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Magnetic phase transitions in samarium iron garnet

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Mössbauer spectroscopy has shown that there are at least three magnetic phases of samarium iron garnet and possibly five, if spin reorientations that are not abrupt are assumed to occur between these phases. The easy magnetic axes are : [111], $560 > T \gtrsim 60$ K; [110], $\sim 45 > T \gtrsim 18$ K; [100], $\sim 10 > T \geqslant 5$ K. The spin reorientations are estimated to occur between ~60 and ~45 K and between ~18 and ~10 K. While the phases with the [111] and [110] easy magnetic axis have been reported before, this is the first report of the lowest-temperature phase with [100] easy magnetic axis, and of the possible spin reorientations. If the latter exist, the lowest-temperature phase *cannot* be tetragonal; it is most likely orthorhomic. The sequence of magnetic space groups is: $R\bar{3}c'$, [111] $\rightarrow F2'/d' \rightarrow Fdd'd'$, [110] $\rightarrow I2'/c' \rightarrow Ibc'a'$, [100].

I. INTRODUCTION

The behavior of the Sm^{3+} ion in the iron garnets has been of particular interest since shortly after their discovery. The first publication[1] of the thermomagnetic behavior of samarium iron garnet (SmIG) indicated that the ion behaved like an $(L+S)$ ion, because right down to 0 K, the spontaneous magnetization was *lower* than theoretical. However, the thermomagnetic data on yttrium iron garnet (YIG) by the same author[1] were also low, so it was concluded by many that the Sm^{3+} ion did not contribute to the magnetization. Several subsequent publications[2] did not alter the situation with regard to thermomagnetic behavior of the Sm^{3+} ion in the iron garnets.

In 1963, unequivocal proof that the Sm^{3+} ion behaved like both an $(L-S)$ ion at low temperature and like an $(L+S)$ ion at high temperature was published.[3] This proof could not be obtained by measurements on polycrystalline material, undoubtedly because of the high anisotropy of this garnet at the lower temperatures. The results that established the contribution of the Sm^{3+} ions to the magnetization of SmIG were obtained by thermomagnetic measurements on spherical crystals allowed to rotate freely in the measuring magnetic field. When the results were compared with those on YIG, a crossover temperature of 330 K was found.[3] This is the temperature at which the orbital and spin contributions cancel and above which the ion acts like an $(L+S)$ ion. White and Van Vleck[4] presented a theory explaining this crossover; a calculation based on this theory gives 313 K for the crossover temperature.[5] Additional theoretical work on the crossover temperatures has been done by Malik *et al.*[6]

The contribution of the Sm^{3+} ion at 0 K was found to be $0.14\mu_B$ and this was corroborated with thermomagnetic measurements by Harrison *et al.*[7] However, they report a crossover temperature of only 200 K. The problem of the exact value of the crossover temperature in SmIG is still not settled; aside from the theoretical fit, which is an approximation, there is no good reason for preferring one or the other of the reported temperatures. Nevertheless, one can be confident that there is a crossover.

For completeness, it should be mentioned also that reference has been made[8] to a 1963 unpublished report by C. H. Nowlin in which he deduced a contribution of $0.13\mu_B$ per Sm^{3+} ion at 0 K, and a change of the easy magnetization axis from [111] to [110] below 60 K.

From torque measurements on an iron garnet containing a 1% substitution of yttrium by samarium, Pearson[9] and Pearson and Cooper[10] found a [110] easy magnetization axis for this material at 4 K, and it has since been tacitly assumed that this should be the easy magnetization axis at 4 K for SmIG itself. Thermomagnetic measurements on single crystals of SmIG, made by Harrison *et al.*,[7] showed that the easy direction of magnetization changed from [111] to [110] at a temperature between 58.6 and 81 K. These investigators did not make measurements on SmIG below 29 K, at which, the easy magnetic axis was found to be [110].

Recently,[11] we have found a broad spin-reorientation-temperature region in uncompensated silicon-substituted yttrium iron garnets. The easy magnetization axis changes gradually from [111] to [100] with decreasing temperature. For a garnet containing 0.3 $Si^{4}+$ per formula unit, the temperature region over which the spin reorientation takes place is 80–265 K.

Spin reorientations occur in rare-earth perovskite-like compounds, as was first discovered[12] in $SmFeO_3$. In these materials the temperature ranges over which the spin reorientations occur are much narrower[13] than in the silicon-substituted YIG. Various rare-earth and mixed-rare-earth orthoferrites have such a spin reorientation, but they have also been found in yttrium orthoferrites in which some of the Fe^{3+} ions are replaced by Mn^{3+} or by Co^{3+} ions.[14] By analogy[15] with the orthoferrites, it was decided to investigate SmIG for a possible spin reorientation. We expected it to occur at temperatures below 80 K and to be not over 20 K wide in analogy with most of the orthoferrites.[13] As in the case of the silicon-substituted yttrium iron garnets, we used the Mössbauer-spectroscopy technique as a tool to follows the transition.

II. EXPERIMENTAL DETAILS

Mössbauer studies were performed on a constant-acceleration spectrometer with a laser velocity calibrator. The resonant radiation was the 14.4-keV γ transition in ^{57}Fe; the source was ^{57}Co in Pd at 297 K. The absorber came from the same polycrystalline specimen on which the thermomagnetic measurements of Ref. 4 had been made. It is also the specimen for which the lattice constant, 12.529 Å, is given in Ref. 16.

The specimen was ground to a fine powder in an agate mortar. Material passing through a 400-mesh sieve was used to make the absorber. The absorber thickness was 12.7 mg/cm^2.

Absorber temperatures were obtained in a cryogenic Dewar. Sample temperature was measured with a Au (3%-Fe)-chromel thermocouple and the temperature was held constant (±0.5°) with a temperature controller which supplied power to a resistance heater as required to maintain the preset temperature.

III. EXPERIMENTAL RESULTS

Spectra have been taken at 298, 86, 78, 65, 60, 55, 50, 40, 30, 20, 16.5, and 5 K. In Fig. 1 we show only those spectra taken at 60, 55, 50, 40, 20, 16.5, and 5 K. At 60 K (and above) all the spectra indicate a [111] easy magnetization axis. At 55 K, the spectrum is different from the one taken at 60 K. At 50 K, there is further change but the spectrum shows that the easy magnetization axis is very close to the [110]. At 40 K, the spectrum shows that the easy magnetization axis is the [110]; this is also the case for the spectrum at 20 K. However at 16.5 K, there is again clear evidence of a change in the spectrum and at 5 K, the easy magnetization axis is shown by the spectrum to be the [100].

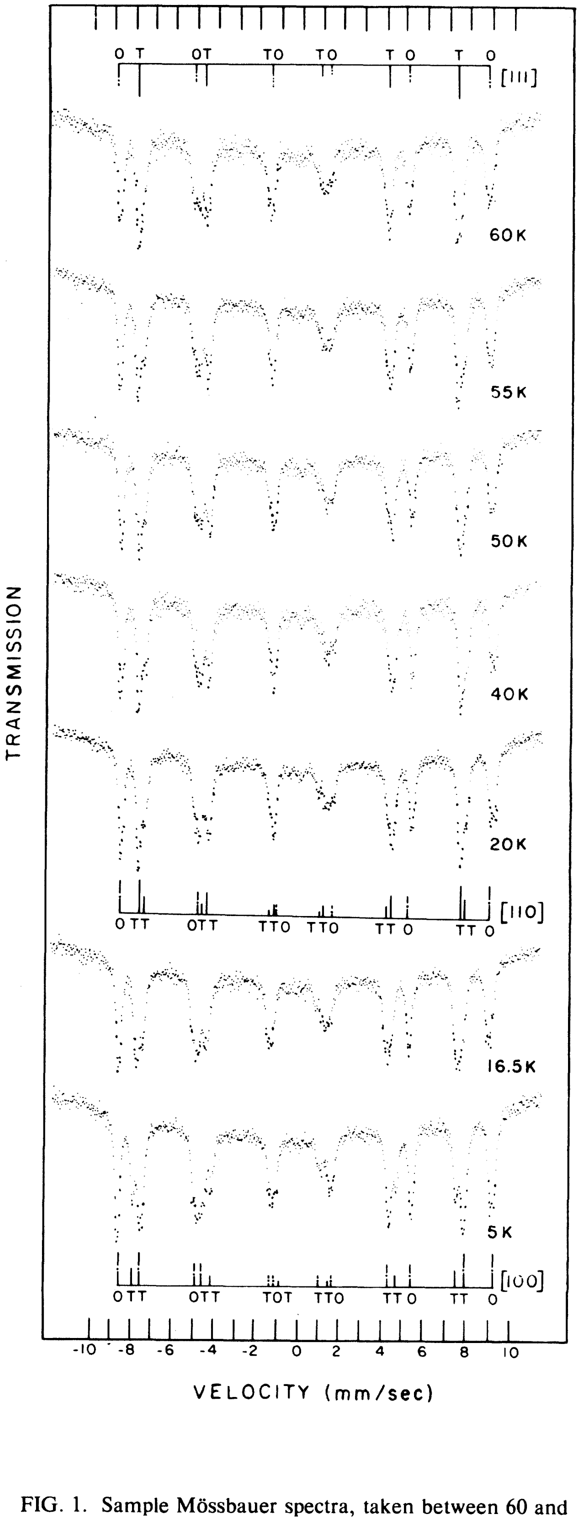

FIG. 1. Sample Mössbauer spectra, taken between 60 and 5 K, of samarium iron garnet with ^{57}Co in Pd source. Stick diagrams (Ref. 24) show theoretical line positions and relative intensities for [111], [110], and [100] easy magnetic axes; where lines overlap, a "broken" stick gives relative contributions from nonequivalent lines.

IV. DISCUSSION

In the case of the silicon-substituted yttrium iron garnets, there is little doubt that spin reorientations take place. The principal alternative is the coexistence of the two magnetic phases. This was essentially eliminated by the absence of hysteresis, by the spectra themselves and by the impossibility of constructing the boundary structure which should be required for the coexistence of the two phases.[17]

In the present case, the temperature ranges over which the spin reorientations take place are very narrow, probably not over 10 K for each, so that a test for hysteresis by coming at the spectra from lower and from higher temperature, would be expensive but not conclusive. Nevertheless, because of the two other reasons given above, we will assume that spin reorientations do take place in SmIG.

We discuss the transitions from a structural point of view. One can be fairly confident that all the magnetic structures can be derived from the subgroups of the nonmagnetic garnet space group $Ia3d(O_h^{10})$. The magnetic structure with [111] easy magnetic axis belongs to the magnetic space group $R\bar{3}c'$. For the [110] easy magnetic axis,[18] the most symmetric magnetic space group is $Fdd'd'$. For a [100] easy magnetic axis, the most symmetric magnetic space group is $I4_1/ac'd'$; this is the applicable group in the silicon-substituted YIG case. However, it will be shown that the most likely magnetic space group to which SmIG belongs when [100] is the easy magnetic axis, is $Ibc'a'$—if a spin reorientation (that is not abrupt) actually occurs. (Throughout this paper, we mean a spin reorientation that is *not* abrupt). In the spin-reorientation region, the magnetic space group must be a subgroup of the two groups at the ends of the spin reorientation.

The picture suggested for the phase transitions is as follows: In the transition from the $\langle 111\rangle$ easy magnetic axis magnetic axis to the $\langle 110\rangle$, $\vec{M}$ rotates through the angle $(\sin^{-1}\sqrt{3}/3)$, 35.3° in a $\{110\}$ plane. In the transition from the $\langle 110\rangle$ easy magnetic axis to the $\langle 100\rangle$, $\vec{M}$ rotates 45° in a $\{001\}$ plane. These indices refer to the original cubic cell. For simplicity, we may still refer the rhombohedral magnetic structure to the body-centered cell. In the transition to the orthorhombic structure, the orthorhombic axes are the [110], $[1\bar{1}0]$, and [001] referred to the cubic cell; this cell has twice the volume of the body-centered-cubic cell. In the transition to the orthorhombic structure at the lowest temperature, the orientations of the axes of the chemical cell are again those of the cubic cell.

In the spin-reorientation region between the rhombohedral ($R\bar{3}c'$) and orthorhombic ($Fdd'd'$) structures, the structure belongs to the magnetic space group $F2'/d'$. The orientation of the axes of the chemical cell are the same as those in the orthorhombic ($Fdd'd'$) structure, but the 2′ axis is along the cubic [110] direction and, by convention, is designated *b*. The monoclinic (010) plane is a cubic $\{110\}$ plane.

In the orthorhombic phase in which the cubic $\langle 110\rangle$ is the easy magnetic axis, this axis is a true twofold axis. The axes perpendicular to it are antisymmetry 2′ axes. As soon as $\vec{M}$ moves off the C_2 axis in the lower-temperature spin reorientation the crystal becomes monoclinic; the twofold axis remaining is 2′ along the cubic [001] direction and the (001) plane becomes a c' glide antireflection plane. The monoclinic magnetic space group is $I2'/c'$. When $\vec{M}$ reaches the cubic [100] direction, the magnetic space group becomes $Ibc'a'$: In the transition from $Fdd'd'$ in which [110] is the magnetic easy axis to the [100] magnetic easy axis, presumably $\vec{M}$ remains in the (001) plane. A 2′ axis of $Fdd'd'$ is perpendicular to this plane and is also coincident with the *b* axis of the monoclinic $I2'/c'$ phase in the spin-reorientation region. Now the (cubic [100]) axis to which $\vec{M}$ becomes paralled must be at least twofold (and not 2′). The 2′ axis of the monoclinic group $I2'/c'$ must be a subgroup of the symmetry elements of the final group, which therefore must have at least a 2′ axis in the same orientation. No tetragonal subgroup of $Ia3d$ satisfies this condition; the orthorhombic group $Ibc'a'$ does. (We have taken the highest symmetry groups derivable from the subgroups of $Ia3d$).

In Table I, we show the equipoint multiplicities and magnetic point symmetries of the paramagnetic ions

TABLE I. Magnetic space group and equipoint transformations of samarium-iron-garnet phases. Point symmetries are in parentheses.

$T > 560$ K $Ia3d$	$560 > T \gtrsim 60$ K $R\bar{3}c'$	$\sim 60 > T \gtrsim 45$ K $F2'/d'$	$\sim 45 > T \gtrsim 18$ K $Fdd'd'$	$\sim 18 > T \gtrsim 10(?)$ K $I2'/c'$	$\sim 10 > T \gtrsim 5$ K $Ibc'a'$
$Sm^{3}+$ in 24*c* (222)	$2\times 6e(2')$	$2\times 8e(2')$ $2\times 16f(1)$	$8a, 8b(22'2')$ $32h(1)$	$2\times 4e(2')$ $2\times 8f(1)$	$8e(2')$ $8c(2), 8d(2')$
Fe^{3+} in $16a(\bar{3})$	$2b(\bar{3})$ $6d(\bar{1})$	$8a, 8b, 8c, 8d, (\bar{1})$	$16c, 16d(\bar{1})$	$4a, 4b, 4c, 4d, (\bar{1})$	$8a, 8b(\bar{1})$
$Fe^{3}+$ in $24d(\bar{4})$	$12f(1)$	$3\times 16f(1)$	$16g(2')$ $32h(1)$	$2\times 4e(2')$ $2\times 8f(1)$	$8e(2')$ $8c(2), 8d(2')$
O^{2-} in $96h(1)$	$4\times 12f(1)$	$12\times 16f(1)$	$6\times 32h(1)$	$12\times 8f(1)$	$6\times 16f(1)$

in the various structures including the cubic paramagnetic one. In a crystal belonging to a ferromagnetic trigonal point group, the spontaneous magnetization $\vec{M}$ must be directed along the threefold axis, but the moments of the ions or atoms in the crystal need not be, unless they lie on the trigonal axis; in $R\bar{3}c'$ only the Fe^{3+} ions in $2b$ are so constrained. There is no symmetry constraint on the moment direction of the other Fe^{3+} ions in the crystal, except, of course, that within the $6d$ and $12f$ sets, the moment directions satisfy the symmetry operations of the space group. (The tutorial paper by Atoji[19] is very helpful to visualization of the moment arrangements.) Needless to say, the moments of the Fe^{3+} ions in $6d$ and $12f$ may be parallel (or antiparalled) to the trigonal axis (or $\vec{M}$), as appears to be the case in the pure iron garnets. The Sm^{3+} ions are in two sets of $6e$, lying on $2'$ axes; the Sm^{3+} ion moments must be perpendicular to these axes. The symmetry operations of $R\bar{3}c'$ *allow* these Sm^{3+} ion moments to be directed along the trigonal axis, even though the crystal field may not permit them to be. In general, the Sm^{3+}-ion moments are tangent to cylindrical surfaces about the $\bar{3}$ axis. In each set of six Sm^{3+} ions, each pair related by $\bar{1}$ point in the same direction,[19] and the three pairs point according to the trigonal axis operation.[19] An important conclusion from the above is that in all ferrimagnetic garnets belonging to $R\bar{3}c'$, canting of all ion moments except those of the two magnetic ions in $2b$ is allowed.

We point out a few important features of the other groups in Table I. In $F2'/d'$ and $I2'/c'$, $\vec{M}$ lies in the plane perpendicular to the twofold antisymmetry axis (these axes are not in the same direction in the two cases). In $Fdd'd'$, there are three mutually perpendicular twofold axes of which two are antisymmetry axes. $\vec{M}$ must be parallel to the (ordinary) twofold symmetry axis. The moments of the Sm^{3+} ions in $8a$ and b *must* lie along the twofold symmetry axis; those in $32h$ may be canted, subject to the symmetry operations of the space group. In $Ibc'a'$, only the moments of the Sm^{3+} and of the Fe^{3+} ions in $8c$ must be directed along the a axis, as must $\vec{M}$.

It is of particular interest that, as the above discussion shows, the magnetic easy axis transition from [111] to [110] to [100], through spin reorientations, results finally in an orthorhombic structure, while the tetragonal structure is entirely compatible with the transition from [111] to [100] through a single spin reorientation as in the case of silicon-substituted YIG.[11]

In the ^{57}Fe Mössbauer spectra of the SmIG belonging to the magnetic space groups of Table I, there should be the number of sets of lines with relative intensity ratios as follows: $R\bar{3}c'$, 3, 1:3:6; $F2'/d'$, 7, 1:1:1:1:2:2:2; $Fdd'd'$, 4, 1:1:1:2; $I2'/c'$, 8, 1:1:1:1:1:1:2:2; $Ibc'a'$, 5, 1:1:1:1:1.

It appears that the relative ionic positions in the garnet may not change measurably from their relative postions in the paramagnetic structure; that is to say, the *chemical* structure may remain close to cubic through the transitions. This means that the symmetry (really pseudosymmetry) axes continue to make the same angles with each other. This causes considerable overlap of the contributions from the many nonequivalent sets of Fe^{3+} ions in the spin reorientation regions.

Another cause of overlap is the rather strange change[20] in the value of the electric quadrupole coupling constant for the independnet octahedral Fe^{3+} ions from the paramagnetic to the ferrimagnetic state. This causes almost complete overlap of the contributions from the two sets of octahedral Fe^{3+} ions in the rhombohedral structure, that is, when the [111] is the easy magnetic axis and also when the [110] is the easy magnetic axis (see Fig. 1).

We have pointed out that we observed the easy magnetic axis beginning to change at 16.5 K and made no measurements between this temperature and 5 K; a spin reorientation here must be very narrow, probably not more than 10 K wide. If what we have observed is hysteresis, then both magnetic transitions must be first order. In fact, all ferromagnetic transitions involving *abrupt* changes in direction of the easy magnetic axis must be first order if they involve only groups with orthorhombic symmetry or higher.[21] In all such ferromagnetic groups, the spontaneous magnetization must lie along a rotation axis.

Specific-heat measurements have been made[22] on SmIG between 1.6 and 20 K. The specimen used was found to have "2% impurity"; the lattice constant was not reported. The results on the transition from [111] to [110] on our specimen are in good agreement with those of Harrison *et al.*[7] and of Nowlin quoted in Ref. 8, and, more important, the lattice constant fits perfectly the plot of lattice constant versus atomic number.[16] In the specific-heat work, the authors apparently had no way of knowing that at 20 K, the easy magnetic axis of SmIG is the [110]. They did observe an anomalous peak below 4 K which they attributed to the impurity. It is possible that this peak is associated with the change in the easy magnetic axis, shifted because of an impurity in their garnet specimen. Further, from their data they calculated energy levels between 8 and 15 K assuming the crystal to have a [111] easy magnetic axis, that is, with two nonequivalent sets of sites for the Sm^{3+} ions with equal population. However, in this temperature range, there is no doubt that the easy magnetic axis was not the [111]; the crystals could actually have been in the spin reorientation region.

For theoretical work on the magnetic anisotropy SmIG, the reader is referred to the paper by White.[23] In view of our present results and some much older,[3] the results of that paper require modification to some extent, a task that seems to be formidable.

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