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Crystalline electric field at the rare-earth site in Chevrel-phase $R\mathrm{Mo}_6\mathrm{S}_8$ and $R\mathrm{Mo}_6\mathrm{Se}_8$ from Mössbauer spectroscopy

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The ^{155}Gd Mössbauer-effect measurements in $\mathrm{GdMo}_6\mathrm{S}_8$ and $\mathrm{GdMo}_6\mathrm{Se}_8$ are reported. A quadrupole interaction of 545 ± 40 and 470 ± 60 MHz is measured at ^{155}Gd in $\mathrm{GdMo}_6\mathrm{S}_8$ and $\mathrm{GdMo}_6\mathrm{Se}_8$, respectively. This indicates the presence of a large $B_2^0\hat{O}_2^0$ term in the crystalline-electric-field (CEF) Hamiltonian in all rare-earth Chevrel-phase sulfides and selenides. The results imply that the previous analyses of CEF effects in these materials based on a cubic Hamiltonian are not valid. The importance of the CEF in understanding various measured magnetic and superconducting properties of the $R\mathrm{Mo}_6\mathrm{S}_8$ compounds, where R denotes rare earth, is discussed.

INTRODUCTION

The rare-earth Chevrel phases ($R\mathrm{Mo}_6\mathrm{S}_8$, and $R\mathrm{Mo}_6\mathrm{Se}_8$, where R denotes rare earth) include many known magnetic superconductor compounds. An ordered lattice of magnetic rare-earth atoms in this structure almost always fails to destroy superconductivity. The interaction between magnetism and superconductivity in these materials is not well understood (for reviews of various aspects of the Chevrel phases, see Ref. 1). This is partly due to our lack of knowledge of the crystalline electric fields (CEF) acting on the rare-earth atoms which can dictate the magnetic behavior of these materials. The CEF effects are important in the rare-earth Chevrel-phase materials because the magnetic ordering temperatures are likely to be less than the overall CEF splittings of the rare-earth electronic states. CEF effects have been shown to be substantial in other ternary magnetic superconductors, such as $R\mathrm{Rh}_4\mathrm{B}_4$ and $R_2\mathrm{Fe}_3\mathrm{Si}_5$ compounds.[2,3]

Previous CEF analysis of Chevrel phases has used inelastic neutron scattering data.[4] A small number of transitions between CEF levels have been observed in each of $\mathrm{TbMo}_6\mathrm{Se}_8$, $\mathrm{HoMo}_6\mathrm{Se}_8$, and $\mathrm{ErMo}_6\mathrm{Se}_8$, but no such transitions were found in $\mathrm{HoMo}_6\mathrm{S}_8$. The rare-earth molybdenum selenide data in Ref. 4 were analyzed using a cubic CEF Hamiltonian, assuming that the distortions of the structure from a cubic point symmetry would not be significant. The extraction of CEF splittings from the presently available heat-capacity data[5] is difficult because of large contributions from the magnetic ordering of impurity phases present in all samples studied and from the $\mathrm{Mo}_6\mathrm{S}_8$ vibrational modes. Indeed, Chevrel phases are difficult to prepare in pure form. Heat-capacity data do show that $\mathrm{TbMo}_6\mathrm{S}_8$ has a doublet electronic ground state, but little beyond that. This paper reports ^{155}Gd Mössbauer-effect measurements of the lattice-generated electric field gradient at the rare-earth site, which show that the principal term in the CEF Hamiltonian ($B_2^0\hat{O}_2^0$) is substantial for both the $R\mathrm{Mo}_6\mathrm{S}_8$ and the $R\mathrm{Mo}_6\mathrm{Se}_8$ series. This means that the rare-earth site is not nearly cubic, and a cubic CEF Hamiltonian is not a useful approximation.

EXPERIMENTAL RESULTS

Samples of $\mathrm{GdMo}_6\mathrm{S}_8$ and $\mathrm{GdMo}_6\mathrm{Se}_8$ were synthesized from $\mathrm{Gd}_2\mathrm{S}_3(\mathrm{Se}_3)$, Mo, and S(Se) by a procedure similar to that reported for $\mathrm{SnMo}_6\mathrm{S}_8$.[6] Because of the low vapor pressure of $\mathrm{Gd}_2\mathrm{S}_3(\mathrm{Se}_3)$ it was necessary to fire the samples three times at 1250 °C (with thorough grinding of powder after each firing) to obtain complete reaction. Powder x-ray diffraction of the $\mathrm{GdMo}_6\mathrm{S}_8$ sample found evidence of $\mathrm{Mo}_2\mathrm{S}_3$ impurity, as well as several lines that could not be identified. X-ray diffraction of the $\mathrm{GdMo}_6\mathrm{Se}_8$ sample indicated some gadolinium selenide impurity phases.

Figure 1 shows a ^{155}Gd Mössbauer spectrum of $\mathrm{GdMo}_6\mathrm{S}_8$ at 4.2 K using the 86.5-keV monochromatic radiation from a SmPd_3 source. This pattern exhibits a substantial quadrupole interaction and unresolved extra intensity due to (probably magnetically ordered) impurity phases in the sample. Because of the rather low Debye temperatures of Chevrel compounds, even a small amount of any impurity phase with a higher Debye temperature is

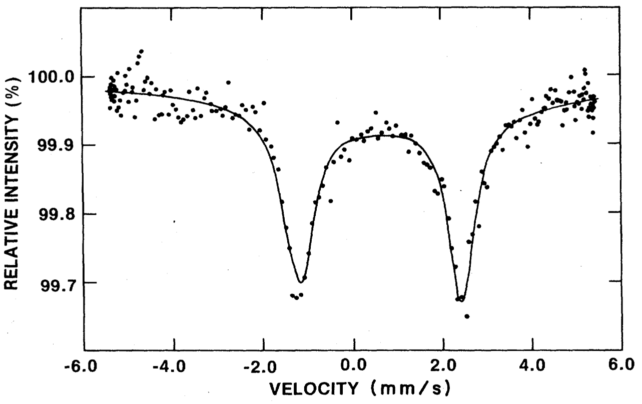

FIG. 1. ^{155}Gd (86.5 keV) Mössbauer absorption spectrum of $\mathrm{GdMo}_6\mathrm{S}_8$ at 4.2 K. The solid line is the least-squares fit to the data. The procedure for such analysis is discussed in detail in Ref. 3.

readily observed in a Mössbauer spectrum because of the large recoil energy associated with the nuclear transition. For a Gd site with an axis of rotational symmetry, the quadrupole coupling is given by the magnitude of e^2qQ, where q is the principal component of the electric field gradient acting on the ^{155}Gd nucleus with a quadrupole moment Q. A least-squares fit to the data, using an appropriate quadrupole Hamiltonian,[2,3] yields the value 545 ± 40 MHz for $|e^2qQ|$. However, the sign of e^2qQ could not be deduced because of the presence of the impurity signal which amounted to about 8% of the total resonance area under the quadrupole pattern.

The ^{155}Gd Mössbauer spectrum of $\mathrm{GdMo_6Se_8}$ measured at 15 K could be decomposed into two quadrupole patterns. At 4.2 K, one of these quadrupole patterns showed considerable broadening, while the other remained unchanged. The first pattern, hence most likely, represents an impurity phase which shows magnetic order between 4.2 and 15 K, while the second represents Gd atoms in the Chevrel phase which does not order in the available temperature range. The quadrupole interaction $|e^2qQ|$ at the ^{155}Gd nucleus in the Chevrel phase was found to be 470 ± 60 MHz.

DISCUSSION OF THE CRYSTALLINE ELECTRIC FIELD

The rare-earth site on the trigonal axis of the Chevrel-phase structure has point symmetry $\bar{3}$, and the crystalline-electric-field Hamiltonian for this case is given by

$$\mathscr{H}_{\mathrm{CEF}}=B_2^0\hat{O}_2^0+B_4^0\hat{O}_4^0+B_4^3\hat{O}_4^3+B_6^0\hat{O}_6^0+B_6^3\hat{O}_6^3$$
$$+B_{6(s)}^3\hat{O}_{6(s)}^3+B_6^6\hat{O}_6^6+B_{6(s)}^6O_{6(s)}^6 \qquad (1)$$

in the notation of Hutchings.[7] If the site is cubic, the CEF parameters B_2^0, B_4^3, and B_6^3 are zero.

The ^{155}Gd Mössbauer measurements unquestionably show that the trivalent-rare-earth site is not cubic for CEF purposes. The lattice-generated electric field gradient at the Gd nucleus is related to CEF parameters through the following relations:[3]

$$q=-4A_2^0(1-\gamma_\infty)/|e| \ , \qquad (2)$$

$$B_2^0=\alpha_J A_2^0\langle r^2\rangle(1-\sigma_2) \ , \qquad (3)$$

where A_2^0 is a coefficient of a spherical harmonic expansion of the electric field at the site (approximately independent of the particular rare earth occupying the site), σ_2 and γ_∞ are shielding parameters,[8] α_J is a "Stevens factor,"[7] and $\langle r^2\rangle$ is the second moment of the $4f$ radial wave function.[9] From the value of $|e^2qQ|$ obtained above, we deduce $|A_2^0|=1900\pm300$ K/a.u. for the $R\mathrm{Mo_6S_8}$ and 1600 ± 300 K/a.u. for $R\mathrm{Mo_6Se_8}$. These values are both larger than in the $R\mathrm{Rh_4B_4}$ series of compounds, where the resulting B_2^0 largely dominates the CEF effects and causes large single-ion magnetic anisotropies that cannot in any way be approximated by a cubic CEF Hamiltonian.[2] The present result suggests that the situation is very different from cubic in rare-earth Chevrel phases.

The behavior of the rare-earth moment in these materials is governed by the sign of A_2^0. Unfortunately, this could not be deduced uniquely from the above experiment. However, the sign of the quadrupole interaction at the ^{170}Yb nucleus in $\mathrm{YbMo_6S_8}$ has been uniquely determined.[10] Since the Yb atom in $\mathrm{YbMo_6S_8}$ is divalent with a $4f^{14}$ configuration, the electric field gradient at the Yb site is produced entirely from the lattice charges, and the procedure described above relating q and A_2^0 should be applicable. Using the measured value of $e^2qQ=+(1000\pm20)$ MHz in $\mathrm{YbMo_6S_8}$ and Eq. (2), one obtains the value of A_2^0, which is identical to that found above from the results on $\mathrm{GdMo_6S_8}$, and the sign of A_2^0 is found to be positive.

The sign of A_2^0 can also be deduced from ESR measurements. Odermatt *et al.*[11] report the zero-field splitting parameter b_2^0 for the $\mathrm{Gd^{3+}}$ atom in $\mathrm{SnMo_6S_8}$ to be -5.1×10^{-2} K. The magnitude of this term is large in comparison to such splittings in other metallic or insulating systems. The value of b_2^0 is related to A_2^0, but in a complex way, with numerous mechanisms which can contribute to the zero-field splitting. The dominant mechanism contributing to the negative value of b_2^0 is linear in the CEF. The matrix elements responsible for this term, which involve a mixing of the $^6D_{7/2}$ and $^6P_{7/2}$ state into $^8S_{7/2}$, can be calculated following Hutchinson *et al.*[12] Using the value of $b_2^0=-5.1\times10^{-2}$ K, we obtain $A_2^0=+258$ K/a.u. This is small in comparison to our measured value of $+(1900\pm300)$ K/a.u. Since all the other mechanisms contributing to b_2^0 will make the A_2^0 value more positive, the value of A_2^0 deduced above from b_2^0 should be considered the lower limit. This reemphasizes the positive sign of A_2^0.

Having established A_2^0 to be positive, we can evaluate its consequences on the magnetic behavior of the rare-earth Chevrel-phase compounds. Assuming that A_2^0 does not vary with the type of rare earth across the isostructural $R\mathrm{Mo_6S_8}$ ($R=$Tb, Dy, Ho, Er, Tm) series, the values of B_2^0 are obtained using Eq. (3). These are given in Table I. In this table, some of the important physical properties of the rare-earth atoms in $R\mathrm{Mo_6S_8}$ obtained experimentally[4,13-16] are summarized and are compared with those predicted by the truncated CEF Hamiltonian containing only the $B_2^0\hat{O}_2^0$ term [see Eq. (1)]. It should be pointed out that the CEF predictions here are similar to those in $R\mathrm{Rh_4B_4}$.[2]

At low temperatures, the magnetic moments of Tb, Dy, and Ho will be nearly free-ion, but will be constrained to lie along the rotational-symmetry axis of the site (the hexagonal c axis). The Er and Tm moments will be constrained to a plane perpendicular to this axis, and their value may be significantly reduced from the free-ion values. These predictions are roughly in agreement with the neutron scattering studies of magnetic ordering in the molysulfides (see Table I). It was found that the Dy and Ho moments in the respective molysulfides order along the hexagonal c axis, but it was not possible to establish the ordered moment direction in $\mathrm{TbMo_6S_8}$ or $\mathrm{ErMo_6S_8}$. Also, the $B_2^0\hat{O}_2^0$ term predicts a doublet ground state for Tb, consistent with the heat-capacity data.[5] ^{160}Dy Mössbauer studies of $\mathrm{DyMo_6S_8}$ at 0.14 K revealed a mag-

TABLE I. Values of B_2^0 and a comparison of available measurements and predictions by $B_2^0\hat{O}_2^0$ Hamiltonian for $R\mathrm{Mo_6S_8}$ (R=Tb, Dy, Ho, Er, Tm). F and AF denote ferromagnetic and antiferromagnetic, respectively.

	B_2^0 (K)	CEF ground state		Ordering and moment direction		Ground-state moment (μ_B)	
R	(±20%)	$B_2^0\hat{O}_2^0$ model	Experiment	$B_2^0\hat{O}_2^0$ model	Experiment	$B_2^0\hat{O}_2^0$ model	Experiment
Tb	-5.8	±6 doublet	doublet[a]	c axis	AF	9.0	8.3[b]
Dy	-3.5	$\pm\frac{15}{2}$ doublet		c axis	c axis AF	10.0	8.8,[b] 9.0[c]
Ho	-1.2	±8 doublet	low degeneracy[b]	c axis	c axis F	10.0	9.0[b]
Er	$+1.3$	$\pm\frac{1}{2}$ doublet		basal plane	AF	$\simeq 5.0$	3.5[b]
Tm	$+4.9$	0 singlet		no ordering		~ 0	

[a] Reference 5.

[b] Reference 4.

[c] Reference 15 and this work.

netic moment of $9\mu_B$ on the Dy atom, which is close to the moment of $10\mu_B$ predicted by the B_2^0 model. This is also in agreement with the neutron diffraction measurements.[14–16]

Although the B_2^0 model for the CEF predicts most of the available results, there are some neutron measurements which cannot be reconciled. One of the important results suggest that the value of the moment on Ho in $\mathrm{HoMo_6S_8}$ is $9.0\mu_B$, and is isotropic under the influence of external field.[17] The field dependence of the moment further indicates that the ground state is a doublet.[4] Unfortunately, all these facts are not consistent with each other. Rubins[18] has shown that for an isolated Kramers-type ground doublet in any point symmetry, the sum of the induced moments in three mutually perpendicular directions is less than or equal to $g_J(J+1)$. Similar arguments hold for non-Kramers doublets. Even allowing high accidental degeneracy of the ground state, the experimental neutron studies cannot be understood.

The other inexplicable result concerns $\mathrm{DyMo_6S_8}$. Lander *et al.*[16] find that in the paramagnetic phase the small-angle elastic neutron scattering intensity is greater when **Q** is parallel to the external magnetic field than when **Q** is perpendicular, contrary to expectation. The result could only be explained by assuming negligible CEF in this compound, in contradiction with the present results.

In both the above neutron studies if it is assumed that there is sample reorientation in the external field, the results would not contradict our measurements and interpretation.[17]

CONCLUSIONS

The results from ^{155}Gd and ^{170}Yb Mössbauer studies of $\mathrm{GdMo_6S_8}$, $\mathrm{GdMo_6Se_8}$, and $\mathrm{YbMo_6S_8}$ have shown the importance of the $B_2^0\hat{O}_2^0$ term in the CEF Hamiltonian. A complete understanding of the CEF effects demands further measurements such as inelastic neutron scattering, single-crystal magnetization,[19] specific heat, critical-field anisotropy, etc. Evaluation of the importance of the other terms in the CEF Hamiltonian and reevaluation of the neutron scattering data should clarify some of the difficulties discussed above.[17]

The low magnetic transition temperatures of rare-earth Chevrel-phase compounds emphasize the importance of the dipolar interaction in these systems[20] and the weak Ruderman-Kittel-Kasuya-Yosida (RKKY) coupling.[21] The prediction of the nature of the magnetic order as well as the transition temperature however requires a proper inclusion of the CEF anisotropies deduced from the present study in addition to the magnetic interactions.

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