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Cr-Gd EXCHANGE COUPLING CONSTANTS IN CR DOPED $GdAlO_3$

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ABSTRACT

The splitting of the fluorescence spectrum of Cr as a function of an external magnetic field in the system $GdAlO_3$ with diluted Cr impurities at Al sites was indicative of a puzzling dependence of the Cr-Gd exchange coupling constant J_1 on the magnetization. Here it is shown that this dependence is an artifact simulated by the existence of an appreciable exchange coupling J_2 between Cr and its next nearest neighbor Gd ions. J_2 has the opposite sign to $J_1(\simeq 2.05\ cm^{-1})$ and it is roughly an order of magnitude smaller.

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INTRODUCTION

The optical and magnetic properties of the antiferromagnet $GdAlO_3$ with Cr^{3+} impurities substituting for Al^{3+} have been extensively studied both experimentally and theoretically. Initially, the interest in this material was connected with its potential application as a medium for a tunable laser.[1-5] Further interest was awakened by the peculiar dependence of its optical spectrum on temperature and magnetic field.[6-10] To the best of my knowledge this is the only substance where a "magnetic Franck-Condon" effect has been observed.[10] While many features of the optical spectrum are understood, a puzzling dependence of the Cr-Gd exchange coupling constant on the external magnetic field, which was apparent when comparing theory and experiment, remains unexplained. Indeed, at high external magnetic fields, with the Gd spins saturated, the splitting of the fluorescence of Cr points to a Gd-Cr exchange coupling of 1.46 cm^{-1}. In the absence of field, however, with the Gd spins randomly distributed, the splitting yields an exchange coupling constant of about 2.1 cm^{-1}.[10] The purpose of this paper is to show that a simple extension of the former theory[8] to include the effects of the next nearest neighbor Gd ions to Cr eliminates the necessity of assuming a variable exchange coupling. Also, more precise exchange constants are determined, as well as a spin correlation parameter which characterizes the spin-flop antiferromagnetic state.

THEORY

The theory presented in Ref. 8 is generalized to include the interaction between the Cr^{3+} impurity and its next nearest neighbor (nnn) Gd spins. The notation of that Reference will be followed, and Eq. (n) therein will be denoted by Eq. (I-n). The ensemble of eight nearest neighbor (nn) Gd ions will be called the nn-cluster and that of the 24 nnn Gd ions the, nnn-cluster.

The Hamiltonian (I-1) is modified accordingly, namely

$$H = H_A' + H_C' + J_1 \vec{s}.\sum_{nn} \vec{S}_j + J_2 \vec{s} \sum_{nnn} \vec{S}_j - g\mu_B \vec{s}.\vec{B} \qquad (1)$$

Here H_A' describes the exchange coupling of the nnn-cluster with the outside antiferromagnetic medium and includes the Zeeman energy of both the nnn- and the nn-cluster in the external magnetic field $\vec{B}$. H_C' contains the antiferromagnetic exchange interactions between neighbor Gd spins belonging to both clusters, this includes the interactions between ions sitting on different clusters (nn and nnn), as well as within the same clusters. $\vec{S}_j$ is the spin operator of the Gd ion at site j and $\vec{s}$ is the spin operator of the Cr ion. J_1 and J_2 are the exchange coupling constants between Cr and the nn and nnn Gd ions respectively. g is the gyromagnetic factor of Cr and μ_B the Bohr magneton. Like in Ref. 8 we put $S_j = S = 7/2$ and s=1/2, and we diagonalize H in the space of the two states

$$|\Psi\uparrow\rangle = |\Psi\rangle_1 \cdot |\Psi\rangle_2 \cdot |\uparrow\rangle \qquad (2)$$

$$|\chi\downarrow\rangle = \left(A_1 |\chi\rangle_1 \cdot |\Psi\rangle_2 + A_2 |\chi\rangle_2 \cdot |\Psi\rangle_1\right) \cdot |\downarrow\rangle \ . \qquad (3)$$

Here $|\Psi\rangle$ stands for a typical cluster (nn+nnn) wavefunction in the temperature ensemble in the sense of Ref. 8. It is here written as the product of two cluster wavefunctions, $|\Psi\rangle_1$ defined by Eq. (I-4) and $|\Psi\rangle_2$ defined analogously for the nnn-cluster. $|\uparrow\rangle$ and $|\downarrow\rangle$ denote the up and down Cr spin states. The quantization axis is taken along the z-direction. $|\chi\rangle_1$ and $|\chi\rangle_2$ are unnormalized wavefunctions defined by

$$|\chi\rangle_1 = \sum_{nn} S_j^+ |\Psi\rangle_1 \quad \text{and} \quad |\chi\rangle_2 = \sum_{nnn} S_j^+ |\Psi\rangle_2 \, . \tag{4}$$

A_1 and A_2 are constants to be determined variationally in such a way that the basis (2-3) gives a maximum splitting. The norm of $|\chi\downarrow\rangle$ is of the form

$$\langle\chi\downarrow|\chi\downarrow\rangle = |A_1|^2 W_1 + |A_2|^2 W_2 + \text{Tvm} \tag{5}$$

where

$$W_i = {}_i\langle\chi|\chi\rangle_i \qquad (i=1,2) \, . \tag{6}$$

Tvm stands for terms with vanishing mean value in the thermal ensemble (as it follows from Ref. 8) and will be neglected. Thus, the constants A_1 and A_2 (which can be taken to be real) must be subject to the normalization condition

$$A_1^2 W_1 + A_2^2 W_2 = 1 \, . \tag{7}$$

The energy matrix in the space of the states $|\Psi\uparrow\rangle$, $|\chi\downarrow\rangle$ reads (with $\underline{B}$ taken along the z-direction),

$$\begin{pmatrix} E + J_1 U_1^z/2 + J_2 U_2^z/2 - g\mu_B B/2 & J_1 A_1 W_1/2 + J_2 A_2 W_2/2 \\ J_1 A_1 W_1/2 + J_2 A_2 W_2/2 & E + \hbar\Omega - J_1(\delta_1 + U_1^z)A_1^2/2 \\ & -J_2(\delta_2 + U_2^z)A_2^2/2 + g\mu_B B/2 \end{pmatrix} \quad (8)$$

Here $E = \langle \Psi\uparrow | H_A' + H_B' | \Psi\uparrow \rangle$, $U_i^z = {}_i\langle \Psi | R_i^z | \Psi \rangle_i$, $\delta_i^z = {}_i\langle \Psi | R_i^- R_i^z R_i^+ | \Psi \rangle_i - U_i^z$ (9)

where

$$R_1^z = \sum_{nn} S_j^z , \qquad R_2^z = \sum_{nnn} S_j^z$$

and analogously for R_i^+ and R_i^- with S_j^+ and S_j^-, respectively. The discussion of the term $\hbar\Omega$ is similar to that of Ref. 8; it represents the energy of a spin wave localized in the nn and nnn clusters and it involves a Zeeman term which practically cancels out the Zeeman energy of the impurity. This cancellation occurs because the basis states (2) and (3) have quite approximately the same z-component of angular momentum and the gyromagnetic factor of Gd, g', equals g.

The diagonalization of the matrix (8) yields the following expression for the splitting ε:

$$\varepsilon = \{[J_1 U_1 + J_2 U_2]^2 + [J_1 A_1 W_1 + J_2 A_2 W_2]^2\}^{1/2} . \quad (10)$$

Terms of order $J_1\delta/\varepsilon$ have been neglected. The values of A_1 and A_2 which maximize ε under the condition (7) are, with $\gamma = J_2/J_1$,

$$A_1 = \left[\frac{1}{W_1 + \gamma^2 W_2}\right]^{1/2} \quad \text{and} \quad A_2 = \left[\frac{\gamma^2}{W_1 + \gamma^2 W_2}\right]^{1/2} , \quad (11)$$

which replaced in (10) leads to

$$\varepsilon = \{[J_1U_1+J_2U_2]^2 + [J_1W_1]^2 + [J_2W_2]^2\}^{1/2} . \qquad (12)$$

Starting from the definitions of U_i and W_i (Eqs.(9) and (6)), their explicit expressions can be immediately obtained from formulae (I-A1) and (I-A9), respectively. A distribution of values of ε can be calculated using the method of Ref. 8 in which the z-component ($\sum_j$) and the azimuthal angle (θ_j) of each Gd spin is considered a random variable within limits compatible with the thermodynamic state of the system. In this paper, however, we will limit ourselves to consider approximate expressions for the most probable values of ε in several cases, along the lines of Ref. 9.

i) Antiferromagnet at T=1.5 K with easy axis along the z-direction (Fig.1a).

For one sublattice we have $\Sigma_1=-S$, and for the other sublattice $\Sigma_2=S-2\sigma$, where σ is the reduced magnetization per spin. Note that the external field is applied in such a way that the spin polarization is in the -z-direction (See Ref. 8). The azimuthal angle is considered a random variable and we approximate

$$\left| \sum_{j=1}^{m} e^{i\theta_j} \right|^2 \simeq m . \qquad (13)$$

In this case the most probable value for the splitting becomes

$$\varepsilon_{af} = 8S\{C^2\sigma^2 + D^2[\sigma(1-\sigma)/4 + (1+\sigma^2)/(8S)]\}^{1/2} \qquad (14)$$

where the exchange constants appear in the combinations

$$C = J_1 + 3J_2$$
$$D = \left(J_1^2 + 3J_2^2\right)^{1/2} \quad . \tag{15}$$

ii) Case of the antiferromagnet at T=1.5 K in the spin-flop state (Fig.1b).

We have now $\Sigma_1 = \Sigma_2 = -\sigma$. The azimuthal angles are now correlated due to the antiferromagnetic ordering in the direction perpendicular to the easy axis and we introduce a new adjustable parameter p to describe this correlation, defined by

$$\left| \sum_{j=1}^{m} e^{i\theta_j} \right|^2 \simeq m\, p \quad . \tag{16}$$

Thus p=0 for strict antiferromagnetism and p=1 for random angle; at finite temperatures $T < T_N$ (where $T_N = 3.9$ K is the Neel temperature) we expect $0 < p < 1$. The most probable value for the splitting in this case becomes

$$\varepsilon_{sf} = 8S\{C^2\sigma^2 + D^2[p(1-\sigma^2)/8 + (1+\sigma)^2/(16S)]\}^{1/2} \quad . \tag{17}$$

iii) Case of the paramagnetic state at T=4.2 K in the presence of a magnetic field.

We have $\Sigma_j = -\sigma$ and θ_j random, therefore

$$\varepsilon_p = 8S\{C^2\sigma^2 + D^2[(1-\sigma^2)/8 + (1+\sigma)^2/(16S)]\}^{1/2} \quad . \tag{18}$$

We note that the coupling constants J_1 and J_2 appear only in the form (15). This has a simple interpretation. The system is des

cribed by a correlated wavefunction which involves both the Gd and Cr spins. This correlation can be visualized in a somewhat classical way as if the Cr ion would feel the instantaneous exchange field produced by the vector sum of the Gd spins. Along the z-direction the components of the Gd spins are driven by the external field producing a finite average magnetization and this is coupled through C, that is, the coupling constants add. In the transverse direction the components of the Gd spins are random and they add in the form of a random walk to produce an instantaneous value of the effective field; in that case the coupling constants add quadratically like in D.

Finally, it is conceivable that alternative explanations for the magnetic field dependence of the exchange parameters might be possible beyond the simple Heisenberg form for the exchange hitherto assumed; the explanation pointed here, however, looks rather plausible in order of magnitude and it is fully consistent with previous models.

COMPARISON WITH EXPERIMENT

The splitting ε for the antiferromagnet at T=1.5 K as a function of the external magnetic field is shown in Fig. 2. The experimental points were taken from Ref. 10. To draw the theoretical curve Eqs.(14) and (17) were used for magnetic fields below and above the spin-flop transition ($H_{sf} \simeq 1.2$ T), respectively. The values for the magnetization were taken from Ref. 3 and are also shown in Fig. 2. The fitting yielded the values C=1.3 cm^{-1}, D=2.1 cm^{-1} and p=0.7, that is J_1=2.05 cm^{-1} and J_2=-0.25 cm^{-1}. The optical spectra and the magnetization were not measured in the same samples and this may account for the slightly different spin-flop fields observed in each case.

The splitting ε in the paramagnetic state at 4.2 K as a function of the external magnetic field is shown in Fig. 3. The experimental points were taken from Ref. 7. The theoretical curve was drawn using Eq.(18) with values for the reduced magnetization σ calculated within the molecular field approximation (also shown in Fig. 3), and with the same values for C and D given above.

Several comparably good fittings obtained by varying the parameters C, D and p indicate that the values given above for J_1, J_2 and p may be reliable within 10%. Errors from theoretical approximations should be smaller.

CONCLUSIONS

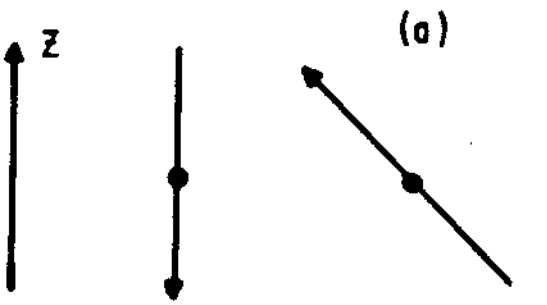
A consistent description of the magnetic field dependence of the splitting of the fluorescence spectrum of Cr doped $GdAlO_3$ requires that the next nearest neighbor interaction between Cr and Gd be taken into account. Fitting to available data yields a nearest neighbor exchange interaction $J_1 \simeq 2.05\ cm^{-1}$ (of the same order as previously reported) and a next nearest neighbor exchange interaction of opposite sign, $J_2 \simeq -0.25\ cm^{-1}$. The spin-flop state is also characterized by the determination of a parameter p which measures the antiferromagnetic spin correlation.

FIGURE CAPTIONS

Fig. 1 - Two-sublattice antiferromagnetic order in the presence of an external magnetic field along the easy axis: a) below the spin-flop transition. b) above the spin-flop transition.

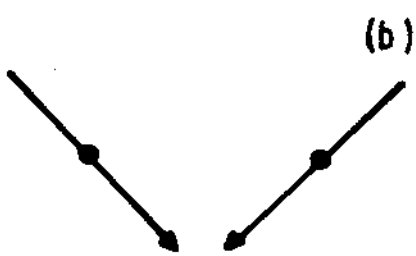
Fig. 2 - Average splitting ε of the fluorescence of $GdAlO_3:Cr$ at T=1.5 K as a function of the magnetic field H. The reduced magnetization σ is also shown with its scale on the right.

Fig. 3 - Average splitting ε of the fluorescence of $GdAlO_3:Cr$ at T=4.2 K as a function of the magnetic field H. The reduced magnetization σ is also shown with its scale on the right.



$\Sigma_1 = -S$ $\Sigma_2 = S - 2\sigma$

θ_i random



$\Sigma_1 = \Sigma_2 = -\sigma$

θ_1, θ_2 correlated

Fig. 1

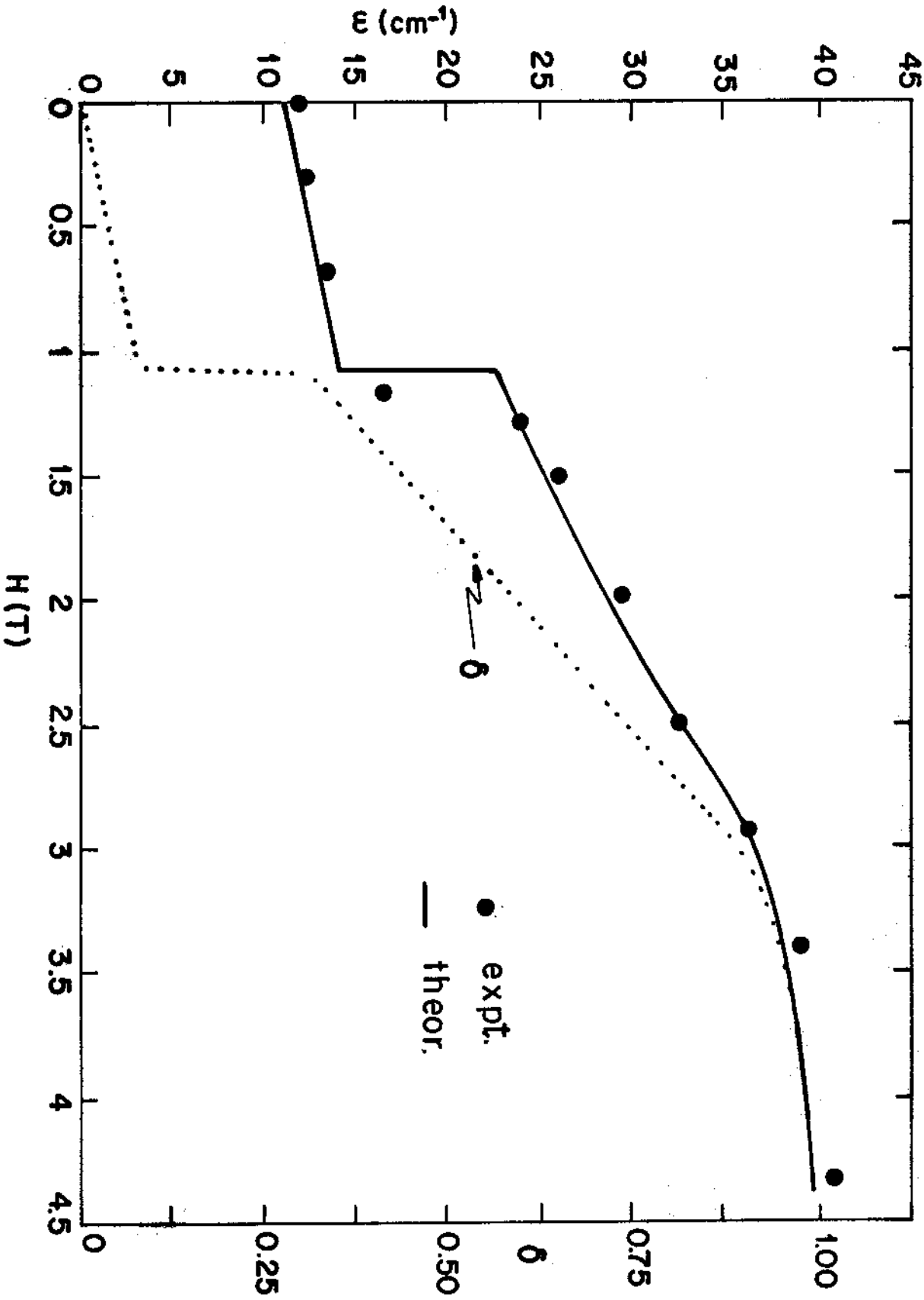

ε (cm⁻¹)
0
5
10
15
20
25
30
35
40
45
H (T)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
σ
0
0.25
0.50
0.75
1.00
2
6
expt.
theor.

Fig. 2

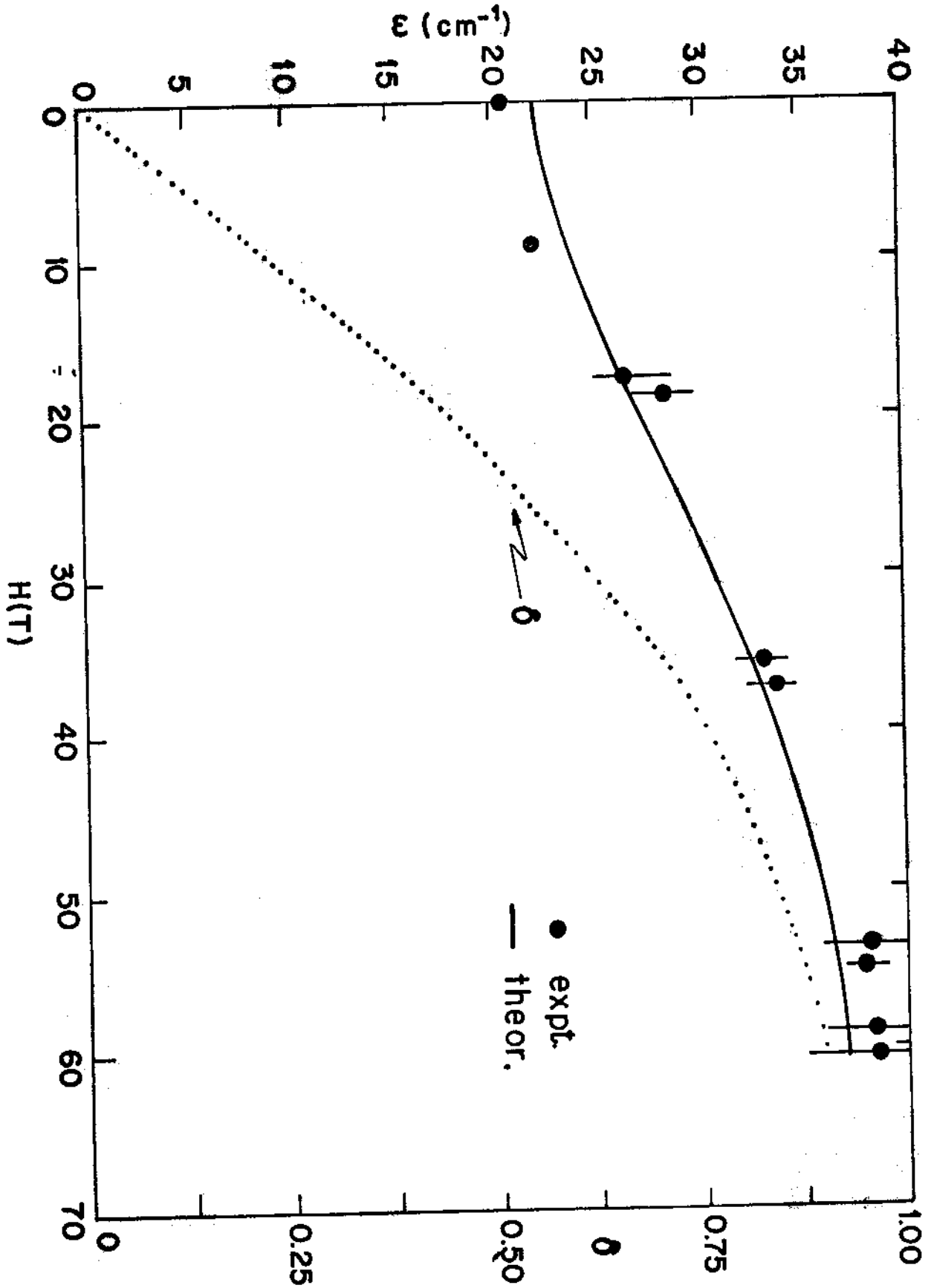

ε (cm⁻¹)
0
5
10
15
20
25
30
35
40
H(T)
0
10
20
30
40
50
60
70
0
0.25
0.50
0.75
1.00
θ
z
θ
expt.
theor.

Fig. 3

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