pling is large (witness the large pressure dependence of the transition temperature[11]) and because the transition is strain dependent, we believe that lattice instability plays an important role. This belief is reinforced by the appearance of the first-order transition below the "strained" second-order transition point which is a feature of the lattice instability model.[12] Clearly, proper allowance for lattice compressibility must be made in the spin-density-wave model[9] before a complete understanding of this unusual phase transition is possible.

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Optical Observation of Stress-Induced Spin Flop in Cr_2O_3 *

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It has been observed that applying sufficiently large uniaxial stress to Cr_2O_3 induces in its ${}^4A_2 \rightarrow {}^2E$ optical-exciton absorption spectrum changes that are nearly identical to those observed when magnetic-field—induced spin flop occurs. This is interpreted as evidence that uniaxial stress induces spin flop in Cr_2O_3. A phenomenological discussion is given.

This Letter reports optical data which constitute strong evidence of uniaxial-stress–induced spin flop in the corundum-structure antiferromagnet Cr_2O_3 ($T_N = 308°K$). Although spin-reorientation phenomena in antiferromagnets and ferrimagnets are well known to occur with the application of magnetic fields or with temperature variations, Cr_2O_3 is the first example of a material in which spin flop can be induced by a uniaxial stress. Experimental evidence of the effect is provided by the observation that uniaxial stress of about 15 kbar applied along the a axis induces in the ${}^4A_2 \rightarrow {}^2E$ optical-exciton absorption spectrum of Cr_2O_3 fairly abrupt changes that are nearly identical to the changes observed when the spins are forced to flop from the c axis to the basal plane by the application of a c-axis magnetic field exceeding the critical value $H_c = 59$ kG. Qualitative support for the contention of stress-induced spin flop is provided by the observations of Dudko, Eremenko, and Semenenko (DES) that H_c in Cr_2O_3 increases linearly with the magnitude of c-axis uniaxial stress,[1] and that when spin flop is induced with a magnetic field, the crystal spontaneously lengthens along the c axis and contracts perpendicular to the c axis.[2]

The optical absorption spectrum of Cr_2O_3 displays in the vicinity of 7000 Å five reasonably sharp, polarized absorption lines. These are shown in the center trace of Fig. 1 and labeled 1 through 5. Lines 1 and 4 are σ and axially polarized, lines 2 and 3 are π polarized, and line 5 is σ and π polarized. The combinations of lines 1 with 4 and 2 with 3 have been assigned and analyzed in detail by Allen, Macfarlane, and White[3] as pairs of Davydov-split Frenkel excitons associated with single-ion Cr^{3+} transitions from the lowest exchange-split ${}^4A_2$ state to the lowest two exchange-spilt ${}^2E$ states.

Application of a magnetic field along the c axis[4] or of uniaxial stress along the a axis induces changes in the spectrum, some of which are shown in Fig. 1. For small values of stress the lines shift linearly and nearly uniformly to lower

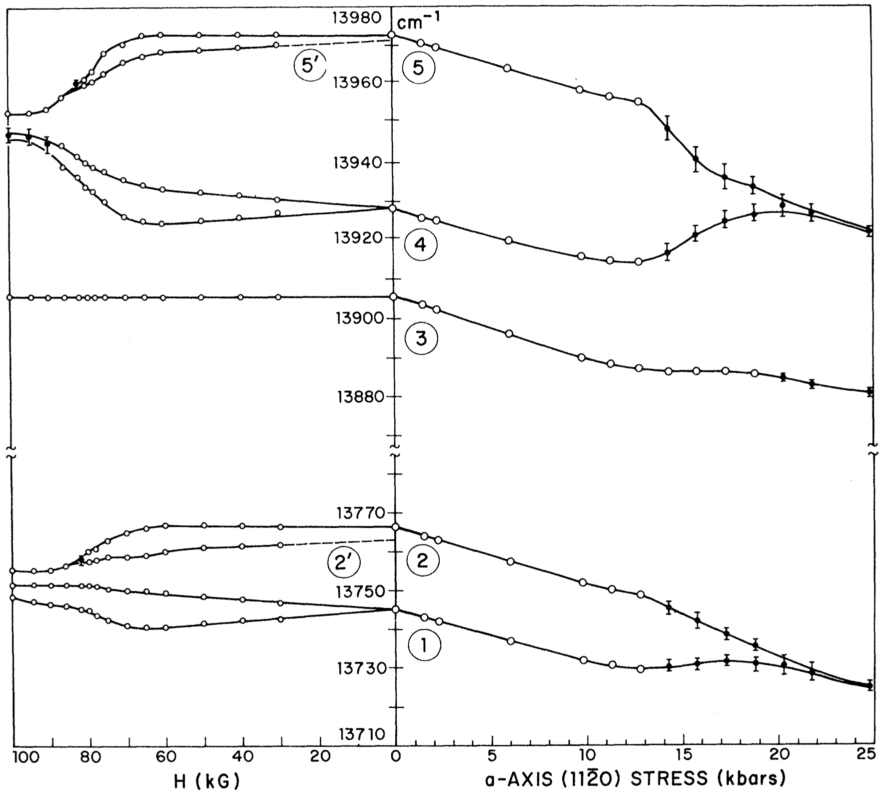

FIG. 1. Variation of positions of $^4A_2 \rightarrow {}^2E$ exciton absorptions in Cr_2O_3 with magnitudes of applied c-axis magnetic field (sample at 15 K) and a-axis uniaxial stress (sample at 2 K). For comments on the meaning of large error bars, see text.

energies, with no changes in intensity or polarization. The shifts are probably due to the effect of the hydrostatic component of induced strain, which varies the crystal-field parameters and interion interactions that govern the single-ion splittings and exciton Davydov splittings. As discussed previously by Allen, Macfarlane, and White,[3] the magnetic field makes the up-spin and down-spin sublattices energetically inequivalent, which, for fields less than H_c, causes lines 1 and 4 to split, and lines 2′ and 5′ to appear and separate from lines 2 and 5. As the field increases through H_c, these effects tend to disappear, as might be expected, since the spins all become oriented perpendicular to the field.

The are additional changes, however, as the field increases through H_c, and these are nearly duplicated in the stress data as the stress is increased through 15 kbar. By pairs, the positions of lines 1 with 2 and lines 4 with 5 become nearly coincident, as shown in Fig. 1. The position of line 3 is unchanged in the magnetic-field data and suffers a small anomalous departure from linear shifting in the stress data. These position changes are accompanied by intensity and polarization changes that are also the same for both the field and the stress data. The intensity of line 5 increases in σ and axial polarization to become as large as that of line 1, the intensity of line 3 first increases in σ and axial polarization and then goes nearly to zero in all polarizations, and the intensity of line 2 increases in σ and axial polarization to become as large as that of line 1. The remarkable similarities in the two sets of data are here interpreted as strong evidence that a-axis uniaxial stress induces spin flop in Cr_2O_3. The difference in behavior of the position of line 3 in the two sets of data (see Fig. 1) suggests that an elastic-constant anomaly occurs when the spins flop.

A detailed analysis of the effect of spin rotation on the optical-exciton absorptions will be postponed for a future publication. Similar changes have been observed in the optical spectra of other magnetic insulators when the spins are forced to reorient by an applied magnetic field[5,6] or a temperature variation.[7] The mechanism for the changes has generally been ascribed to anisotropy of the interion exchange interaction,[5] or the dependence of certain single-ion matrix elements of the spin-orbit interaction upon the spin direction.[6,7] The latter of these will certainly be important in Cr_2O_3.

A point that deserves comment is the failure, in either set of data, to observe an abrupt spin flop. In the magnetic-field case, this is due to small misalignment of the field with the crystal c axis. It is known that any misalignment changes the transition from first to second order and causes the spins to reorient gradually.[8] As much as 5° misalignment smears out the transition to occur from about $0.6H_c$ to about $1.4H_c$. There is some advantage in a slight misalignment in that it is much easier to observe the changes taking place. The failure to observe a sharp transition at some critical stress is almost certainly due to inhomogeneities in the strain produced. The stress was observed to broaden the lines by about 5 cm^{-1} and from the observed shifts of the lines, this implies a stress distribution of about 4 kbar, which is nearly the width of the observed transition region. In the transition region, where the line positions are very stress sensitive, the lines become quite broad, some with asymmetric line shapes, which is the meaning of the large error bars in Fig. 1. Inhomogeneities in the stress are hard to avoid, because Cr_2O_3 is so opaque as to require the use of very thin samples (less than 100 μm thick) in an optical absorption experiment. To avoid breaking the samples, the stress must be applied in the same direction as the light is propagated, so a stresser was built in which the light enters a hollow vertical stress rod horizontally, is reflected down the center of the rod through two pieces of transparent sapphire, and then is reflected out of the rod horizontally again. The thin sample is placed between the two pieces of sapphire, which may not transmit a completely homogeneous stress to it even though samples of small area (about 1 mm^2) are used.

As mentioned in the introductory paragraph, DES have measured[1] the c-axis stress dependence of H_c and the magnetostrictive strains induced as spin flop occurs in Cr_2O_3.[2] Since the effect of stress in promoting spin flop and the existence of magnetostrictive strains when spin flop is forced are both phenomena that have their origins in the magnetoelastic interaction, they are clearly related. In fact, the two quantities measured, the critical stress and the magnetostrictive strain, are related very simply and directly. To illustrate, it is convenient to discuss a simple two-parameter magnetoelastic interaction introduced by DES to describe their data. The anisotropy energy in Cr_2O_3 can be written $K(\alpha_x^2+\alpha_y^2)$, where the α_i are direction cosines of the vector difference of the two sublattice magnetizations. For K positive, the spins lie along the c axis. It is presumed that K is given by a positive constant K_0 plus terms linear in strains u_{ij} that preserve the crystal symmetry, namely, u_{zz} and $u_{xx}=u_{yy}$, which gives a two-parameter magnetoelastic energy. The equilibrium values of the strains in terms of $\alpha_x^2+\alpha_y^2$ and the magnetoelastic and elastic constants are readily found by solving the equations $\partial E/\partial u_{ii}=0$, where E is the sum of the elastic and magnetoelastic energies. When spin flop occurs, $\alpha_x^2+\alpha_y^2$ changes from 0 to 1 and the strains change from 0 to new values $\bar{u}_{xx}=\bar{u}_{yy}$ and $\bar{u}_{zz}$. The critical stresses T_{ii} for spin flop are those producing strains such that K is driven from K_0 to 0. These are readily found in terms of K_0 and the magnetoelastic and elastic constants. The result can be expressed entirely in terms of K_0 and the $\bar{u}_{ii}$:

$$T_{zz}=K_0/\bar{u}_{zz}, \quad T_{xx}=T_{yy}=K_0/\bar{u}_{xx}. \qquad (1)$$

From antiferromagnetic resonance[9] K_0 is known to be 2×10^5 erg/cm^3. The experimental value of $\bar{u}_{zz}$ found by DES[2] is $+2.8\times10^{-5}$, which implies $T_{zz}=+7.14$ kbar (a positive T is tensile). This agrees well with the value 7 kbar obtained by linear extrapolation to $H_c=0$ of the data of DES[1] for the increase of H_c with compressive c-axis stress. DES[2] report an experimental value of -0.4×10^{-5} for $\bar{u}_{xx}=\bar{u}_{yy}$. They state that this value is actually the average of the strains measured with a small basal-plane component of the applied magnetic field oriented parallel and perpendicular to the unspecified axis of measurement in the basal plane. It implies a T_{xx} of -50 kbar, in considerable disagreement with the value of about -15 kbar reported here.

Unless a large error is assumed to exist in either strain measurements of DES or the present stress measurements, this discrepancy implies the need to consider a less restrictive magnetoelastic interaction that allows for $\bar{u}_{xx}\neq u_{yy}$ and the presence of other strains. An analysis of the magnetoelastic strains and the possible critical stresses has been carried out using the full magnetoelastic interaction allowed by symmetry. Simple interrelations of the type given in Eq. (1) are found. The results, which will be described elsewhere, are flexible enough to remove the discrepancy between the measurements of

DES and those reported here, but there are insufficient data to obtain a unique description of the Cr_2O_3 magnetoelastic interaction. Some intriguing possible basal-plane stress behaviors emerge. For example, it may be that compressive (tensile) stress along or perpendicular to an a axis induces the spins to flop into the basal plane perpendicular to (along) or along (perpendicular to) the stressed a axis, respectively. An experimental search for effects of this kind would help clarify the basal-plane magnetoelastic interaction in Cr_2O_3. Probably some other-than-optical technique, perhaps measuring magnetic susceptibilities while uniaxially stressing, would be best in order to avoid the use of thin samples and the concomitant difficulties of strain inhomogeneities encountered in the experiments reported here.

The origin of the Cr_2O_3 anisotropy constant K_0 has been discussed by Artman, Murphy, and Foner.[10] Assuming the exchange anisotropy to be negligibly small, which is probably right since Cr^{3+} has an orbital singlet ground state, they set $K_0 = K_{MD} + K_{FS}$ where K_{MD} is due to the magnetic dipolar interaction and K_{FS} is the single-ion anisotropy. K_{MD} is computed theoretically to be 1×10^5 erg/cm^3 so K_{FS} is deduced to be 1×10^5 erg/cm^3. K_{MD} was found theoretically to be very sensitive to the positions of the metal ions along the c axis, which are not fixed by the corundum symmetry. K_{FS} is proportional to the ground-state splitting $2D$ of the paramagnetic Cr^{3+} ion, which in Al_2O_3:Cr^{3+} is found to be quite stress sensitive.[11] These results suggest that a sizable magnetoelastic interaction in Cr_2O_3 is reasonable, so that K_0, which is quite small, can be driven through zero by stresses that do not shatter the crystal. A more detailed analysis of the microscopic origins of the magnetoelastic interaction in Cr_2O_3, of the type done by Phillips and White for certain of the garnets,[12] has been carried out and will be described in a future publication.

In summary, this Letter has presented experimental evidence that spin flop in Cr_2O_3 can be induced by the application of about 15 kbar of compressive uniaxial stress along the a axis. It was pointed out that the critical stress is directly related to magnetostrictive-strain changes occurring when spin flop is induced by a magnetic field. Further measurements are needed to clarify the nature of the basal-plane magnetoelastic interaction in Cr_2O_3 and the exact relation of the present work to that of DES. Favorable circumstances for observing stress-induced spin flop may well exist in other materials, and it can be hoped that the possibility of such stress studies will promote a wider range of spin-flop experiments than previously since large uniaxial stresses are rather simply and inexpensively produced in comparison with the large magnetic fields usually needed to study spin flop. Detailed analyses of the optical data, the phenomenological description, and the microscopic origin of the magnetoelastic interaction in Cr_2O_3 will be presented in future publications.

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