splitting. In this compound there is no magnetic ordering down to at least 4.2 K so that there are no complications arising from exchange fields. The spectra from different runs and at different angles were normalized to each other by using the scattering from a vanadium standard. X-ray-diffraction measurements confirmed that all the three compounds were single phase with all diffraction lines consistent with the ThMn_{12} tetragonal crystal structure.

The scattering function obtained for $\text{SmFe}_{11}\text{Ti}$ at $T=20$ K, with an incident energy of 400 meV and full scattering angle $\Phi=5^\circ$, is shown in Fig. 1. A dispersionless electronic excitation was observed at $175.5(5)$ meV with a full width at half maximum $\text{FWHM} = 8(1)$ meV corresponding to the spectrometer resolution. No peaks are observable in the same energy region for YFe_{11}Ti (see inset of Fig. 1) ruling out the possibility that the excitation arises from dispersionless Fe modes. In Fig. 2 is shown the measured spectra at 25 K for SmMn_4Al_8 clearly showing the spin-orbit splitting of about 130 meV characteristic of Sm^{3+} . When the temperature was raised to 290 K the peak position for $\text{SmFe}_{11}\text{Ti}$ shifted to $169.1(5)$ meV while its FWHM increased to about 13 meV.

III. ANALYSIS AND DISCUSSION

The Q dependence of the integrated intensity of the magnetic peak, as obtained from data taken at higher scattering angles and different incident energy, is compared in Fig. 3 with the theoretical inelastic form factor for the $J=\frac{5}{2} \rightarrow J=\frac{7}{2}$ dipole transition in Sm^{3+} . This is calculated by Balcar and Lovesey¹⁴ as,

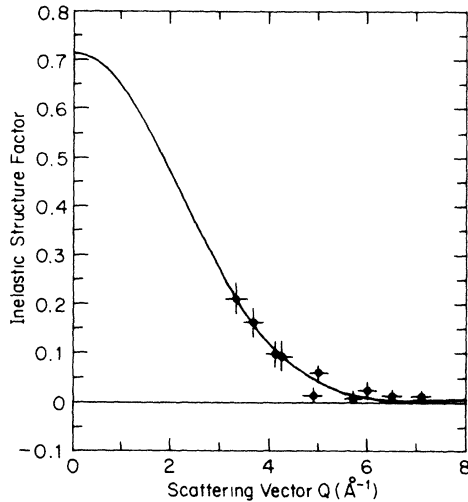


FIG. 3. Dependence of the magnetic peak integrated intensity on the scattering vector Q . Data are obtained from measurements at different scattering angles and different incident neutron energies. The solid line represents the inelastic structure factor calculated for the $J = \frac{5}{2} \rightarrow J = \frac{7}{2}$ dipolar transition in Sm^{3+} (Ref. 14).

$G(Q, J, J')$

$$= \sum_{kk'} a_{kk'} \langle j_k(\mathbf{Q}) \rangle \langle j_{k'}(\mathbf{Q}) \rangle (k, k' = 0, 2, 4, 6). \quad (1)$$

The coefficients $a_{kk'}$ are given in Ref. 14 and the radial integrals are defined as

$$\langle j_k(\mathbf{Q}) \rangle = \int_0^\infty r^2 f^2(\mathbf{r}) j_k(\mathbf{Q}\mathbf{r}) d\mathbf{r}, \quad (2)$$

where $j_k(x)$ is a spherical Bessel function and $f(\mathbf{r})$ is the radial part of the one-electron states. Accurate fully relativistic calculations of the $j_k(\mathbf{Q})$ integrals are given for all the rare-earth free ions by Freeman and Desclaux.¹⁵ The excellent agreement between the experimental data and the theoretical curve further support the assignment of the observed excitation to a transition between levels of the ground- and first-excited Sm^{3+} J multiplets split by the very strong Sm-Fe exchange field. In order to account for the neutron spectroscopy results presented above, a model incorporating the spin-orbit interaction and both exchange and crystal fields was used. The total Hamiltonian may be written as,^{11,12}

$$H = \lambda \mathbf{L} \cdot \mathbf{S} - 2\mu_B \mathbf{B}_{\text{ex}} \cdot \mathbf{S} + H_{\text{CEF}}, \quad (3)$$

$$H_{\text{CEF}} = A_2^0 \langle r^2 \rangle U_2^0 + A_4^0 \langle r^4 \rangle U_4^0 + A_6^0 \langle r^6 \rangle U_6^0. \quad (4)$$

The first term above represents the spin-orbit coupling where $\lambda = 35.4$ meV, assuming a bare spin-orbit splitting of 129 meV for the $J = \frac{5}{2} \rightarrow J = \frac{7}{2}$ multiplet.⁹ The second term represents the molecular field of the Fe sublattice on the Sm site; using an exchange coefficient $n_{\text{Sm-Fe}} = 266\mu_0$, as deduced from the Curie temperature, one obtains at $T = 20$ K, $2\mu_B B_{\text{ex}} = 40.85$ meV. The third term in the Hamiltonian is the crystal-field potential for the $2a$ site in

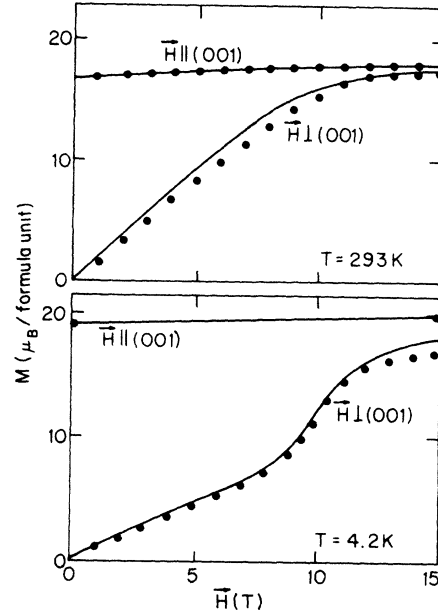


FIG. 4. The single-crystal magnetization curves of $\text{SmFe}_{11}\text{Ti}$ at 4.2 and 293 K with the magnetic field applied parallel and perpendicular to the tetragonal c axis. The points represent the theoretical fit with the parameters given in the text and the solid lines are the experimental data taken from Ref. 16.

the tetragonal ThMn_{12} structure with point symmetry $4/mmm$ (the omission of the other symmetry allowed terms U_4^4 and U_6^4 has a negligible effect on the energy-level scheme). The terms A_4^q are the crystal-field coefficients and $\langle r^n \rangle$ are the expectation values of the r^n operator over the $4f$ wave function as obtained by Freeman and Desclaux¹⁵ by fully relativistic Dirac-Fock calculations. The Racah operators U_k^q are deduced using $3-j$ and $6-j$ symbols and in absence of J mixing reduce to the classical Stevens operators. The crystal-field coefficients A_4^q may be estimated from a fit of the magnetization curves of single crystal $\text{SmFe}_{11}\text{Ti}$.¹⁶ A Zeeman term $\mu_0 \mathbf{H} \cdot (\mathbf{L} + 2\mathbf{S})$, where \mathbf{H} is the externally applied magnetic field, is added for this purpose to the total Hamiltonian. The values obtained are $A_2^0 = -11.37$ meV/ a_0^2 , $A_4^0 = 0.34$ meV/ a_0^4 , and $A_6^0 = 0.60$ meV/ a_0^6 , where a_0 is the first Bohr radius. The fitted experimental curves are shown in Fig. 4.

The diagonalization of the total Hamiltonian yields immediately the eigenvalues and eigenfunctions. Three levels are found in the energy range from 0 to 250 meV which are coupled to the ground state in the dipole approximation. Their wave functions and corresponding energies are reported in Table I. As nondipole transitions should have much smaller intensities than the transitions allowed in the dipole approximation, we should expect to observe three peaks in the inelastic magnetic neutron-scattering cross section, namely at 31, 176, and 207 meV. However, an estimate of the transition probabilities (given by the square of the matrix elements of the magnetic neutron-electron interaction operator in the dipole

approximation) shows that the peak at 207 meV should be an order of magnitude less intense than the one at 176 meV. A further reduction of a factor 2 in the intensity arises from the Q dependence of the inelastic structure factor (for $E_i = 400$ meV, $Q = 3.65 \text{ \AA}^{-1}$ at $\hbar\omega = 176$ meV and $Q = 4.36 \text{ \AA}^{-1}$ at $\hbar\omega = 207$ meV). The corresponding peak height would then be comparable to the statistical fluctuations and the peak could not be observed. On the other hand, the transition at 31 meV, although the most intense, is in a region with a very large phonon background. A reliable subtraction of the vibrational part of the neutron spectrum using the YFe_{11}Ti results was not possible due to the large difference in the neutron absorption for the two compounds. After taking this into account, the agreement with the experimental results is satisfactory.

When the temperature was increased to 290 K, the position of the inelastic magnetic peak shifts towards a lower energy, reflecting the temperature renormalization of the molecular field. However, as the exchange fields acting on the ground and the excited state are not necessarily the same, two independent values for the molecular-field constant should be used in order to fit the temperature dependence of the level splitting. This would give a unique way to measure the exchange strength on the excited multiplet in metallic compounds, but as only two temperatures have been examined in our experiment, no conclusions concerning this point can be made. Further measurements at different temperatures and on different Sm compounds with medium and weak exchange are planned for this purpose.

In conclusion, our neutron spectroscopy experiment on $\text{SmFe}_{11}\text{Ti}$ has revealed, for the first time, an electronic transition between single components of the ground and excited J multiplets in a rare-earth metallic compound.

TABLE I. Largest components of the J -mixing wave functions for some selected states of the $\text{Sm}^{3+}4f$ electrons in $\text{SmFe}_{11}\text{Ti}$. Only those levels lying below 250 meV which are coupled to the ground state in the dipole approximation are reported. The corresponding eigenvalues are given in the last column.

J -mixing eigenfunction	Energy (meV)
$-0.970 \frac{5}{2}, -\frac{5}{2}\rangle + 0.237 \frac{7}{2}, -\frac{5}{2}\rangle - 0.049 \frac{9}{2}, -\frac{5}{2}\rangle$	0.0
$+0.963 \frac{5}{2}, -\frac{3}{2}\rangle - 0.269 \frac{7}{2}, -\frac{3}{2}\rangle + 0.016 \frac{9}{2}, -\frac{3}{2}\rangle$	31.1
$+0.979 \frac{7}{2}, -\frac{7}{2}\rangle - 0.204 \frac{9}{2}, -\frac{7}{2}\rangle$	176.0
$+0.259 \frac{5}{2}, -\frac{3}{2}\rangle - 0.909 \frac{7}{2}, -\frac{3}{2}\rangle + 0.325 \frac{9}{2}, -\frac{3}{2}\rangle$	207.1

The results allow a direct verification of the Hamiltonian adopted to describe the $4f$ electron states in iron-rich ThMn_{12} structure rare-earth alloys.⁷ The J -mixing eigenfunctions for the $\text{Sm}^{3+}4f$ electrons in $\text{SmFe}_{11}\text{Ti}$ have been determined. This is of particular interest because J -mixing effects play a fundamental role in the determination of the basic magnetic properties of this compound. Further utilization of the epithermal spectrum presently available at advanced spallation neutron sources can be expected to yield a wealth of information on the electronic state of rare-earth ions in Fe- and Co-rich intermetallic compounds.

ACKNOWLEDGMENTS

The authors are grateful to D. Kennedy of Rare Earth products for providing the $\text{SmFe}_{11}\text{Ti}$ and YFe_{11}Ti samples and the Science and Engineering Research Council, U. K. for provision of the neutron-scattering facilities.

*Present address: Istituto di Struttura della Materia del Consiglio Nazionale delle Ricerche, Via E. Fermi 38, 00044 Frascati, Roma, Italy.

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