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Spin-flop transition in samarium metal investigated by capacitance dilatometry in a steady magnetic field of 45 T

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The longitudinal and transversal forced magnetostrictions of a single crystal of samarium metal have been investigated in a static magnetic field up to 45 T. The data show pronounced features of a spin-flop transition initiating at an applied field of about 30 T. The measured forced magnetostriction is about 1 order of magnitude smaller than the spontaneous magnetostriction. Based on a model calculation of the magnetic phase diagram these features have been interpreted within the exchange striction model. The moments of the quasi-succicubic Sm sites enter a spin-flop phase at about 30 T and ferromagnetic saturation is predicted at 60 T. Similarly the model predicts a spin-flop phase for the hexagonal Sm sites at 140 T and ferromagnetic saturation at 300 T.

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I. INTRODUCTION

Samarium is probably the most widely used rare earth element; applications range from advanced permanent magnetic materials to nuclear medicine. Yet, many riddles have still to be solved. The compensation of orbital and spin moment in SmAl$_2$ with 1% of Sm substituted by Gd (Ref. 1) gives rise to exchange bias and suggests the use of Sm based materials for the design of spin resolved nanodevices. Today Sm is used widely in the form of SmCo$_5$ as a permanent magnetic material. The magnetic anisotropy of this important material has been studied by ab initio methods. Recently, the observation of a pressure induced magnetic order associated with the appearance of a trivalent Sm in a metallic state in SmS (Refs. 4 and 5) and SmB$_6$ (Ref. 6) raised interest in the relation of strain and magnetic properties in Sm based systems. A direct probe for this is the measurement of magnetostriction. It is the most powerful macroscopic method to study the interaction of electronic and lattice degrees of freedom. For such an investigation antiferromagnetic systems are favorable. In contrast to ferromagnets, in antiferromagnets a large variety of magnetic structures can be stabilized at different temperatures and magnetic fields, which enables the different mechanisms of magnetostriction to be separated and distinguished. Yet few magnetostriction data are available on rare earth elements; for a review, see Ref. 7. Here we report a study on Sm metal.

The crystal and the magnetic structures of Sm metal have been determined by x-ray and neutron scattering. Early x-ray measurements by Daane et al. determined the crystal structure to be rhombohedral, space group $R\bar{3}m$ with three atoms in the unit cell. It can be envisaged as a nine-layer stacking sequence $\text{ABCABCAC}$... of closed packed hexagonal layers. There is a second structural domain which is turned by $180^\circ$ about the $c$ axis (so the stacking is $\text{ACACBCBAB}$...). Two-thirds of the atoms have a surrounding similar to that found in the hexagonal-stacking sequence, $\text{ABAB...}$, and one-third is in a nearly cubic closed packed local symmetry ($\text{ABCA}$... stacking). For simplicity the sites are denoted as the hexagonal and cubic sites, respectively, in the further text. Sm has the following hexagonal lattice parameters: $a = 0.3621$ nm and $c = 2.625$ nm. Several structural phase transitions under pressure up to 100 GPa have been reported (to hcp-, fcc-distorted, fcc-, hexagonal-, tetragonal phases). By quenching a metastable hcp phase can be obtained, which orders ferromagnetically at $T_C = 160$ K with a small moment of $0.1 \mu_B$.

Koehler and Moon performed neutron diffraction measurements on a Sm single crystal. They used the isotope $^{154}$Sm to lower the high absorption cross section of natural Sm. They confirmed that the phase transitions at 106 and 13.8 K arise from magnetic ordering, as deduced by electrical resistivity and specific heat measurements. Below 106 K the magnetic moments at the hexagonal sites order in ferromagnetic sheets. The second transition can be assigned to the antiferromagnetic ordering of the cubic sites. The distance between two cubic site layers is 0.9 nm. The spin sequence
within one layer is $++--$ along the hexagonal $a_1$ axis. Recent resonant magnetic x-ray scattering experiments indicate that the moments at the cubic and hexagonal sites are of similar magnitude.\textsuperscript{13} Interestingly in a 750 nm dhcp film the ordering of hexagonal and cubic sites occurs at the same temperature (25 K).\textsuperscript{14}

The magnetization of Sm has already been studied in 1974,\textsuperscript{15} in pulsed magnetic fields. These measurements revealed the existence of a magnetic transition for field parallel to the crystallographic $c$ axis at about 28 T. Because the magnetostriction signal of Sm metal is expected to be small\textsuperscript{16} it is necessary to combine the highest steady magnetic fields with the best resolution available for measuring length changes thus pushing the frontiers of this experimental technique. The aim of this work is to explore the magnetism of Sm in high magnetic fields by (i) performing magnetostriction measurements up to 45 T and (ii) modeling both the magnetization and the magnetostriction and obtain the magnetic phase diagram, and (iii) confronting the results of this model calculation with the experimental data.

II. DESCRIPTION OF THE EXPERIMENTAL METHOD

The design of a miniaturized capacitance dilatometer (outer diameter 20 mm)\textsuperscript{12} allows the measurement of longitudinal as well as transversal components of magnetostriction with unprecedented resolution and field range. Therefore, the complete magnetostriction tensor can be analyzed. The dilatometer was installed in the 45 T hybrid magnet of the National High Magnetic Field Laboratory (Tallahassee, FL) equipped with a $^4$He cryostat. For the best resolution of about $10^{-6}$ it is important to damp mechanical vibrations and electric noise. In addition, the signal was corrected for artifacts due to eddy currents. To exclude effects caused by the crystal growing process two different high quality Sm crystals were used; details can be found in Ref. 11. The magnetostriction results of both crystals are identical in the limit of the experimental error.

III. MAGNETOSTRICTION DATA

Figure 1 summarizes the longitudinal and transversal magnetostriction data along the three fundamental crystallographic axes at a temperature of 4 K, obtained in magnetic fields up to 45 T. The $a$ axis is taken along the direction joining a pair of nearest neighbors in the hexagonal plane, the $c$ axis is normal to the plane, and the $b$ axis is orthogonal to the other two.\textsuperscript{18} In Fig. 1 the field was oriented parallel or perpendicular to the crystallographic $c$ axis. The magnetostrictions of the $a$ and $b$ axes are shown in the two upper graphs. The behavior is similar: the sample length shrinks in fields parallel to the $c$ axis by $4 \times 10^{-5}$ at about 30 T. It stays nearly unchanged in fields parallel to $a$ (the only difference is a small upturn with field for the $b$ direction and a small downward change for the $a$ direction). The opposite behavior is found for the $c$ axis, presented in the graph below: the sample length jumps up by $7 \times 10^{-5}$ when a field parallel to $c$ is applied, whereas the magnetostrictive effect in field parallel to $a$ is small and does not show any anomaly. Moreover, the moment at the cubic and hexagonal sites is of similar magnitude.\textsuperscript{13}

Figure 1. Forced magnetostriction data of a Sm single crystal (lower graph) is 1 order of magnitude smaller. From these measurements it can be seen that for fields parallel to $c$ the sample clearly reflects the phase transition which had been observed in pulsed field magnetization measurements and was attributed to a reorientation of the moments of the quasicubic sites. The line shape of the transition also suggests a field-induced spin-flop state. The lack of any anomaly in our data when the field is applied perpendicular to the $c$ axis agrees with the magnetization measurements,\textsuperscript{15} too. The curves of Fig. 1 illustrate that the main magnetoelastic effect of Sm is a structural distortion of the hexagonal plane (the longitudinal magnetostriction is negative and the transversal is positive).

The transversal magnetostriction for field parallel to $c$ was studied at different temperatures in the antiferromagnetically ordered state. The results in the high field range between 11 and 45 T are presented in Figs. 2 and 3. A monotoneous shift of the transition into the spin-flop phase to lower critical fields with increasing temperature is visible as expected for the case of a constant magnetic moment (see Fig. 3). Note that in contrast to our data on Sm metal in some Sm compounds the compensation of the orbital and spin moments leads to an anomalous temperature dependence of the magnetic moment, for instance, in ferromagnetic SmAl\textsubscript{2}.\textsuperscript{1} In antiferromagnetic SmCu\textsubscript{2} this compensation leads to an anomalous increase of the transition field from the antiferromagnetic to the ferromagnetic state when the temper...
FIG. 2. Temperature dependence of the transversal magnetostriction and parastriction $\varepsilon^b$ for magnetic field along the $c$ axis. For comparison, the thermal expansion data $\varepsilon^b$ in zero field are shown in the inset.

Moreover, the magnetostriction curves at temperatures below 5 K are very different compared to the 9 K curves. Whereas the first ones show a simple jump and small (negative) magnetostriction in the spin-flop phase, in the latter a much bigger jump and positive magnetostriction at higher fields can be seen. The parastriction, measured along $a$ up to 10 T (which is sufficient because no transition is expected), is negligible (shown in Fig. 2). Additionally, a hysteresis was observed. Figure 3 also shows the temperature dependence of this hysteresis. At low temperature the hysteresis is larger. This is due to the fact that the relaxation processes for the formation of the collinear antiferromagnetic state upon decreasing the applied field require thermal energy of the order of several Kelvin.

As already visible in Fig. 1 the magnetoelastic behavior of the crystal is anisotropic. When the magnetic field is applied parallel to $c$, the $c$ axis expands, whereas the plane perpendicular to the $c$ axis shrinks. The volume magnetostriction effect is small. This anisotropic behavior is also reflected by the zero field data of thermal expansion, which is shown in Fig. 4. On cooling the $c$ axis contracts at $T_1 = 14$ K, whereas the $a$ and $b$ axes expand leading to a very small magnetoelastic volume change. Application of a magnetic field along the easy direction reverses the effect of cooling, i.e., the $c$ axis expands and the $a$ and $b$ axes contract. This is shown for $\varepsilon^b$ in Fig. 2. In contrast to many other systems, the magnitude of the spontaneous magnetostriction (i.e., the magnetic contribution to the thermal expansion, which is about $A_l^s / 10^4$) is much larger than that of the forced magnetostriction (i.e., the strain induced by an external magnetic field, which is of the order of $10^{-5}$). When the magnetic moments are aligned parallel by an external field usually a similar order of magnitude for the forced magnetostriction as for the spontaneous magnetostriction near $T_N$ is observed for other compounds (see, e.g., Refs. 7 and 20).

IV. ANALYSIS OF THE MAGNETIC PHASE DIAGRAM

In order to understand this particular behavior of Sm metal, the magnetic phase diagram has been modeled within the framework of the standard model of rare earth magnetism. Numerical calculations have been performed using the MCPHASE program package. The model is based on a Hamiltonian consisting of a sum of the crystal field, the two-ion interaction, and the Zeeman term as follows:

$$H = \sum_{i,j,m} B_i^m(i) O_j^m(J_i) - \frac{1}{2} \sum_{i,j} \left( J_a^a(\epsilon, ij) 0 0 \right) J_j - \sum_{i} \varepsilon_i \mu_B H_i$$

(1)
Here the indices $i$ and $j$ refer to the different Sm atoms and $J_i$ denotes the total angular momentum of Sm atom $i$. $g_J$ is the Landé factor and $\mu_B$ the Bohr magneton.

A. Crystal field

The $B_{ij}^m$ and $Q_{ij}^m$ denote the crystal field parameters and Stevens operators, respectively. In order to obtain reasonable values for the crystal field parameters, we consider some available experimental data: (i) From the data of the susceptibility shown in Fig. 5 we conclude that the magnetic single ion anisotropy produced by the crystal field in Sm is small (see curves for $T > 106$ K). (ii) Further evidence for the small energy splitting by the crystal field can be found from the entropy of Sm as determined from specific heat data. At 25 K it clearly exceeds the value of $\frac{1}{2} R \ln 2$ expected for a crystal field doublet ground state on the cubic sites. In order to account for this small crystal field anisotropy, the crystal field parameters for both the quasicubic and hexagonal Sm sites were estimated from the point charge model: a small point charge of $0.011 |e|$ was put on the six nearest neighbors in the adjacent hexagonal planes ($e$ denotes the elementary charge).

B. Two-ion interaction

Next we consider the components of the two-ion interaction $J^{(e,ij)}$ and $J^{(c,ij)}$ in the Hamiltonian (1). The experimental susceptibility data shown in Fig. 5 indicate some anisotropy of this two-ion interaction: the moments order along $c$, although just above $T_N$ the susceptibility in the hexagonal plane is larger than that in the $c$ direction (see Fig. 5 in Ref. 41). Such a behavior is not uncommon in rare earth based systems, in particular, some puzzling details of this anisotropy in a Sm based system have been reported. In the case of Sm metal we model the anisotropy of the two-ion interaction by putting $J^{(e)} = J^{c} \neq J^{c}$ for the two antiferromagnetic quasicubic sublattices and thus neglecting any anisotropy in the hexagonal planes. For a description of the macroscopic properties it is sufficient to introduce anisotropy for one of the interactions, which we chose to be the interaction between the two antiferromagnetic quasicubic sublattices. By tuning this anisotropy it is possible to describe correctly the experimentally observed value of the critical field of the transition to the spin-flop phase.

C. Obtaining the model parameters

The complex antiferromagnetic structure of Sm is not fully considered in the model. The magnetic structure is modeled by simple antiferromagnetism, with a two sublattice mean field model for both the quasicubic and the hexagonal sites. This simplification was made because neutron spectroscopy is hampered by the strong absorption of Sm (Refs. 35 and 36) and therefore currently no information about details of the magnetic two-ion interactions in Sm are available. The values of the point charges and the two-ion interaction have been tuned in order to reproduce (i) the experimental values of the antiferromagnetic ordering temperatures, (ii) the spin-flop field observed in the magnetostriction, and (iii) the magnitude of the magnetic susceptibility. The values obtained in this way for the interaction constants are summarized in Table I. Note that the temperature dependence of the measured susceptibility in the $c$ direction (see Fig. 5) yields a finite value at very low temperatures. If the magnetic moment also points in the $c$ direction (as observed by neutron scattering), such a finite value can be explained by the admixture of higher multiplets leading to a Van Vleck type of susceptibility. In our calculations we have therefore assumed a temperature independent isotropic paramagnetic susceptibility of $\chi_0 = 0.0009 \mu_B / T$.

D. Results of the model calculation

Within a mean field approximation the magnetic moment per Sm ion was calculated by

$$M = \frac{1}{N} \sum_i g_i \mu_B \langle J_i \rangle_{T,H} + \chi_0 \mathbf{H}. \quad (2)$$

Here $i$ runs over all atoms and $N$ is the number of atoms (quasicubic and hexagonal); the $\langle J_i \rangle_{T,H}$ are the thermal expectation values for the angular momentum operator of the Sm ions.

A comparison of the calculated susceptibility and magnetization with the experimental data is shown in Figs. 5 and 6. Considering the experimental error and the approximations...
SPIN-FLOP TRANSITION IN SAMARIUM METAL

FIG. 6. Experimental data of magnetization (Ref. 15) (symbols) and results of the model calculation (solid lines) described in the text.

involved in the model we find reasonable agreement of the results of the calculation and the experimental data. Applying a magnetic field along the $c$ direction at $T=4$ K leads to a transition from the collinear antiferromagnetic state into the spin-flop phase at about 30 T. Note that the experimental data of magnetization taken in pulsed magnetic fields shows this transition at a lower field than our steady field magnetostriction data. From our data the temperature dependence of the transition to the spin-flop phase has been determined. In order to compare these experimental data to the predictions of the model calculation the phase diagram of Sm metal has been calculated and is shown in Fig. 7: transitions from a collinear phase into a noncollinear spin-flop phase are expected for both the hexagonal and quasicubic sites. For the quasicubic sites this transition is at about 30 T in good agreement with the experimental magnetostriction data. For the hexagonal sites it is predicted at the high field of 135 T and still needs to be confirmed experimentally. Due to the low magnetic moment of Sm the boundaries of the antiferromagnetic and spin-flop phases are predicted at fields up to 400 T. According to the calculation the ferromagnetic saturation is reached at 65 (390) T for the quasicubic (hexagonal) sites.

V. EXCHANGE OR CRYSTAL FIELD STRICTION?

Having established a simple model for the magnetic phase diagram of Sm metal we apply this model to the magnetostriction and confront its results with our experimental data. In this way it is possible to make important conclusions about the mechanism of the magnetoelastic coupling in this rare earth element. Among the rare earth elements a similar analysis has only been performed for Ho metal.36

Restricting ourselves to first order $\alpha$-type magnetoelastic couplings and neglecting the small changes in the atomic positions in the unit cell19 the magnetoelastic Hamiltonian can be written as a sum of crystal field and two-ion contributions39 as follows:

$$H_{me} = H_{me}^{CF} + H_{me}^{EX},$$

$$H_{me}^{CF} = - \sum_i (B_i^{a1} e^{a1} + B_i^{b2} e^{b2}) O^{a1}_i (J_i),$$

$$H_{me}^{EX} = - \sum_{ij} [D_{i,j}^{a1} (ij) e^{a1} + D_{i,j}^{b2} (ij) e^{b2}] J_i J_j - \sum_{ij} [D_{i,j}^{a1} (ij) e^{a1} + D_{i,j}^{b2} (ij) e^{b2}] \times [2\langle J_i \rangle_o (J_j)_o - (J_j)_o (J_i)_o - (J_i)_o (J_j)_o].$$

Here the $B$ and $D$ denote the magnetoelastic coupling and the $\alpha$ strains are defined by $\epsilon^{a1} = \frac{1}{3}(\epsilon^x + \epsilon^y + \epsilon^z)$ (volume strain) and $\epsilon^{b2} = \sqrt{\frac{2}{3}} [\epsilon^z - \frac{1}{3}(\epsilon^x + \epsilon^y)]$ (anisotropic strain).

Following the methods of Refs. 7 and 39 the magnetoelastic energy can be combined with the elastic energy and the total free energy may be minimized with respect to the strains. This procedure leads to the following expression for the magnetostrictive strains, which can be used for the analysis of our experimental data:

$$\epsilon = \epsilon^b = K^{a0}_{20} \langle O^a_2 \rangle_{T,H} + \sum_{i,k} L_{ik}^a [2J_{i,j} (ik) - J_{i,j} (ik) + J_{j,i} (ik)]$$

$$+ \sum_{i,k} M_{ik}^a [2J_{i,j} (ik) - J_{i,j} (ik) - J_{j,i} (ik)],$$

$$\epsilon = K^{a0}_{20} \langle O^a_2 \rangle_{T,H} + \sum_{i,k} L_{ik}^a [2J_{i,j} (ik) + J_{j,i} (ik) + J_{j,i} (ik)]$$

$$+ \sum_{i,k} M_{ik}^a [2J_{i,j} (ik) - J_{i,j} (ik) - J_{j,i} (ik)].$$

The strains are given by a linear combination of (i) thermal expectations values of Stevens operators ($\langle O^a_2 \rangle_{T,H}$) and (ii) two-ion correlation functions $[J_{i,j} (ik) - J_{i,j} (ik)]$. Both (i) and (ii) can be calculated from the numerical model. By comparison with the experimental data the parameters $K$, $L$, and $M$ in Eq. (6) can be estimated.
sample volume are observed. This leads to the conclusion that $K_t \sim -2K_a$, $L_c \sim -2L_a$, and $M_c \sim -2M_a$. Furthermore, our analysis indicates a small crystal field striction contribution and the dominant importance of the (isotropic) exchange striction mechanism (i.e., $K \sim 0$, $M \sim 0$). Note that a small crystal field striction is expected from the small crystal field anisotropy in this compound (compare the discussion of the susceptibility in Sec. IV above).

The full lines in Figs. 1 and 4 indicate the results of a model calculation using the exchange striction parameters given in Table II. In contrast to the crystal field striction contribution the exchange striction contribution is able to explain the experimental observation of the large difference between the spontaneous magnetostriction at the ordering temperature of the quasicubic sites and the field-induced magnetostriction at the transition to the spin-flop phase (see Fig. 2): this feature can be explained under the assumption that the exchange interaction between quasicubic ions on the same sublattice is much more sensitive to strain than the exchange interaction between ions on the other [antiferromagnetic (AFM)] sublattice (see Table II).

The extension of the field range of our experimental data to 45 T allows us to also reinvestigate the role of anisotropic magnetoelastic interactions in Ref. 11. From the small signal of the magnetostriction with field parallel to $a$, it was concluded that the isotropic contribution [parameters $L$ in Eq. (6)] is small in comparison to the anisotropic magnetoelastic interaction [parameters $M$]. However, the experimental data taken above the field $H_a \sim 30$ T show that the forced magnetostriction is not constant at larger fields. We demonstrated that all the data can be reasonably well described by isotropic magnetoelastic interactions ($L$), and anisotropic magnetoelastic interactions ($M$) are probably small. Moreover, the difference in the signal in $a$ and $b$ directions when applying field parallel to $a$ indicates an orthorhombic distortion of the crystal in high magnetic fields. Such a distortion is not included in the current model. If such an orthorhombic distortion is indeed caused by exchange striction effects it (i) should disappear when all the moments are aligned ferromagnetically above 390 T, and (ii) it should be present also in zero field (compare the magnetoelastic paradox).

VI. CONCLUSION

In conclusion, extending the magnetic field range of magnetostriction measurements on Sm metal shows the occurrence of a magnetoelastic distortion at $H_c \sim 30$ T. This distortion is associated with the transition to a spin-flop phase, where the moments at the quasicubic sites undergo a spin-flop transition. Spontaneous and forced magnetovolume effects are small in Sm metal. However, large anisotropic strains have been observed. A model analysis of the magnetic and magnetovolume data allows predictions of the magnetic phase diagram for this element. Exchange striction is identified as the dominant magnetoelastic interaction mechanism in Sm metal. In contrast to the case of Ho, the data on Sm indicate anisotropy in the magnetic two-ion interactions.

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TABLE II. Magnetoelastic parameters in Eq. (6) used for the model calculation of the magnetostriction.

<table>
<thead>
<tr>
<th>Neighbor</th>
<th>$L_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexagonal site</td>
<td>Same sublattice</td>
</tr>
<tr>
<td>Quasicubic site</td>
<td>Same sublattice</td>
</tr>
<tr>
<td>Quasicubic site</td>
<td>Other sublattice</td>
</tr>
</tbody>
</table>

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If the two-ion interactions are isotropic the susceptibility just above $T_n$ has to be explained by crystal field effects. An easy plane crystal field anisotropy will also lead to an ordered state with moments in the plane, which is not found in the experiment.

The expectation value of $\Theta^2$ shows a change of similar magnitude at the ordering temperature of the quasicubic sites and at the transition to the spin-flop state at about 30 T parallel to c and thus is in contrast to the experimental data shown in Fig. 2.