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Magnetic properties of D-$Er_2Si_2O_7$ at low temperatures

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The low field magnetic susceptibility and the high field magnetic moment of D-$Er_2Si_2O_7$ at low temperatures are measured by an inductance method. The susceptibility results show that D-$Er_2Si_2O_7$ undergoes a transition from a paramagnetic to an antiferromagnetically ordered state at $T_N = 1.9 \pm 0.1$ K. The magnetic moment data is analysed on the basis of a four-sublattice antiferromagnetic spin model. The *g*-values obtained from magnetic susceptibility and moment experiments are compared with those of optical measurements.

1. Introduction

Single crystals of $R_2Si_2O_7$ (R = Tm, Er, Ho, Dy) have been grown using a flux method by Maqsood *et al.* [1]. $Er_2Si_2O_7$ exists in three modifications, a triclinic low temperature phase (Type B), a monoclinic modification (Type C) and a high temperature monoclinic modification (Type D). D-$Er_2Si_2O_7$ was selected as the first compound of the series to study the magnetic and optical behaviour [2] because of the simplicity of its chemical structure. Substitutional flux impurity levels were determined by electron probe microanalysis (EPMA); the results showed that D-$Er_2Si_2O_7$ contained 0.06% lead and 0.01% potassium. This paper is concerned with the magnetic properties of the compound.

1.1. Crystal structure

The crystal structure of the Type D disilicates was first described for $Y_2Si_2O_7$ [3, 4] which is isostructural with $R_2Si_2O_7$ (R = Er, Ho) [1]. The D-$Er_2Si_2O_7$ crystal is monoclinic with the lattice parameters $a_0 = 4.683$ Å, $b_0 = 5.56$ Å, $c_0 = 10.79$ Å, $\gamma = 96°$ and space group $P2_1/b$. The interesting unit in this structure, as shown in Fig. 1a, is the (Si_2O_7) double tetrahedral group. Its centrosymmetry and 180° Si–O–Si angle follow directly from the space group $P2_1/b$. Four-fold general positions and two-fold special positions at the centre of symmetry are possible in this space group. Since the unit cell with the two formula units contains only two pyrosilicate groups, they necessarily occupy these special positions. Evidence for the linearity of Si–O–Si therefore does not depend on the accuracy of the intensity data applied during the structure refinement, as was the case with Type C $Sc_2Si_2O_7$ [5] and $Yb_2Si_2O_7$ [6].

2. Measurements

2.1. Susceptibility measurements

A mutual inductance method [7] was used for all the measurements. The magnetic susceptibilities of the compound were measured as a function of temperature from 4.2 down to 1.3 K and from 20.4 to 13.94 K at only one value of the measuring field, usually 4 Oe.

2.2. Polycrystalline measurements

Because the magnetic and optical properties of this compound have not previously been studied, the preliminary measurements were carried out on polycrystalline specimens. The measurements were made on a sample of approximately 200 mg. The powder susceptibility χ_p as a function of temperature is shown in Fig. 2. The result is that expected for a compound which undergoes a transition to an antiferromagnetically ordered state. The transition temperature, T_N, as the point of maximum positive slope, is 1.9 ± 0.1 K.

Fig. 2 shows a plot of the inverse powder susceptibility per Er atom against temperature. Above 4 K, the experimental points fall on a straight line corresponding to

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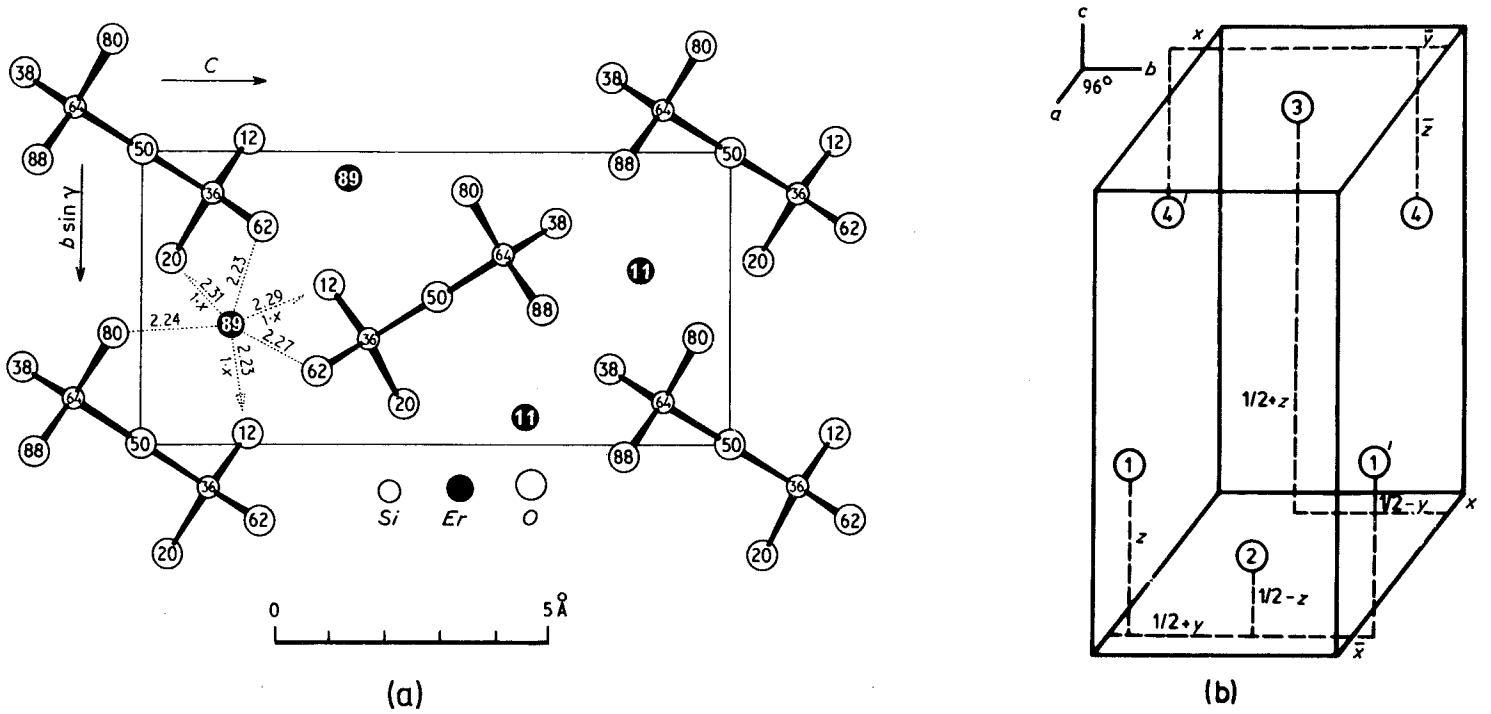

Figure 1 The structure of D-$Er_2Si_2O_7$ (a) projected along the *a*-axis (b) only the Er atoms are shown diagrammatically. The cell dimensions are $a_0 = 4.683$ Å, $b_0 = 5.56$ Å $c_0 = 10.79$ Å and $\gamma = 96°$ (5). Considering ion 1 as the origin there are three sets of neighbours, two at 3.509 Å (1–2), two at 5.748 Å (1–3) and one at 3.585 Å (1–4).

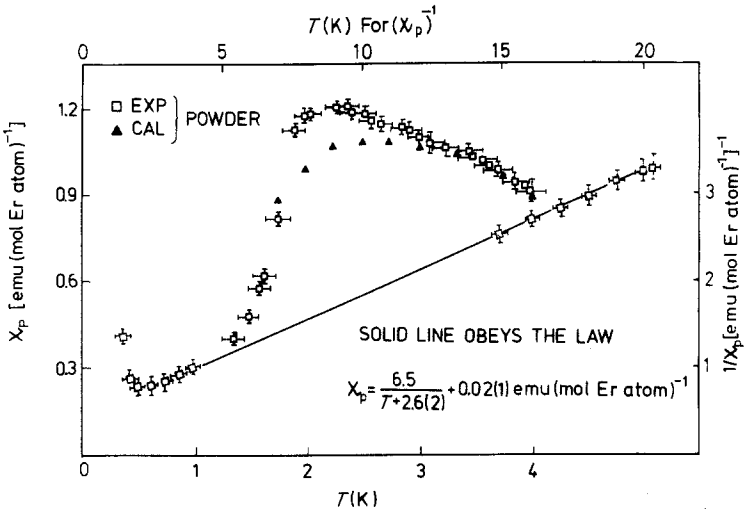

Figure 2 The susceptibility and the reciprocal of susceptibility of D-$Er_2Si_2O_7$ as a function of temperature.

$$\chi_p = \frac{6.5}{T + 2.6\,(2)} + 0.02\,(1)\,\text{emu (mol Er atom)}^{-1}. \quad (1)$$

For an effective spin (of the ground state doublet) $S = 1/2$, the Curie constant leads to $g_p = 8.3 \pm 0.3$. The negative value (− 2.6 K) of the Weiss constant θ indicates the predominance of antiferromagnetic exchange interaction. The existence of a rather high value of θ suggests that probably the next excited states lie quite near to the ground state doublet of the Er^{3+} ion in this compound.

The straight line represents the computer fitted plot for a linear least-square fit. With this preliminary information obtained from the polycrystalline susceptibility measurements it was decided to carry out measurements on single crystal specimens.

2.3. Single crystal measurements

The susceptibilities parallel to the principal axis and parallel to the a-axis for a needle-shaped specimen are shown in Fig. 3 as a function of temperature. As the temperature is lowered they reach a maximum and thereafter decrease, tending to zero as $T \to 0$. This is the typical behaviour of an antiferromagnetic material. Fig. 3 also shows a plot of the reciprocal susceptibility, χ_a^{-1}, over a wider range of temperature. Above 10 K, the plot is linear and a computer fitted result is of the form

$$\chi_a = \frac{12.4}{T + 2.5\,(2)} + 0.045\,(5)\,\text{emu (mol Er atom)}^{-1}. \quad (2)$$

The Curie constant 12.4 corresponds to an effective (i.e. $S = 1/2$) g-value of $g_a = 11.5 \pm 0.4$. The negative value of the Weiss θ again suggests the predominance of the antiferromagnetic interactions in this compound. Again, a quite high value of the Van Vleck temperature-independent susceptibility, was observed.

Meanwhile Tapster [2] reports preliminary results of the spectroscopic measurements on D-$Er_2Si_2O_7$, according to which the ground state $^4I_{15/2}$ of the Er^{3+} ions is split by the crystalline electric field into eight Kramers doublets, with the first excited doublet lying only 29 cm^{-1} above the ground doublet. The axis of the high g-value $g_\parallel$ lies in the a–b plane and is 28° ± 2° away from the a-axis (clock-wise sense of Fig. 1b). The observed values of the g-tensor at 4.2 K along the principal axis ($g_\parallel$), the axis perpendicular to the principal axis ($g_\perp$) and the c-axis (g_c) are

$$g_\parallel = 12.2 \pm 0.2, \quad (3)$$

$$g_\perp = 2.0 \pm 0.5 \quad (4)$$

and

$$g_c = 4.7 \pm 0.4. \quad (5)$$

The spectroscopic measurements also show that there are two magnetically inequivalent Er^{3+} ions. Application of a high magnetic field at 4.2 K reveals that the moment points ± 14° ± 1° to the principal axis, and does not lie in either the a–b, a–c or b–c planes.

The above results suggest that Er^{3+} ions behave like an approximate Ising antiferromagnetic in the compound D-$Er_2Si_2O_7$, and the magnetic properties must be analysed with the aid of at least a four-sublattice spin model. In addition, the first excited doublet lying only 29 cm^{-1} above the

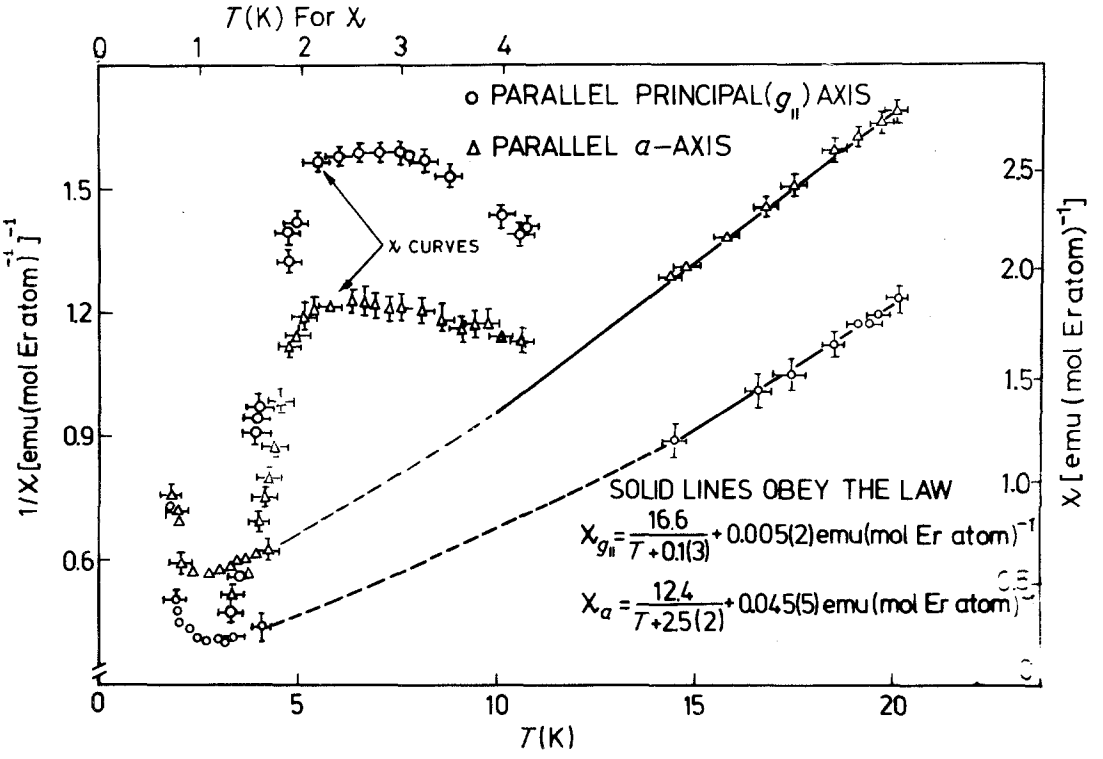

Figure 3 Molar susceptibility and reciprocal of molar susceptibility per Er atom of single crystals of D-$Er_2Si_2O_7$ as a function of temperature.

ground doublet is consistent with the observation of eight values of the temperature-independent part of the susceptibility. The g-values along the a-axis ($g_a = 11.5 \pm 0.4$) obtained from the susceptibility measurement, and the spectroscopic observation that $g_{\|}$ lies $28° \pm 2°$ away from the a-axis, suggest that an expected g-value for the principal axis should be $g_{\|} = g_a/\cos 28° = 13$.

The susceptibilities as a function of temperature measured along (a) the principal axis, (b) perpendicular to the principal axis and (c) parallel to the c-axis are shown in Figs 3 and 4. For the principal axis and c-axis, χ falls rapidly below the transition temperature whilst $\chi_{\perp}$ remains almost constant and is very small. The plots of the reciprocal susceptibilities for the principal axis, the axis perpendicular to the principal axis and the c-axis obey, respectively, the Curie–Weiss–Van Vleck law of the forms

$$\chi_{\|} = \frac{16.6}{T + 0.1\,(3)} + 0.005\,(2)\,\text{emu}\,(\text{mol Er atom})^{-1}. \quad (6)$$

$$\chi_{\perp} = \frac{0.16}{T + 2.1\,(1)} + 0.03\,(1)\,\text{emu}\,(\text{mol Er atom})^{-1}. \quad (7)$$

$$\chi_c = \frac{1.85}{T + 0.6\,(2)} + 0.001\,(4)\,\text{emu}\,(\text{mol Er atom})^{-1}. \quad (8)$$

The results have not been corrected for the demagnetizing effect. From the observed Curie constants, the effective g-values along the principal axis, along the axis perpendicular to the principal axis and along the c-axis are

$$g_{\|} = 13.4 \pm 0.6, \quad (9)$$

and

$$g_{\perp} = 1.3 \pm 0.06 \quad (10)$$

$$g_c = 4.3 \pm 0.1. \quad (11)$$

The g-value along the principal axis agrees with the predicted value and with the values obtained from optical measurements, while g_c and $g_{\perp}$ values are in agreement with those obtained from optical measurements.

2.4. Magnetic moment measurements

Magnetic measurements have been made on single crystal specimens in fields up to 30 kOe at 0.6 K, using a cryostat cooled by liquid He^4 or He^3, which has been described by Cashion *et al.* [8].

To avoid errors which might arise because of

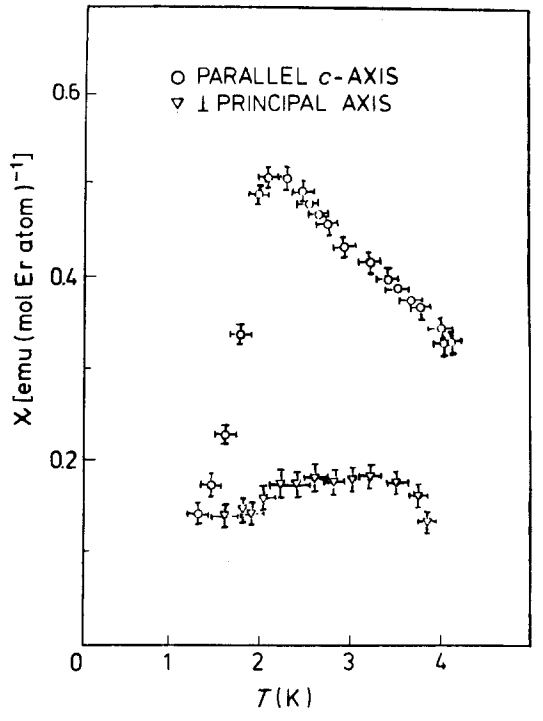

Figure 4 Molar susceptibility per Er atom of single crystals of D-$Er_2Si_2O_7$ as a function of temperature.

of crystal misorientation, inaccuracy in weighing and possibly misalignment of the samples in the specimen containers, the same specimens on which susceptibility measurements had been made were used for moment measurements.

Because of the large anisotropy observed in D-$Er_2Si_2O_7$, application of a strong magnetic field may induce a "flip" in which one or more sublattices simply reverse their direction of magnetization. In a pure Ising system, each individual moment is constrained to lie along a line, but may point in either direction along it; below the ordering temperature, there is an internal field at each site preferring one direction over the other. If an external field is then applied along this constraining direction of the internal field, all the moments which were originally antiparallel to the field will now find it energetically more favourable to "flip" over and become parallel to it. This means that the full saturation moment is obtained immediately on passing throught the critical field. In D-$Er_2Si_2O_7$ the situation does not exactly correspond to the simple Ising model since $g_\perp \neq 0 \neq g_c$.

The simplest experimental results which can be expected are therefore obtained when the applied field is parallel to the principal or c-axis, in which all four sublattices are equivalent. Fig. 5 shows the results of magnetic moment as a function of internal field parallel to the principal axis. The results have been corrected for a long needle-shaped specimen. It is evident from the figure that the moment rises steeply and smoothly when the applied field exceeds 5.2 kOe. The moment is saturated at a field of 8 kOe, with a saturation value of 37 000 emu (mol Er atom)$^{-1}$, corresponding to a g-value of 13.2 ± 0.4 in agreement with the susceptibility result. Along the c-axis (Fig. 6), much higher fields were required for saturation. Above 12 kOe, saturation is almost achieved, with a moment of 12 000 emu (mol Er atom)$^{-1}$, corresponding to $g_c = 4.3 \pm 0.1$, again consistent with the susceptibility data. A single "flip" at a critical field of 3.5 kOe was again observed along this direction.

In contrast, the second curve in Fig. 6 shows the magnetic moment obtained for an applied field along the a-axis. A stepped double "flip" was observed showing that the four sublattices are no longer equivalent. The process is shown schematically in Fig. 7, as first spins in one and then in a

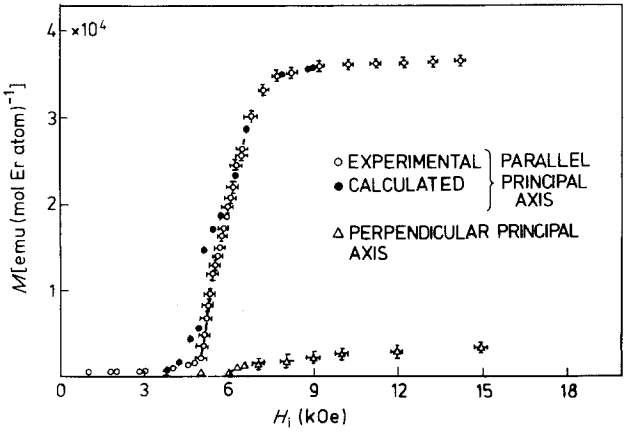

Figure 5 Magnetic moment against internal field of D-$Er_2Si_2O_7$, at 0.6 K.

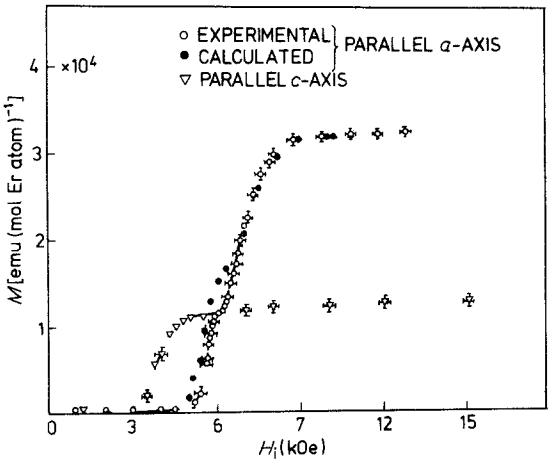

Figure 6 Magnetic moment against internal field of D-$Er_2Si_2O_7$, at 0.6 K.

second sublattice reverse their directions. At this stage it is interesting to calculate the angle between the principal axis and a-axis from their saturation moment values, i.e.

$$\theta = \cos^{-1}\frac{32\,500}{37\,000} = 27.7°, \qquad (12)$$

in good agreement with the optical measurement of $28° \pm 2°$.

A comparison of the results obtained from the magnetic moment and susceptibility experiments with those from the optical measurements is given in Table I.

3. The exchange interaction constants

The analysis was carried out in molecular field approximation [9], and compared with the Monte Carlo calculations [10]. The calculated points on the moment against field curves are shown in Figs 5 and 6. The exchange constants are:

$$J_{11}/k = 0.15\,(5);$$
$$J_{12}/k = 0.13\,(5);$$
$$J_{13}/k = -0.80\,(5);$$
$$J_{14}/k = -0.48\,(5),$$

where the subscripts on J refer to ion numbers.

On the basis of the molecular field theory [9], the Weiss θ is related to the sum of the interaction energies, which is found to be -2.8 K. The observed Weiss θ for the polycrystalline specimen is -2.6 ± 0.1 K. This comparison of the observed Weiss θ, obtained from the susceptibility measurements, with that obtained from exchange interaction energies, shows that the choice of only four sublattices was approximately correct.

Magnetic transitions in C-$Er_2Si_2O_7$ at low temperatures were also studied. The magnetic susceptibility experiments showed that it became antiferromagnetic at 2.50 ± 0.1 K. Details of the magnetic anisotropy will be published elsewhere.

4. Conclusions

(1) The susceptibility results show that D-$Er_2Si_2O_7$ undergoes a transition to an antiferromagnetically ordered state at $T_N = 1.9 \pm 0.1$ K, and at these

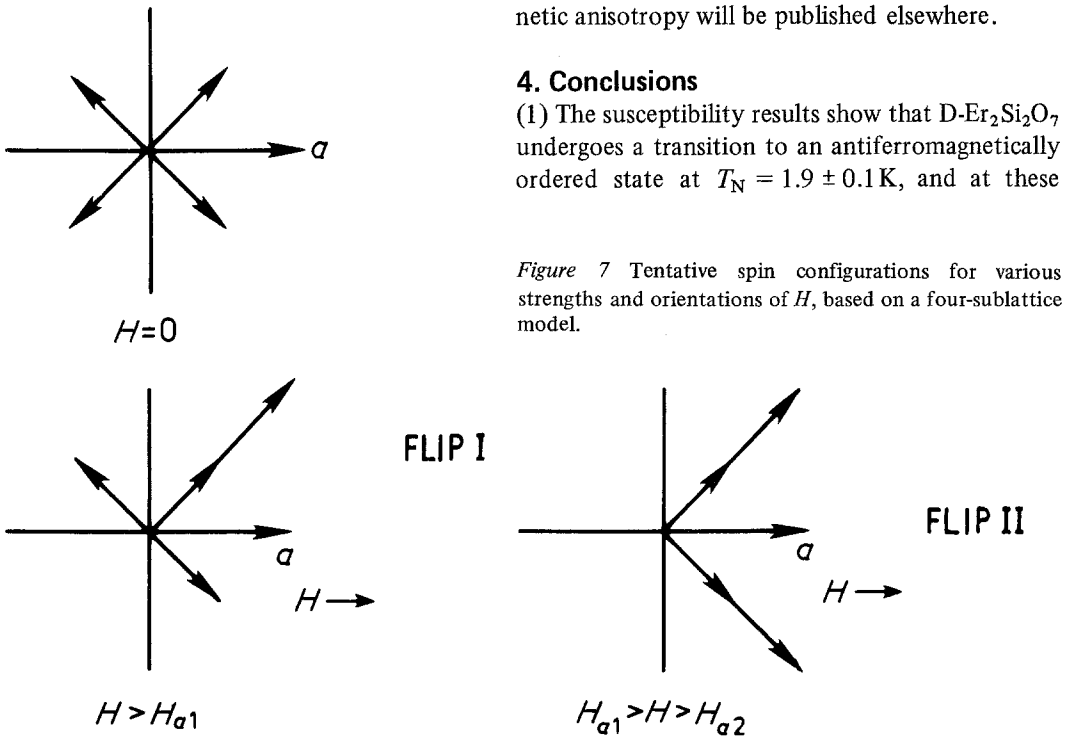

Figure 7 Tentative spin configurations for various strengths and orientations of H, based on a four-sublattice model.

TABLE I Comparison of the results obtained from magnetic and optical measurements

Field direction	Moment (M against H)	Susceptibility ($1/\chi$ against T)			Optical results	
	g	g	θ (K)	α (emu per mol Er atom)	g	α (emu per mol Er atom)
Polycrystalline	–	8.3 ± 0.3	−2.6 (2)	0.02 (1)	–	–
a-axis	11.7 ± 0.3	11.5 ± 0.5	−2.5 (2)	0.045 (5)	–	0.04
$g_{\parallel}$	13.2 ± 0.4	13.3 ± 0.6	−0.1 (3)	0.005 (2)	12.2 ± 0.2	–
$g_{\perp}$	1.2 ± 0.03	1.3 ± 0.06	−2.1 (1)	0.03 (1)	2.0 ± 0.5	–
c-axis	4.3 ± 0.1	4.4 ± 0.2	−0.6 (2)	0.001 (4)	4.7 ± 0.4	–

temperatures only the lowest doublet state of the Er^{3+} ions is populated to any appreciable extent. Therefore, the Ising approximation should be valid.

(2) Both the magnetic and optical measurements show that the direction of the maximum g-value is $28^\circ \pm 2^\circ$ away from the a-axis in the a–b plane.

(3) The g-values obtained from magnetic susceptibility and moment experiments are in agreement with those from optical measurements (Table I).

(4) The moment measurements show that phenomenon of "spin flip" expected in an anisotropic antiferromagnet; one or two "spin flips" are observed depending upon the direction of the applied field.

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