

# Crystal-Field Effects and the Anisotropic Magnetization of TmSb

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(Received 19 September 1969)

We show that the experimental results for the susceptibility and high-field anisotropic magnetization of TmSb can be understood on the basis of crystal-field effects. The absence of any exchange effects is verified by experiments on  $\text{Tm}_{0.53}\text{Y}_{0.47}\text{Sb}$  giving the same susceptibility and high-field anisotropic magnetization per Tm ion as in TmSb. The theory and calculation of the anisotropic magnetization are described, and the use of such measurements to determine crystal-field parameters is discussed. Such anisotropic magnetization experiments are particularly valuable in determining the relative importance of fourth- and sixth-order contributions to the crystal field. Analysis of the present susceptibility and high-field magnetization experiments shows that the crystal field is predominantly fourth order, and gives an energy splitting of  $26.6^\circ\text{K}$  from the  $\Gamma_1$  singlet ground state to the  $\Gamma_4$  triplet first excited state of  $\text{Tm}^{3+}$  in TmSb.

## 1. INTRODUCTION

FOR rare-earth compounds it commonly occurs that the crystal-field-only ground state of the rare-earth ion is a singlet. (This is possible for those rare-earth ions with integral  $J$  in the ground state multiplet of the free ion. These are  $\text{Tb}^{3+}$  and  $\text{Tm}^{3+}$  with  $J=6$ ,  $\text{Pr}^{3+}$  with  $J=4$ , and  $\text{Ho}^{3+}$  with  $J=8$ .) Then at low temperature, the magnetization develops through a polarization or induced-moment process (i.e., the admixture of a crystal-field-only excited state wave function to the crystal-field ground-state wave function. In the paramagnetic regime, at low temperature this gives a Van Vleck susceptibility). In order for magnetic ordering, even at zero temperature, to occur in such an induced moment system, the ratio of exchange interaction to crystal-field energy must exceed a certain threshold value.<sup>1</sup> For values of exchange below threshold the system is always paramagnetic; but since such systems can be concentrated in the magnetic species, it is possible to develop quite large magnetization in rather moderate applied magnetic fields.<sup>2-4</sup> In the low-field region where the magnetization varies linearly with applied field, for a cubic material the magnetization must be isotropic. However, in the higher-field nonlinear regime the magnetization can show marked anisotropy.<sup>2,4,5</sup>

The anisotropic magnetization is both an interesting phenomenon in its own right, and as shown in the following paper<sup>6</sup> is a valuable tool to study the develop-

ment of exchange effects as one approaches the critical value of exchange for magnetic ordering. For both these reasons, it is desirable to have a "model" material exhibiting the crystal-field-only behavior for the anisotropic induced magnetization. This need is fulfilled by the behavior of TmSb, one of the NaCl structure compounds of rare earths with group-V anions. The behavior of TmSb, for which there is no detectable exchange, serves as a basis of comparison in discussing exchange effects in  $\text{Tb}_x\text{Y}_{1-x}\text{Sb}$  in the following paper.<sup>6</sup>

As discussed in the present paper, the absence of exchange effects in TmSb is documented in two ways. First, for TmSb the behavior of the susceptibility as temperature varies, and of the low-temperature anisotropic magnetization at high fields, are in excellent agreement with crystal-field-only theory. (These results have been partially reported previously,<sup>4</sup> and the present paper completes that report.) Second, we show that the susceptibility and high-field anisotropic magnetization per Tm ion are essentially unchanged on diluting the Tm with almost 50% Y.

In Sec. 2 we present the crystal-field-only theory for the susceptibility and high-field anisotropic magnetization. This theory is used both in Sec. 3 of this paper where comparison is made with the experimental behavior of TmSb and  $\text{Tm}_{0.53}\text{Y}_{0.47}\text{Sb}$ , and in the following paper<sup>6</sup> where for  $\text{Tb}_x\text{Y}_{1-x}\text{Sb}$  the addition of significant exchange leads to antiferromagnetic ordering.

## 2. CRYSTAL-FIELD-ONLY THEORY OF THE MAGNETIZATION

The crystal-field Hamiltonian for a rare-earth ion in an octahedral crystal field has the form

$$\mathcal{H}_{\text{CF}} = B_4(O_4^0 + 5 \times O_4^4) + B_6(O_6^0 - 21 \times O_6^4). \quad (2.1)$$

Here,  $O_4^0$ ,  $O_4^4$ ,  $O_6^0$ , and  $O_6^4$  are specified operators for a given  $J$  ( $J=6$  for  $\text{Tm}^{3+}$  and  $\text{Tb}^{3+}$ ), and the axis of quantization has been chosen parallel to a crystal axis. The operators  $O_4^0$  and  $O_4^4$  are fourth order in the com-

<sup>1</sup> G. T. Trammell, J. Appl. Phys. **31**, 362S (1960); Phys. Rev. **131**, 932 (1963); B. Bleaney, Proc. Roy. Soc. (London) **A276**, 19 (1963); B. R. Cooper, Phys. Rev. **163**, 444 (1967); Y. L. Wang and B. R. Cooper, *ibid.* **172**, 539 (1968); **185**, 696 (1969). For a review see B. R. Cooper, J. Appl. Phys. **40**, 1344 (1969).

<sup>2</sup> B. R. Cooper, I. S. Jacobs, R. C. Fedder, J. S. Kouvel, and D. P. Schumacher, J. Appl. Phys. **37**, 1384 (1966).

<sup>3</sup> G. Busch, A. Menth, O. Vogt, and F. Hulliger, Phys. Letters **19**, 622 (1966).

<sup>4</sup> O. Vogt and B. R. Cooper, J. Appl. Phys. **39**, 1202 (1968).

<sup>5</sup> B. R. Cooper, Phys. Letters **22**, 24 (1966); **22**, 244 (1966).

<sup>6</sup> B. R. Cooper and O. Vogt, following paper, Phys. Rev. B **1**, 1218 (1970).

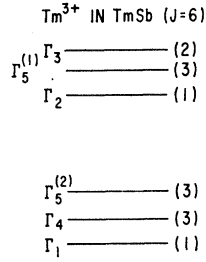


FIG. 1. Crystal-field level scheme for  $Tm^{3+}$  in a site of octahedral symmetry. Order of levels shown is for predominantly fourth-order anisotropy.

ponents of  $\mathbf{J}$ , while  $O_6^0$  and  $O_6^4$  are sixth order in  $\mathbf{J}$ . Thus the crystal-field Hamiltonian is completely determined by symmetry considerations except for the constants  $B_4$  and  $B_6$ . Rather than deal with  $B_4$  and  $B_6$ , it is often more convenient to treat two other parameters,<sup>7</sup>  $x$  and  $W$ . The ratio of fourth-to-sixth-order anisotropy is given by  $x$ ; while  $W$  gives the absolute scaling of the crystal-field energy levels.

$$\frac{B_4}{B_6} = \frac{x}{1-|x|} \frac{F(6)}{F(4)}, \quad (2.2)$$

$$B_4 F(4) = Wx. \quad (2.3)$$

Here  $F(4)$  and  $F(6)$  are numerical factors known for a given  $J$ .

If the crystal field is completely fourth order and is due to an octahedron of negative charges (i.e., at the nearest anion sites) surrounding the  $Tm^{3+}$  ion, then  $x = -1$  and  $W$  is negative, and the level scheme is as shown in Fig. 1. As  $x$  varies between  $-1$  and  $+1$ , the relative splittings of the levels change, and for sufficiently great departures from  $x = -1$  (for  $x \gtrsim -0.55$ ) there are level crossings.<sup>7</sup> The wave functions and relative separations of the energy levels are specified for a given  $x$ , so that  $W$  serves solely as an absolute scaling factor. The wave functions and energy values for the  $\mathcal{H}_{CF}$  of Eq. (2.1) can be determined by diagonalizing the  $13 \times 13$  secular determinant corresponding to  $\mathcal{H}_{CF}$ . Since there is only one state present of each symmetry type except for  $\Gamma_5$ , the wave functions other than  $\Gamma_5$  do not vary with  $x$ , and the corresponding energy levels vary linearly with  $x$ . On the other hand, there are two triplet states of  $\Gamma_5$  symmetry present, denoted as

$$\begin{aligned} \chi_p/\mu_B = (2g^2\mu_B/Z) & \left\{ \frac{\langle \Gamma_{4b} | J_z | \Gamma_1 \rangle^2}{E(\Gamma_4) - E(\Gamma_1)} \exp(-E(\Gamma_1)/kT) \right. \\ & + \left[ \frac{2\langle \Gamma_{5a}^{(2)} | J_z | \Gamma_{4a} \rangle^2}{E(\Gamma_5^{(2)}) - E(\Gamma_4)} + \frac{2\langle \Gamma_5^{(1)} | J_z | \Gamma_{4a} \rangle^2}{E(\Gamma_5^{(1)}) - E(\Gamma_4)} + \frac{\langle \Gamma_1 | J_z | \Gamma_{4b} \rangle^2}{E(\Gamma_1) - E(\Gamma_4)} + \frac{\langle \Gamma_{3a} | J_z | \Gamma_{4b} \rangle^2}{E(\Gamma_3) - E(\Gamma_4)} \right] \exp(-E(\Gamma_4)/kT) \\ & \left. + \left[ \frac{2\langle \Gamma_{4a} | J_z | \Gamma_{5a}^{(2)} \rangle^2}{E(\Gamma_4) - E(\Gamma_5^{(2)})} + \frac{2\langle \Gamma_{5a}^{(1)} | J_z | \Gamma_{5a}^{(2)} \rangle^2}{E(\Gamma_5^{(1)}) - E(\Gamma_5^{(2)})} + \frac{\langle \Gamma_2 | J_z | \Gamma_{5b}^{(2)} \rangle^2}{E(\Gamma_2) - E(\Gamma_5^{(2)})} + \frac{\langle \Gamma_{3b} | J_z | \Gamma_{5b}^{(2)} \rangle^2}{E(\Gamma_3) - E(\Gamma_5^{(2)})} \right] \exp(-E(\Gamma_5^{(2)})/kT) \right\} \end{aligned}$$

<sup>7</sup> K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).

$\Gamma_5^{(1)}$  and  $\Gamma_5^{(2)}$  in Fig. 1. Therefore the  $\Gamma_5$  wave functions do not vary with  $x$  and the corresponding energies vary nonlinearly with  $x$ .

To find the magnetization at specified magnetic field, the  $13 \times 13$  determinant for  $\mathcal{H}$  is first diagonalized, where

$$\mathcal{H} = \mathcal{H}_{CF} - g\mu_B H J_z. \quad (2.4)$$

Here  $g$  is the Landé factor and  $\mu_B$  is the Bohr magneton. Then the magnetization (Bohr magnetons per ion) is calculated using the eigenfunctions and eigenvalues for each value of  $H$ .

$$M = g \text{Tr}[J_z \exp(-\mathcal{H}/kT)] / \text{Tr}[\exp(-\mathcal{H}/kT)]. \quad (2.5)$$

The contribution to  $M$  linear in applied field is obtained easily by considering the applied field as a perturbation on the crystal-field energy. The susceptibility so obtained is isotropic for a cubic material and is given by

$$\chi = \chi_R + \chi_P. \quad (2.6)$$

Here  $\chi_R$  is the part of the susceptibility arising from the population difference caused by a magnetic field, between states having a permanent moment in the absence of magnetic field.

$$\begin{aligned} \chi_R/\mu_B = (2g^2\mu_B/kTZ) & \left[ \langle \Gamma_{4a} | J_z | \Gamma_{4a} \rangle^2 \exp(-E(\Gamma_4)/kT) \right. \\ & + \langle \Gamma_{5a}^{(2)} | J_z | \Gamma_{5a}^{(2)} \rangle^2 \exp(-E(\Gamma_5^{(2)})/kT) \\ & \left. + \langle \Gamma_{5a}^{(1)} | J_z | \Gamma_{5a}^{(1)} \rangle^2 \exp(-E(\Gamma_5^{(1)})/kT) \right], \quad (2.7) \end{aligned}$$

Where the subscripts  $a$  and  $b$  on the triplet wave functions are used to denote the lower and middle Zeeman-split triplet wave functions, respectively, and

$$Z = \sum_n e^{-E_n/kT} \quad (2.8)$$

is the crystal-field-only single-ion partition function. (Here  $E_n$  is the energy of the  $n$ th crystal-field state of the single ion.)

$\chi_R$  is the usual sort of susceptibility encountered for magnetic systems having small crystal-field effects. The second contribution,  $\chi_P$ , is that caused by that part of the moments of the states that is induced by the field. Then  $\chi_P$  is the polarization or Van Vleck-type contribution to the susceptibility.

$$\begin{aligned}
& + \left[ \frac{\langle \Gamma_{5b}^{(2)} | J_z | \Gamma_2 \rangle^2}{E(\Gamma_5^{(2)}) - E(\Gamma_2)} + \frac{\langle \Gamma_{5b}^{(1)} | J_z | \Gamma_2 \rangle^2}{E(\Gamma_5^{(1)}) - E(\Gamma_2)} \right] \exp(-E(\Gamma_2)/kT) \\
& + \left[ \frac{2\langle \Gamma_{4a} | J_z | \Gamma_{5a}^{(1)} \rangle^2}{E(\Gamma_4) - E(\Gamma_5^{(1)})} + \frac{2\langle \Gamma_{5a}^{(2)} | J_z | \Gamma_{5a}^{(1)} \rangle^2}{E(\Gamma_5^{(2)}) - E(\Gamma_5^{(1)})} + \frac{\langle \Gamma_2 | J_z | \Gamma_{5b}^{(1)} \rangle^2}{E(\Gamma_2) - E(\Gamma_5^{(1)})} + \frac{\langle \Gamma_{3b} | J_z | \Gamma_{5b}^{(1)} \rangle^2}{E(\Gamma_3) - E(\Gamma_5^{(1)})} \right] \exp(-E(\Gamma_5^{(1)})/kT) \\
& + \left[ \frac{\langle \Gamma_{5b}^{(2)} | J_z | \Gamma_{3b} \rangle^2}{E(\Gamma_5^{(2)}) - E(\Gamma_3)} + \frac{\langle \Gamma_{5b}^{(1)} | J_z | \Gamma_{5b} \rangle^2}{E(\Gamma_5^{(1)}) - E(\Gamma_3)} + \frac{\langle \Gamma_{4b} | J_z | \Gamma_{3a} \rangle^2}{E(\Gamma_4) - E(\Gamma_3)} \right] \exp(-E(\Gamma_3)/kT) \}. \quad (2.9)
\end{aligned}$$

At low temperature,  $\chi_p$  is the dominant part of the susceptibility. In particular, at  $T=0$  for values of  $x$  between  $-1$  and approximately  $-0.55$  where the order of levels shown in Fig. 1 applies,

$$\frac{\chi(T=0)}{\mu_B} = \frac{\chi_p(T=0)}{\mu_B} = \frac{2g^2\mu_B \langle \Gamma_{4b} | J_z | \Gamma_1 \rangle^2}{E(\Gamma_4) - E(\Gamma_1)}. \quad (2.10)$$

Since the wave functions  $|\Gamma_{4b}\rangle$  and  $|\Gamma_1\rangle$  are independent of  $x$ , the susceptibility at  $T=0$  depends only on the energy splitting from the  $\Gamma_1$  ground state to the  $\Gamma_4$  first excited state. For specified  $x$ , this splitting depends only on  $W$ ; and thus matching the experimental susceptibility at  $T=0$  for specified  $x$  determines  $W$ . (Actually, the same sort of determination of  $W$  holds for  $x$  between  $-0.55$  and  $0$  where, however, the singlet ground state is then the  $\Gamma_2$  state.)

As  $H$  increases, the nonlinear contribution to the magnetization becomes important. The magnetization is then obtained from (2.5) where the trace is taken over the 13 exact eigenstates of the ground state multiplet for specified  $\mathbf{H}$ . The diagonalization of the Hamiltonian and the calculation of  $\mathbf{M}$  are most easily obtained in a coordinate system where the direction of magnetization (i.e., of applied field) is always taken as the  $z$  axis. Then (2.4) applies, and the crystal-field Hamiltonian is given by (2.1) for  $\mathbf{H}$  in a  $\langle 100 \rangle$  direction, and by (2.11a) and (2.11b) for  $\mathbf{H}$  in the  $\langle 110 \rangle$  and  $\langle 111 \rangle$  directions, respectively. (See the review article by Hutchings<sup>8</sup> for a derivation of these forms.)

$$\begin{aligned}
\langle 110 \rangle: \quad 3\mathcal{C}_{CF} = & -\frac{1}{4}B_4[O_4^0 - 20 \times O_4^2 - 15 \times O_4^4] \\
& - \frac{13}{8}B_6 \left[ O_6^0 + \frac{105}{26} \times O_6^2 - \frac{105}{13} \times O_6^4 \right. \\
& \left. + \frac{231}{26} \times O_6^6 \right], \quad (2.11a)
\end{aligned}$$

$$\begin{aligned}
\langle 111 \rangle: \quad 3\mathcal{C}_{CF} = & -\frac{2}{3}B_4[O_4^0 - 20\sqrt{2} \times O_4^3] \\
& + \frac{16}{9}B_6 \left[ O_6^0 + \frac{35}{4} \times \sqrt{2} \times O_6^3 + \frac{77}{8} \times O_6^6 \right]. \quad (2.11b)
\end{aligned}$$

<sup>8</sup> M. T. Hutchings, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. 16, pp. 227-273.

Here,

$$O_4^0 = 35J_z^4 - 30J(J+1)J_z^2 + 25J_z^2 - 6J(J+1) + 3J^2(J+1)^2, \quad (2.12a)$$

$$O_4^4 = \frac{1}{2}[J_+^4 + J_-^4], \quad (2.12b)$$

$$\begin{aligned}
O_6^0 = & 231J_z^6 - 315J(J+1)J_z^4 + 735J_z^4 \\
& + 105J^2(J+1)^2J_z^2 - 525J(J+1)J_z^2 + 294J_z^2 \\
& - 5J^3(J+1)^3 + 40J^2(J+1)^2 - 60J(J+1), \quad (2.12c)
\end{aligned}$$

$$O_6^4 = \frac{1}{4}[(11J_z^2 - J(J+1) - 38)(J_+^4 + J_-^4)]_+, \quad (2.12d)$$

$$O_4^2 = \frac{1}{4}[(7J_z^2 - J(J+1) - 5)(J_+^2 + J_-^2)]_+, \quad (2.12e)$$

$$\begin{aligned}
O_6^2 = & \frac{1}{4}[\{33J_z^4 - (18J(J+1) + 123)J_z^2 + J^2(J+1)^2 \\
& + 10J(J+1) + 102\}(J_+^2 + J_-^2)]_+, \quad (2.12f)
\end{aligned}$$

$$O_6^6 = \frac{1}{2}[J_+^6 + J_-^6], \quad (2.12g)$$

$$O_4^3 = \frac{1}{4}[J_z(J_+^3 + J_-^3)]_+, \quad (2.12h)$$

$$\begin{aligned}
O_6^3 = & \frac{1}{4}[(11J_z^3 - 3J(J+1)J_z - 59J_z) \\
& (J_+^3 + J_-^3)]_+, \quad (2.12i)
\end{aligned}$$

where  $[A, B]_+$  indicates the anticommutator.

Once the crystal-field Hamiltonian is specified by (2.1), (2.11), and (2.12), using the  $J_z$  representation it is a straightforward matter to exactly diagonalize the  $13 \times 13$  secular determinant for  $\mathcal{H}$  given by (2.4). Thus for a given value of  $H$  applied in a given direction, the magnetization is completely specified once  $B_4$  and  $B_6$

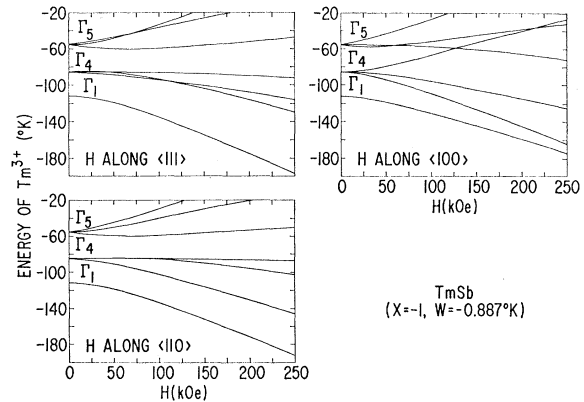


FIG. 2. Variation of crystal-field energy levels for  $Tm^{3+}$  in TmSb under influence of applied magnetic field in principal crystal directions.

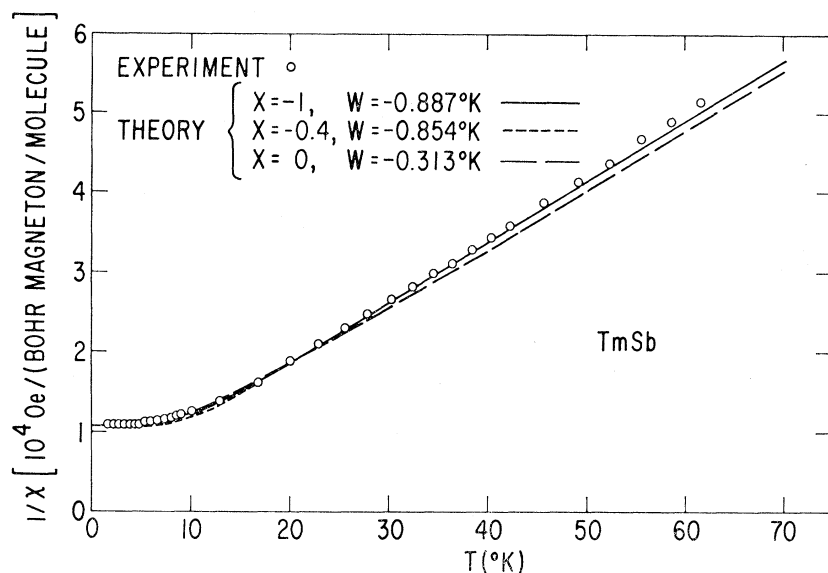


FIG. 3. Inverse susceptibility as temperature varies in TmSb. Experimental results are compared to crystal-field-only theory for several sets of parameters.

(or  $x$  and  $W$ ) are specified. For a  $\langle 100 \rangle$  direction, the  $13 \times 13$  secular determinant reduces to one  $4 \times 4$  and three  $3 \times 3$  determinants. For  $\langle 110 \rangle$ , there is one  $7 \times 7$  and one  $6 \times 6$ ; while for  $\langle 111 \rangle$ , there is one  $5 \times 5$  and two  $4 \times 4$  determinants to diagonalize.

The variation of the energy with field for the parameters pertinent to TmSb (as found in Sec. 3) is shown in Fig. 2 for the lower-energy levels. For large field, the behavior is quite anisotropic. (The unit of energy used is  $^\circ\text{K}$ , and this figure serves to show the behavior of the levels predominantly occupied at low temperature. Of course, for the higher-field values shown, the wave functions differ radically from the crystal-field-only wave functions. The ground-state level crossing and consequent sharp jump in magnetization expected<sup>6</sup> for  $\mathbf{H}$  in a  $\langle 100 \rangle$  direction would occur for  $H$  approximately 380 kOe for the crystal-field splitting pertinent to TmSb used in Fig. 2.)

### 3. EXPERIMENTAL RESULTS AND DISCUSSION

In Fig. 3, the experimental susceptibility as reported in Ref. 4 is shown compared to the theoretical result obtained from (2.6) for several values of  $x$ . The value of  $W$  used in each case was chosen to match the experimental susceptibility at the lowest temperature. (If the crystal field is octahedral, as opposed to some other cubic coordination—say tetrahedral—then  $x$  is negative, independent of the sign and magnitude of the effective charge giving the crystal field. In a point-charge model, presumably an oversimplification in the present case, the value of  $x$  depends only on the lattice parameter.)

The agreement of experiment and crystal-field-only theory for the susceptibility is excellent. Measurements up to 300°K maintain this excellent agreement,

approaching a Curie law at the highest temperatures. Thus there is no evidence for any significant exchange effects. (The approach to the Curie Law as temperature increases for the theoretical curves in Fig. 3 is, of course, asymptotic. While the  $x = -1$  and  $x = 0$  curves in Fig. 3 appear to the eye to be almost parallel at the upper part of the temperature range shown, by the time room temperature is reached they are quite close together. As already pointed out,<sup>2</sup> care should be taken in systems like this to avoid identifying apparent Curie-Weiss behavior, unless the temperatures for which such behavior arises are comparable to the over-all crystal-field splitting. The best and safest way to detect exchange effects on the inverse susceptibility for induced moment systems is to fit the over-all curve of  $1/\chi$  versus  $T$ , rather than just examining the higher temperature behavior.)

As can be seen from Fig. 3, once one chooses  $W$  to match the experimental  $1/\chi$  at the lowest temperature, the agreement between theory and experiment is not very sensitive to the choice of  $x$ . (This has been further documented for values of  $x$  intermediate to those shown in Fig. 3.) At most, one would discriminate against values of  $x$  quite close to zero. On the other hand, as shown in Fig. 4, the high-field anisotropic magnetization is much more sensitive to the choice of  $x$ . (The values of  $\langle 100 \rangle$  magnetization for  $x = -1$ ,  $W = -0.887^\circ\text{K}$  and  $x = -0.6$ ,  $W = -1.255^\circ\text{K}$  coincide, and the magnetization values for the  $\langle 110 \rangle$  direction are quite similar, so we do not show separate  $x = -0.6$  curves for  $\langle 100 \rangle$  and  $\langle 110 \rangle$ .) Agreement with the pulsed-field experimental results reported in Ref. 4 is best for values of  $x$  where the fourth-order anisotropy is predominant,  $x$  between  $-0.6$  and  $-1$ . Within that range, the  $\langle 111 \rangle$  behavior somewhat favors  $x = -1$ . (This is consistent with the paramagnetic resonance

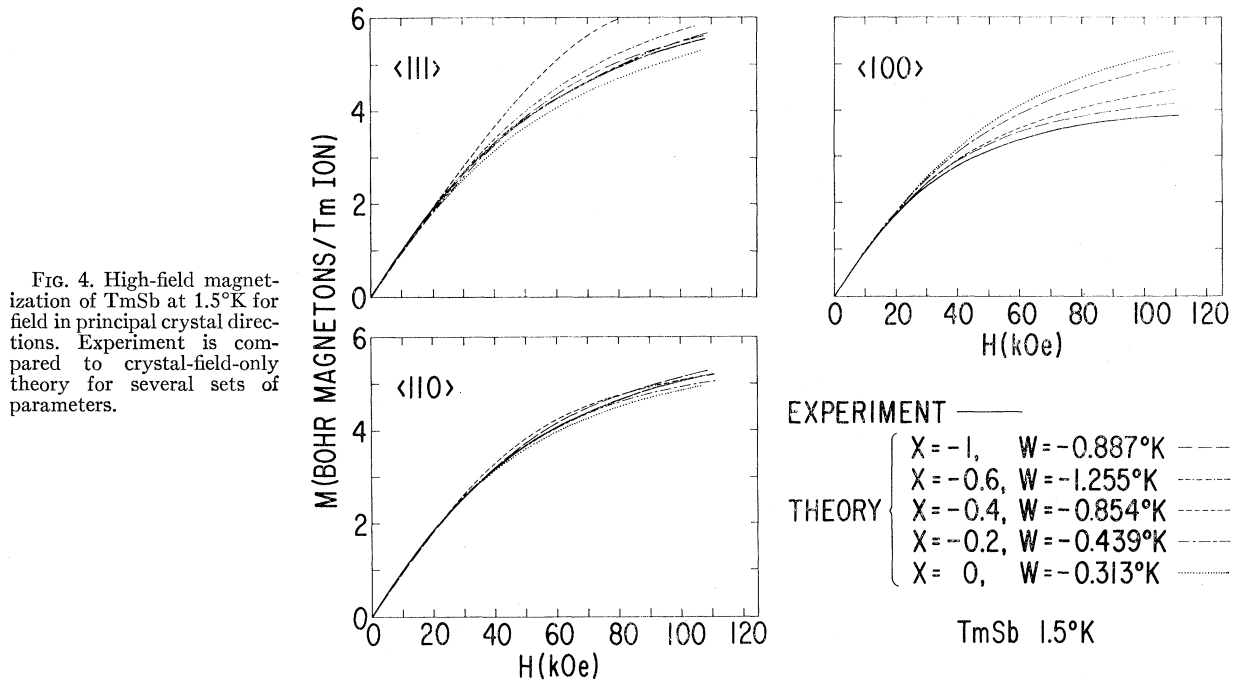


FIG. 4. High-field magnetization of TmSb at 1.5°K for field in principal crystal directions. Experiment is compared to crystal-field-only theory for several sets of parameters.

studies<sup>9</sup> on TmN where the resonance  $g$  behavior for the  $\Gamma_5^{(2)}$  excited state indicates a value of  $x$  very close to  $-1$ .)

For  $x \approx -1$ , the difference at low temperature between the magnetization with field in a  $\langle 111 \rangle$  direction and in a  $\langle 100 \rangle$  direction occurs because for a  $\langle 100 \rangle$  direction, the only significant admixture into the  $\Gamma_1$  state is from the  $\Gamma_4$  state. On the other hand, for  $\mathbf{H}$  along  $\langle 111 \rangle$ , in the nonlinear regime there is significant admixture from the second excited state, of  $\Gamma_5$  symmetry.

It is the anisotropic nature of the high-field magnetization that makes it particularly useful in determining the value of  $x$ . For example, for  $x = -0.2$  in Fig. 4 the agreement between theory and experiment is good for a  $\langle 111 \rangle$  direction, but quite poor for a  $\langle 100 \rangle$  direction. Also the anisotropic behavior found experimentally makes it easy to eliminate values of  $x$  near zero, sixth-order-only anisotropy. The  $x = 0$  theoretical behavior shown in Fig. 4 is almost isotropic, and indeed the hard directions are  $\langle 110 \rangle$ . This use of high-field magnetization experiments to study the crystal-field properties of rare-earth ions in crystals might be valuable in other situations in conjunction with the usual paramagnetic resonance experiments, or in situations where paramagnetic resonance cannot be observed.

All the theoretical curves shown in Fig. 4 are for negative  $W$  (corresponding to negative charge on the anion sites). Positive  $W$ , giving a  $\Gamma_3$  nonmagnetic

doublet ground state near  $x = -1$ , can be quickly eliminated since this would interchange the  $\langle 111 \rangle$  and  $\langle 100 \rangle$  directions as the axes of easy and hard magnetization, as well as giving rise to other distinctive behavior.<sup>10</sup>

Thus the experimental high pulsed-field magnetization results on TmSb at 1.5°K are in excellent agreement with the crystal-field-only theory for  $x = -1$  and a value of  $W$  which gives excellent agreement with the experimental temperature dependence of the susceptibility. (This value,  $W = -0.887^\circ\text{K}$ , gives a splitting of 26.6°K between the  $\Gamma_1$  ground state and the first excited  $\Gamma_4$  state.)

The applicability of the crystal-field-only picture for TmSb has been further documented by performing susceptibility and high pulsed-field magnetization experiments on  $\text{Tm}_{0.53}\text{Y}_{0.47}\text{Sb}$ . Yttrium is essentially identical to the heavy rare earths in its valence electron behavior, but has an empty  $4f$  shell. Thus substituting Y for Tm essentially does not change the crystal field, but would reduce any effective exchange field, because of neighboring  $\text{Tm}^{3+}$  ions, acting on a given  $\text{Tm}^{3+}$  ion.

In Fig. 5, the inverse susceptibility (per  $\text{Tm}^{3+}$  ion) versus temperature for  $\text{Tm}_{0.53}\text{Y}_{0.47}\text{Sb}$  is compared to the experimental results for TmSb and the crystal-field-only theory. There is a difference of at most a few percent between the experimental results for TmSb and those for  $\text{Tm}_{0.53}\text{Y}_{0.47}\text{Sb}$ ; and both sets of data give excellent agreement with crystal-field-only theory. This indicates an absence of any exchange effects. [The inverse susceptibility for  $\text{Tm}_{0.53}\text{Y}_{0.47}\text{Sb}$  was

<sup>9</sup> B. R. Cooper, R. C. Fedder, and D. P. Schumacher, Phys. Rev. Letters **18**, 744 (1967); Phys. Rev. **168**, 654 (1968).

<sup>10</sup> B. R. Cooper, Helv. Phys. Acta **41**, 750 (1968).

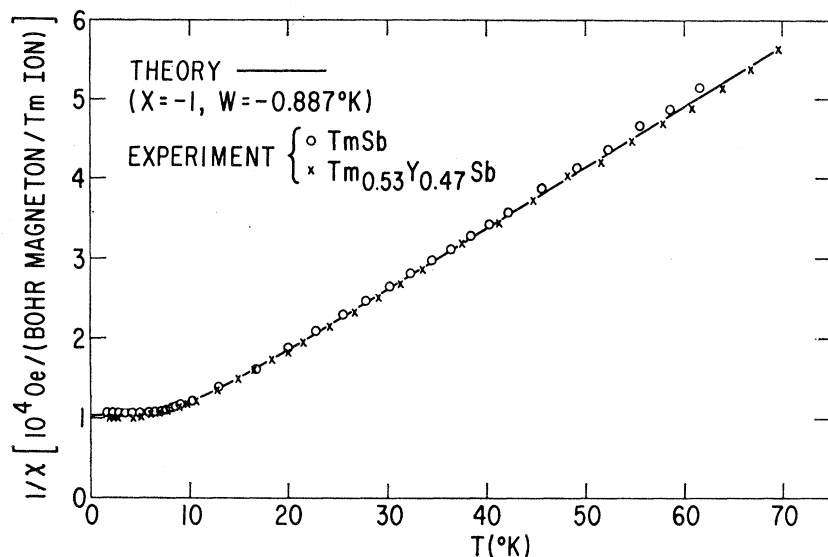


FIG. 5. Experimental inverse susceptibility versus temperature for TmSb and  $Tm_{0.53}Y_{0.47}Sb$  compared to crystal-field-only theory for purely fourth-order anisotropy.

measured up to 300°K and approaches a Curie law behavior. The sample was prepared from equal quantities of Tm and Y. The concentration of Tm in the crystal was then determined from the slope of the  $1/\chi$ -versus- $T$  curve (i.e., effective molar moment) at high temperature.] The small change in  $1/\chi$  at low temperature between TmSb and  $Tm_{0.53}Y_{0.47}Sb$  is of the expected size for the small change in lattice parameter which occurs. Specific-heat measurements by Stutius<sup>11</sup> of the Schottky anomaly in TmSb and  $Tm_{0.53}Y_{0.47}Sb$  also confirm that the crystal-field splitting changes at most by a few percent.

The high-field magnetization per Tm ion for  $Tm_{0.53}Y_{0.47}Sb$ , as shown in Fig. 6, is also in close agreement with that for TmSb and the crystal-field-only theory. Thus the measurements on  $Tm_{0.53}Y_{0.47}Sb$  strongly support the applicability of crystal-field-only theory to understanding the magnetic behavior of TmSb.

It should be pointed out that the excellent agreement of the TmSb and  $Tm_{0.57}Y_{0.43}Sb$  high-field magnetizations with each other and with crystal-field-only theory for the same crystal-field parameters eliminates the possibility of any significant magnetostriction effects

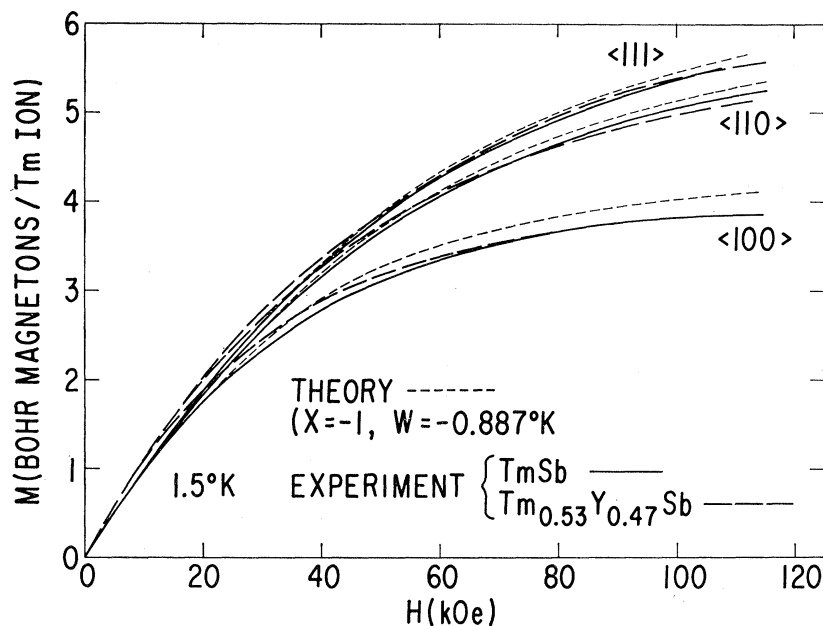


FIG. 6. High-field anisotropic magnetization of TmSb and  $Tm_{0.53}Y_{0.47}Sb$  at 1.5°K compared to crystal-field-only theory for purely fourth-order anisotropy.

<sup>11</sup> W. Stutius (private communication).

on the observed magnetization. Besides giving rise to significant departures from octahedral symmetry of the crystal field, such effects would be expected to depend on the magnetization per unit volume (rather than per ion), and thus to change significantly with yttrium dilution.

As pointed out in Ref. 4, at high fields the pulsed-field experimental results at 20.4°K had a significant difference with the isothermal theory. In Ref. 4 it was suggested that this difference might result from the spin-lattice relaxation time being comparable to the pulse time, so that the experimental magnetization would fall between the isothermal and adiabatic results. Indeed, the experimental results at high fields fell roughly halfway between the two theories. (There is essentially no difference between the isothermal and adiabatic magnetizations at low temperature, so such effects would not enter into the behavior at 1.5°K.) Direct-current magnetization measurements to resolve this question are currently in progress.

It is difficult to see any other possible explanation of the 20.4°K pulsed-field behavior than the mixture of adiabatic and isothermal behavior. As discussed above, the possibility of significant exchange effects in TmSb

has been eliminated. Also, any significant change of the crystal-field parameters with applied magnetic field seems unlikely since such magnetostriction effects are absent at 1.5°K. (A significant temperature dependence of  $W$ , without change of symmetry, can be ruled out by the over-all excellent agreement of the experimental and theoretical  $1/\chi$ -versus- $T$  behavior for  $X = -1$  and  $W = -0.887^\circ\text{K}$ .)

Thus the anisotropic high-field magnetization of TmSb can be well understood on the basis of crystal-field-only theory. Comparison with experiment of the theoretically expected behavior as exchange becomes significant is used in the following paper to discuss the nature of the effective exchange forces in  $\text{Tb}_x\text{Y}_{1-x}\text{Sb}$ .

#### ACKNOWLEDGMENTS

The authors wish to thank Miss Elise Kreiger for her aid with the numerical calculations, and Miss I. Schneider for her aid in preparing the crystals and performing the measurements. We are most grateful to Professor G. Busch for his stimulating interest and to Dr. I. S. Jacobs and Professor W. P. Wolf for much interesting discussion.