Crystal fields of dilute Tb, Dy, or Er in Sc obtained by magnetization measurements

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Crystal-field parameters for dilute Sc-Tb, Sc-Dy, and Sc-Er alloys have been obtained by fitting theoretical expressions to the experimentally measured paramagnetic susceptibility. The initial susceptibility was measured and corrected for the effects of ordering at the lowest temperatures in the hard direction, as investigated by neutron spectroscopy. The crystal-field parameters divided by Stevens factors B_{20}/α, B_{40}/β, B_{60}/γ, and B_{66}/γ are within the accuracy of their determination independent of the rare-earth solute. A comparison to parameters obtained for dilute Y and Lu rare-earth alloys shows that B_{40}, B_{60}, and B_{66} are almost independent of the host. B_{20}/α depends smoothly on the c/a ratio of the host in the decreasing order Y, Lu, Sc.

In earlier publications,[1,2,3] the crystal-field parameters of dilute Tb, Dy, or Er in Y or Lu have been reported. These parameters were obtained by fits to the initial susceptibility measured at a low constant field as a function of temperature. The parameters have been compared to other magnetization measurements[2,3,4] and to a neutron-spectroscopy experiment on a Y-Er alloy.[5] The data for all Er alloys are consistent. For Dy and Tb alloys, derivations have been found which have been attributed to effects of ordering. As has been demonstrated by a recent neutron-spectroscopy experiment on a Y-Dy alloy,[6] this ordering may drastically change the experimental initial

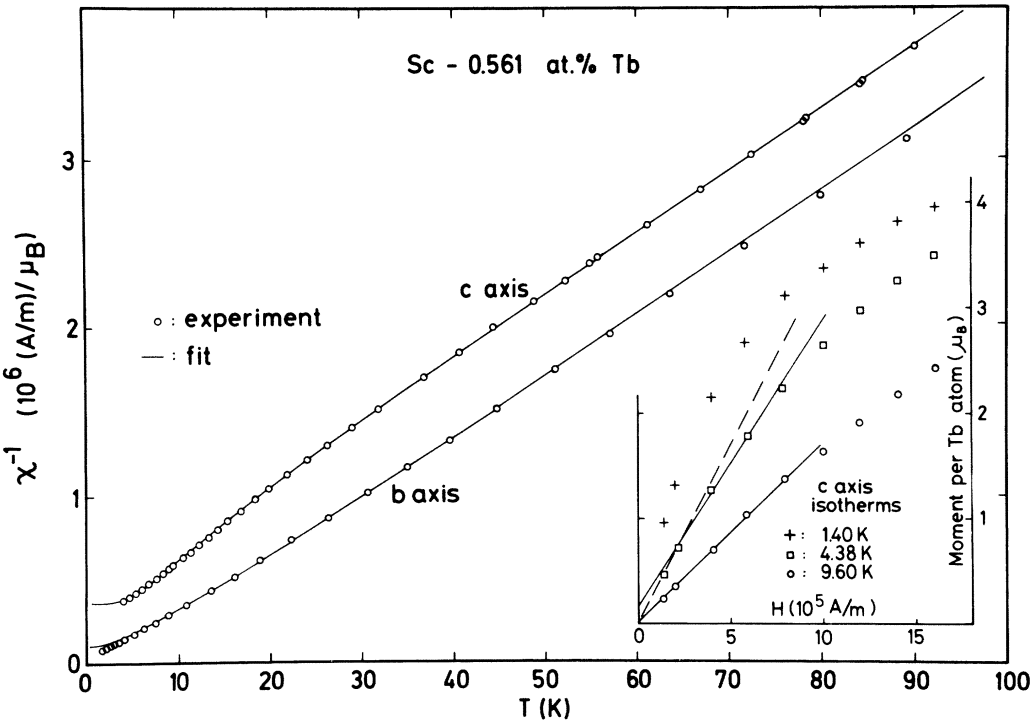

FIG. 1. Reciprocal susceptibility for Sc-0.561-at.% Tb. The full curves are theoretical fits. The susceptibility measured as the ratio $\chi_H = M/H$ at $H = 1.35\times10^5$ A/m has been corrected in the c direction below 9 K to the differential susceptibility χ_{CF} obtained from isothermal magnetization curves as illustrated in the inset. The dashed line and the upper full line have the slopes χ_H (4.38 K) and χ_{CF} (4.38 K), respectively. The lower full line has the slope χ_H (9.60 K) $=\chi_{CF}$ (9.60 K). At 4 K the accuracy of χ_{CF} is ± 7%. Below 4 K χ_{CF} cannot be obtained with reasonably accuracy.

TABLE I. Deduced crystal-field parameters divided by Stevens factors (Ref. 12). For all alloys B_{66} has the value $-\frac{77}{8} B_{60}$, as described in the text. The exchange parameters $\gamma_\perp$ and $\gamma_\parallel$ have been set equal to zero in the Sc-Dy and Sc-Er fits. For Sc-Tb, exchange parameters different from zero give the best fit. The theoretical curves in the figures are calculated using the parameters in this table. The parameters for Lu-Er and Y-Er given here have been obtained by the fitting procedure described in the present paper and differ insignificantly from those published earlier (Refs. 2 and 3).

	Units	Sc-0.561-at.% Tb	Sc-0.562-at.% Dy	Sc-0.528-at.% Er	Lu-0.553-at.% Er	Y-0.307-at.% Er Y-0.142-at.% Er
B_{20}/α	K	-31.0 ± 4	-29.9 ± 3	-29.0 ± 3	-55.7 ± 7	-111 ± 13
B_{40}/β	K	13.4 ± 5	14.6 ± 4	8.2^{-2}_{+5}	9.6 ± 2	13.5 ± 6
B_{60}/γ	K	24.4^{+2}_{-5}	20.9 ± 3	18.1 ± 2	16.1 ± 2	12.0 ± 3
γ	10^5 (A/m)/(μ_B/atom)	-0.2 ± 0.2	0	0	0	0
γ	10^5 (A/m)/(μ_B/atom)	-1.0 ± 1.0	0	0	0	0

susceptibility at low temperatures in the hard direction, thus giving rise to errors in the fitted parameters. However the correct paramagnetic susceptibility can be obtained from isothermal magnetization curves as the slope of the linear part of the curves following the initial high-slope range. Parameters fitted to the susceptibility measured in this way are consistent with the neutron results. Y and Lu resemble the magnetic rare earths with respect to both lattice constants and electronic band structure, while Sc is significantly different. For instance, the width of the d conduction bands in Sc, Y, Tb, and Lu are approximately 0.28, 0.48, 0.59, and 0.61 Ry, respectively.[7] It is therefore of interest to determine the crystal-field parameters in Sc also. In this paper we present magnetization measurements on Sc-Tb, Sc-Dy, and Sc-Er alloys and compare them with theoretical curves calculated from deduced crystal-field parameters.

The measurements were performed on hcp single crystals grown by recrystallization techniques.[8] Sublimed materials of 99.99% purity for Sc and 99.9% for Tb, Dy, and Er were used. Pure-Sc single crystals were grown, samples cut out for measuring, and the Sc crystals then remelted and used as a host metals for the alloys. In this way the measurements on the pure-Sc samples were representative for the Sc in the alloys. The measurements were performed using a Faraday magnetometer[1] for measuring initial susceptibilities, a 5-Hz vibrating-sample magnetometer[1] for measuring isothermal magnetization curves, and a 169-Hz vibrating-sample magnetometer[2,9] for measuring basal-plane anisotropies. In the latter instrument, the magnetic moment $M_\perp$ in the basal plane perpendicular to the magnetic field (also in the basal plane) was measured as a function of the crystal rotation angle ϕ about the vertical c axis. The large sixth-order Fourier component of $M_\perp(\phi)$ was used as a measure of the basal-plane anisotropy.

The experimental data were analyzed using a total single-ion Hamiltonian which contained the hexagonal crystal-field operator and an effective Zeemann operator:

$$H = B_{20}O_{20} + B_{40}O_{40} + B_{60}O_{60} + B_{66}O_{66} + g_J \mu_B \vec{J} \cdot (\vec{H} + \bar{\bar{\lambda}} \cdot \vec{M}). \quad (1)$$

The latter term includes the relatively small exchange interactions in the molecular-field approximation. The parameters to fit were the four crystal-field parameters B_{20}, B_{40}, B_{60}, and B_{66}, two molecular-field parameters $\lambda_\perp$ and $\lambda_\parallel$, and the actual concentration. The data for the Sc alloys contain less structure than those for the Y and Lu alloys. In order to avoid any ambiguity in

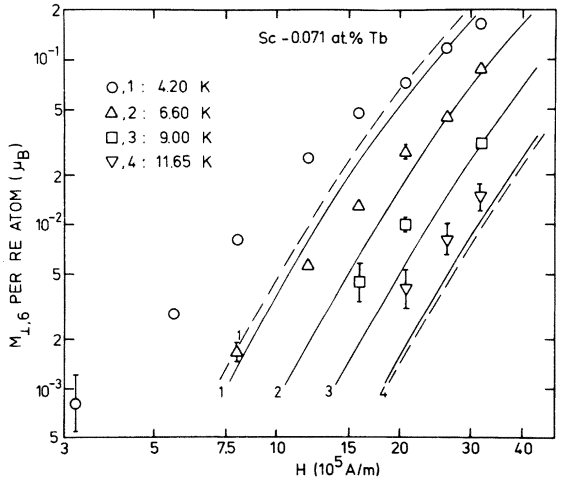

FIG. 2. Sixth-order harmonic of the perpendicular-basal-plane magnetization versus field and temperature for Sc-0.071-at.% Tb. The full curves are calculated. The effect of a 20% decrease of B_{60} and B_{66} is illustrated by the dashed curves.

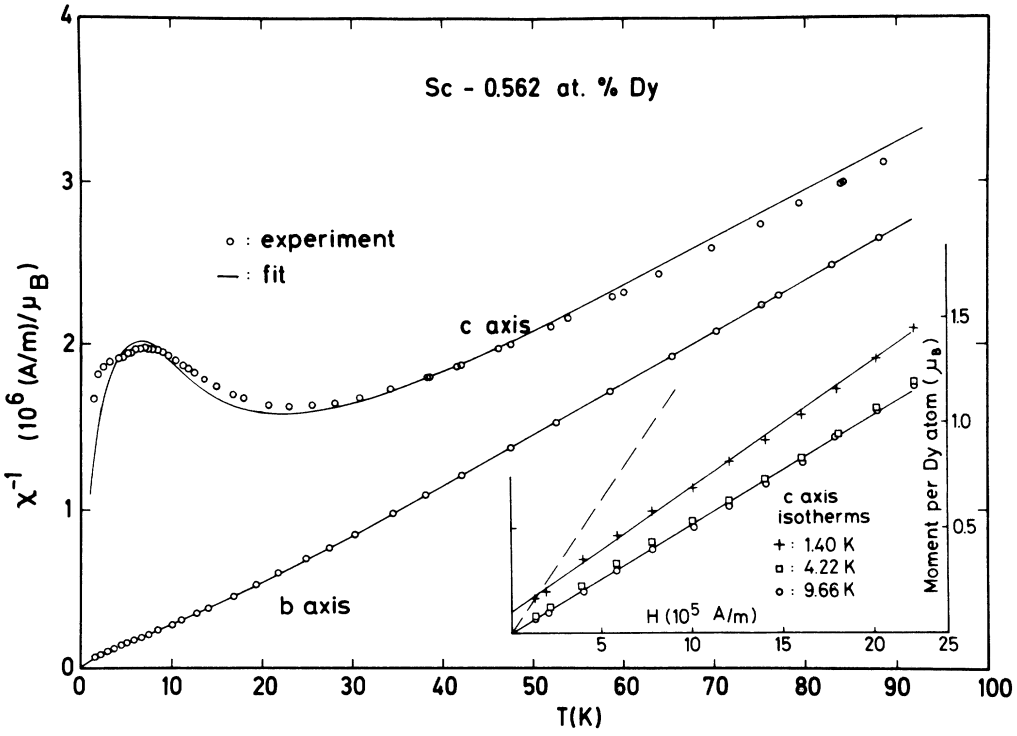

FIG. 3. Reciprocal susceptibility for Sc-0.562-at.% Dy. The full curves are theoretical fits. The susceptibility measured as the ratio $\chi_H = M/H$ at $H = 1.35 \times 10^5$ A/m has been corrected in the c direction below 9 K to the differential susceptibility χ_{CF} obtained from isothermal magnetization curves as illustrated in the inset. The dashed line and the upper full line have the slopes χ_H (1.40 K) and χ_{CF} (1.40 K), respectively. The lower full line has the slope χ_H (9.66 K) $= \chi_{CF}$ (9.66 K). Experimental data at 4.22 K are also shown.

the deduced parameters a fitting procedure different from that published earlier[1,2] was used. First the exchange parameters $\gamma_\perp$ and $\gamma_\parallel$ were so small that they could be set equal to zero without changing the crystal-field parameters by an amount greater than the final quoted uncertainties. Secondly the concentration and B_{20} were determined from the very-high-temperature data. The concentration was given by the slope of the $1/\chi$ curves and B_{20} was given by $1/\chi_c - 1/\chi_b$ since this difference only depends on B_{20} in the high-temperature limit. After all parameters had been deduced it was checked that the highest temperatures in the experiment were sufficiently high for this determination. Finally in order to interpret the very featureless data for Sc-Tb and Sc-Er the ratio B_{66}/B_{60} was set equal to $-\frac{77}{8}$. This relation is valid for nearest-neighbor interactions in the point-charge model, and also in the much more general superposition model.[10] Experimentally it is found to be valid within the uncertainty of determination for Sc-Dy and for many Y and Lu alloys[1,2,3,11] for which B_{60} and B_{66} can be determined separately. A calculation of the susceptibility in a range of the parameters B_{40} and B_{60}

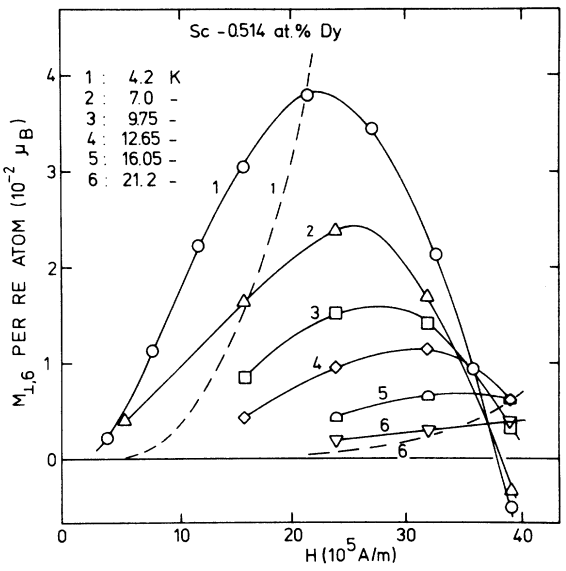

FIG. 4. Sixth-order harmonic of the perpendicular-basal-plane magnetization versus field and temperature for Sc-0.514-at.% Dy. The full curves are drawn through the experimental points. The dashed curves are calculated.

(and for Sc-Dy B_{66}) of several orders of magnitude and for both signs indicated only one minimum in the least-squares deviation between experimental and theoretical results. This was used to determine the starting values for these parameters in the final detailed fitting to the experimental results.

In Fig. 1 the reciprocal susceptibilities for Sc-0.561-at.% Tb are plotted. Of all Y, Lu, and Sc alloys measured, Sc-Tb alloys contain the least structure in the susceptibility curves. However, with the fitting procedure described above which contains only B_{40} and B_{60} as substantive unknowns a unique fit can be obtained. A difference between the experimental and theoretical reciprocal susceptibility is observed at low temperatures in the b direction. This is expected since the susceptibility in the easy direction cannot be corrected for ordering by the method used for the hard direction.[6] Fortunately the susceptibility at low temperatures in the easy direction is not important in determining the crystal-field parameters. The errors in the parameters given in Table I have for all alloys been estimated from the variation of the parameters when (a) data below a temperature T_{cut} were excluded with T_{cut} varied in the range 4–10 K, (b) the concentration and B_{20} were varied within the limits determined from the high-temperature data, and (c) nonzero exchange parameters were included in the fit. To check the parameters, further measurements on the basal-plane anisotropy have been performed (Fig. 2). Sc-Tb alloys show strong tendencies towards ordering and the latter measurements which are very sensitive to ordering had to be performed on the more dilute 0.071-at.%-Sc Tb alloy. Even for this low concentration the effects of ordering are seen, especially at the lowest fields and temperatures. Sc-0.562-at.% Dy has reciprocal susceptibility curves with characteristic features (Fig. 3), which allow a separate determination of both B_{60} and B_{66}. The ratio B_{66}/B_{60} is found to be within 10% of $-\frac{77}{8}$. The anomalies in the basal-plane-anisotropy measurements (Fig. 4) are also seen in[2] Y-Dy and[3] Lu-Dy alloys and in pure Dy.[13]

The reciprocal susceptibility curves for Sc-0.528-at.% Er also show characteristic features (Fig. 5). The Sc-Er alloys show the least tendency for ordering compared to Sc-Tb and Sc-Dy alloys and correction for ordering in the hard direction is not necessary for Sc-0.528-at.% Er. However, the basal-plane-anisotropy measurements in Fig. 6 show effects of ordering at the lowest temperatures and fields.

The experimental and theoretical curves for Sc-RE alloys are similar to those for Y-RE and Lu-RE alloys, but the characteristic features are observed at lower temperatures compared to the

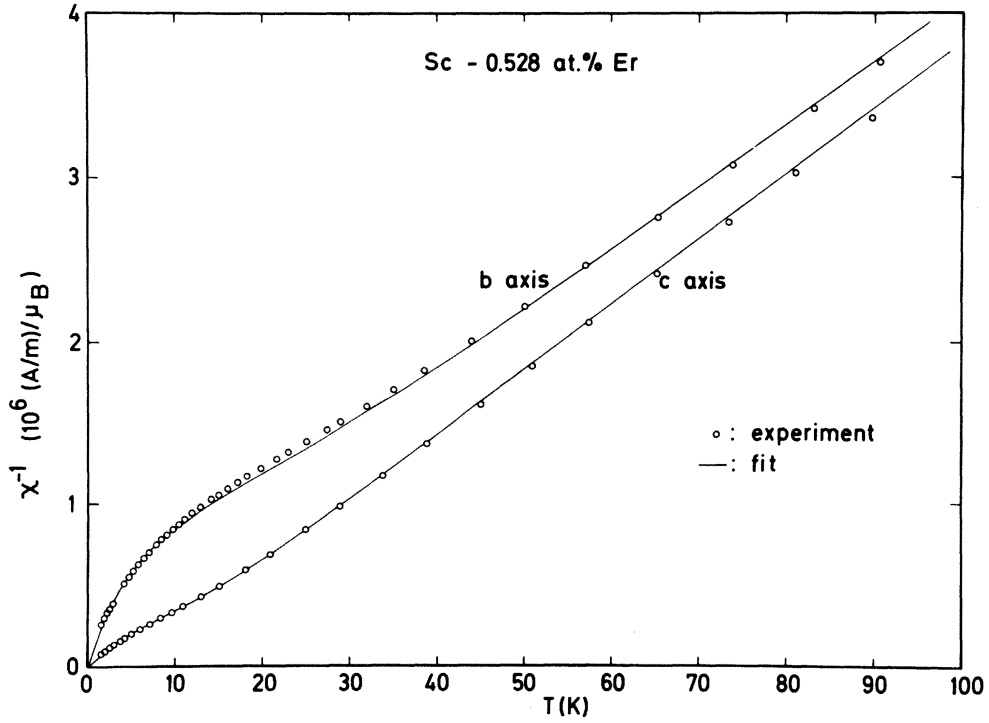

FIG. 5. Reciprocal susceptibility for Sc-0.528-at.% Er. The full curves are theoretical fits.

latter. This reflects a decrease in the crystal-field-level splittings from Y and Lu to Sc alloys. This decrease is mainly due to a decrease in B_{20} which is apparent from the experimental anisotropy of the susceptibility at higher temperatures. Except for variations arising from this difference in B_{20}, the Y, Lu, and Sc alloys show very similar magnetic properties. This is even true for the ordering phenomena observed at low temperatures which are best illustrated in the basal-plane-anisotropy measurements. The change in sign of the basal-plane anisotropy at low temperatures in applied fields is seen for Sc-0.514-at.% Dy and Lu-0.481-ar.% Dy,[3] but develops first at a concentration of 3-at.% Dy in Y.[2] This is consistent with the conclusion by Wohlleben[14] that the exchange interactions in Sc-RE alloys are of longer range than those in Y-RE alloys. The crystal-field parameters for the Sc alloys are summarized in Table I. Within the accuracy of their determination they are independent of the rare-earth solute. To explore the variation with the host the parameters for the Sc alloys may be compared to those for Y-Er and Lu-Er also given in Table I. The experimental data for these alloys need no correction for ordering and the earlier deduced parameters are therefore expected to be reliable. Only a small variation with the host is observed for B_{40}, B_{60}, and B_{66}. The parameter B_{20} decreases in the order Y, Lu, Sc corresponding to a smooth dependence on the c/a ratio of the host.

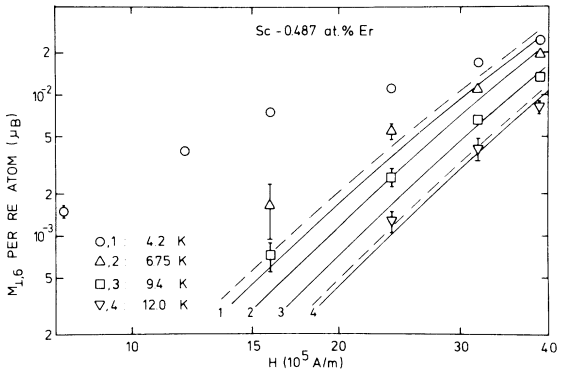

FIG. 6. Sixth-order harmonic of the perpendicular-basal-plane magnetization versus field and temperature for Sc-0.487-at.% Er. The full curves are calculated. The effect of a 10% increase in B_{66} is illustrated by the dashed curves.

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