from similar measurements on thick crystals, and by comparison with the molecular properties, $n=1/k_e$ can be found. n may also be determined from a comparison of the molecular and technical photofluorescence spectra. The technical scintillation properties t_I and q_I can also be observed directly, and the related quantities m, t_P, and $(t_P)_0$ deduced. The direct measurement of these latter parameters is difficult. An experimental investigation is in progress to determine the main properties of interest for a large group of related organic fluorescent compounds.

The photon cascade theory provides a quantitative description of the fluorescence and scintillation properties of organic phosphors which is in excellent agreement with experiment. When considered in conjunction with the other experimental data discussed elsewhere,[1] the results provide strong evidence of the validity of the photon theory of energy transfer.

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Moduli and Internal Friction of Magnetite as Affected by the Low-Temperature Transformation

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The low-temperature ordering transformation in magnetite is the source of large nonelastic effects. For example, Young's modulus for the ⟨111⟩ direction at 108°K is 30 percent lower than the value one would estimate from higher-temperature measurements; an internal friction peak occurs near 95°K. We have attributed the nonelastic effects to stress-induced ordering of Fe^{++} and Fe^{+++} among the octahedral sites in the lattice.

A SECOND-ORDER transformation with critical temperature near 115°K occurs in magnetite[1–14] and has been attributed to ordering[2,3] of Fe^{++} and Fe^{+++} among the octahedral sites of the magnetite structure (spinel type). The symmetry changes from cubic to orthorhombic on cooling.[5] In certain crystallographic directions this transformation, we find, is accompanied by large effects in the moduli and internal friction. Stress-induced ordering is proposed as the explanation.

For our measurements two rods were prepared from a natural occurring magnetite single crystal containing 20.7 percent Fe^{++} and, as an impurity, 1.2 percent Zn (stochiometric Fe_3O_4 has 24.2 percent Fe^{++}). The long direction of one rod was parallel to a ⟨100⟩ direction; the long direction of the other was parallel to a ⟨111⟩ direction. Young's modulus of ⟨111⟩ and ⟨100⟩, the torsion modulus of ⟨100⟩, and the internal friction in each case were determined as functions of temperature and external magnetic field by the resonant vibration method. Both electromagnetic[15,16] and piezoelectric[17,18] excitation and detection of vibrations were employed. The strain amplitudes were approximately 10^{-7}, the frequency range, 50 to 130 kc/sec.

DATA AND INTERPRETATION

The moduli of crystalline solids are expected to increase on cooling approaching asymptotically a maximum value at very low temperatures, provided there is no change of state and all of the strains are elastic. Magnetite has a transformation. Furthermore, two sources of nonelastic strain are probably present, stress-induced domain motion (magnetostriction)[19,20] and stress-induced ordering of Fe^{++} and Fe^{+++} among the octahedral sites. Thus, for a given applied stress (σ), the total strain (ϵ) is given by (1).

$$\epsilon=\epsilon_{\text{elastic}}+\epsilon_{\text{domain-motion}}+\epsilon_{\text{ordering}}=\epsilon_1+\epsilon_2+\epsilon_3. \tag{1}$$

The observed modulus,

$$M=\frac{\sigma}{\epsilon}=\frac{\sigma}{\epsilon_1+\epsilon_2+\epsilon_3}, \tag{2}$$

is thus less than the truly elastic value.

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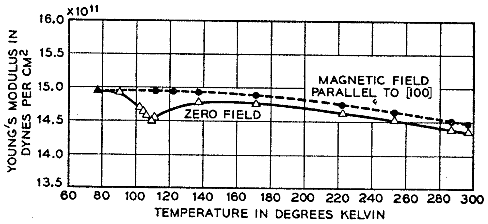

FIG. 1. Young's modulus of ⟨100⟩ in magnetite. Length = 3.8 cm, $w=t=0.4$ cm. Frequency of measurement—approximately 70 kc sec^{-1}.

Domain motion ϵ_2 may be prevented by measuring specimens in a saturating magnetic field; the field has little effect on elastic strains and would not prevent ordering.

The moduli of magnetite, Figs. 1, 2, and 3, do not vary with temperature in the usual manner. The moduli are minima near the critical temperature of the transformation. Furthermore, positive temperature coefficients of G_{100} (the torsion modulus in ⟨100⟩), and E_{111} (Young's modulus in ⟨111⟩), are observed substantially above the critical transformation temperature. Stress-induced ordering ϵ_3, we propose, is an important strain contribution to these two moduli.

Domain motion ϵ_2 is totally responsible for the abnormal temperature variation of E_{100}, Fig. 1, because when a saturating field is applied parallel to [100] the long direction of the rod, Young's modulus behaves normally. The internal friction is independent of magnetic field and is small throughout the temperature range, Fig. 4. The temperature variation of the domain motion effect, the difference between the two curves in Fig. 1, may arise as follows: At room temperature ϵ_2 for a given applied stress is small because ⟨111⟩ is the direction of easy magnetization[11] and the four ⟨111⟩'s are inclined equally to the stress direction ⟨100⟩. But on cooling the anisotropy constant diminishes reaching zero near 130°K; below 130°K ⟨100⟩ is the direction of easy magnetization.[9–12] When ⟨100⟩ is the magnetic axis, the relative lowering of modulus by ϵ_2[19,20] is proportional to $\mu_0\lambda^2$ (μ_0 is the initial permeability, λ is the magnetostriction). Maximum μ_0 occurs near 130°K but then λ is small.[11] As the temperature is lowered, λ increases but μ_0 becomes small.[11,13] Consequently, the maximum product, that is the minimum modulus, is expected at an intermediate temperature. The minimum occurs at 118°K.

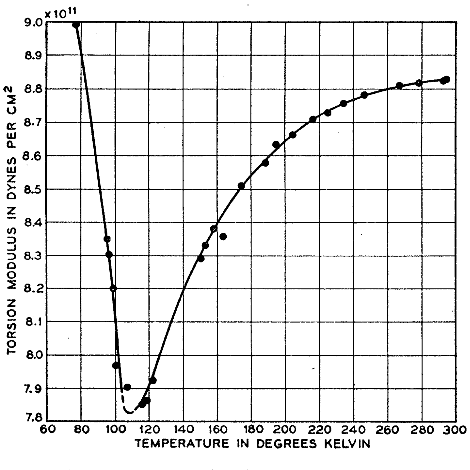

FIG. 2. Torsion modulus of ⟨100⟩ in magnetite. Length = 3.1 cm, diam. = 0.4 cm. Frequency of measurement—approximately 50 kc sec^{-1}.

The transformation has a much larger effect on G_{100}, Fig. 2, and E_{111}, Fig. 3. The slope of the E_{111} curve is positive well above room temperature and both slopes increase on cooling until a sharp minimum near 108°K. Furthermore, the internal friction for the ⟨111⟩ rod in longitudinal vibration and the ⟨100⟩ rod in torsional vibration are maximum near 95°K, Figs. 4 and 5. Neither the internal friction peaks nor the moduli minima are removed by placing the rods in a magnetic field parallel to their long directions. Actually the minimum in E_{111} is even sharper for the saturated condition. Thus the principal effect is not domain wall motion; another source of nonelasticity is indicated.[21]

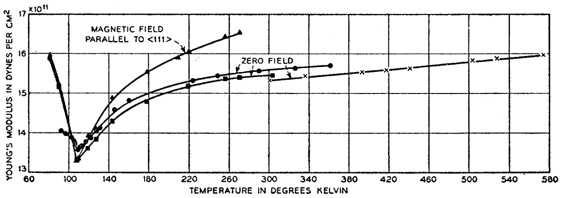

FIG. 3. Young's modulus of ⟨111⟩ in magnetite. Length = 2.1 cm, $w=t=0.4$ cm. Frequency of measurement—approximately 130 kc sec^{-1}.

As previously mentioned stress-induced ordering ϵ_3 is probably present. On first consideration it may seem unreasonable to conclude that effects in the moduli occurring several hundred degrees above the critical ordering temperature arise from stress-induced ordering. However, the low resistivity at room temperature and above has been attributed[2,3] to a change in the distribution of Fe^{++} and Fe^{+++} induced by an applied electric field and occurring by electron motion. Increase in local ordering of Fe^{++} and Fe^{+++} interferes with this electron motion, and consequently, the increase in resistivity due to cooling below 360°K is evidence for a building up of order.

We next consider the question of how the local order changes to give a strain component. Figure 6(a) shows the stacking of octahedral sites in consecutive {100} planes in the magnetite (spinel) structure. In the ordered arrangement suggested by Verwey and Haay-

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[21] The true elastic modulus may be affected from temperature variation by change in the average configuration of local order. However, this would not be a source of internal friction. Furthermore, the elastic modulus would be expected to gradually change from that for the disordered to that for the ordered phase and give an inflection in the modulus-temperature curve at the critical temperature, not a sharp minimum as observed.

man[2] alternate (001) layers are Fe^{++} and Fe^{+++}. Such ordering would change the symmetry to orthorhombic in the manner shown in Fig. 6(b). This was verified experimentally.[5,13] When the crystal becomes orthorhombic, the dimensions of the cubic lattice change, according to Bickford,[13] as follows: The c axis, direction of easy magnetization in the orthorhombic phase and normal to the plane of Fig. 6, shrinks 0.03 percent. One face diagonal AC shrinks 0.07 percent becoming the a axis of the orthorhombic phase while the other face diagonal DB increases 0.06 percent becoming the b axis of the orthorhombic phase. The changes in body diagonals are -0.06 percent (AF and CG) and $+0.03$ percent (BE and DH).

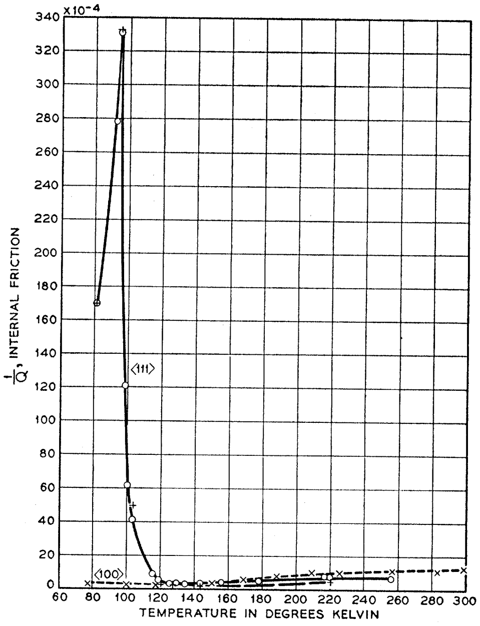

FIG. 4. Internal friction of ⟨111⟩ and ⟨100⟩ in magnetite, longitudinal vibrations. ×⟨100⟩, no external magnetic field. ○⟨111⟩, no external magnetic field. +⟨111⟩, large magnetic field parallel to the ⟨111⟩ of the rod. Frequency for ⟨100⟩ approximately 70 kc sec^{-1}. Frequency for ⟨111⟩ approximately 130 kc sec^{-1}.

Bickford[13] further concludes that if a single crystal is cooled through the transformation in a demagnetized condition, below T_c it is not a true single crystal; different cubic axes became the orthorhombic c axis in different regions. Furthermore, the regions may be twinned since the a and b axes can be interchanged. A cubic single crystal will remain a single crystal after transformation if it is cooled in a magnetic field parallel to a ⟨100⟩ (that ⟨100⟩ direction becomes the orthorhombic c axis) and tension or compression is applied in one of the ⟨110⟩ directions perpendicular the magnetic field direction. The hybrid orthorhombic crystals revert back to single cubic crystals on heating above T_c.[5,13]

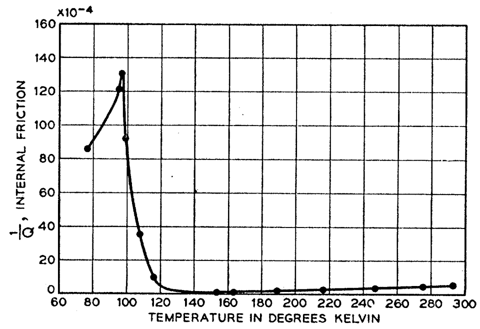

FIG. 5. Internal friction of ⟨100⟩ in magnetite for torsional vibrations. Frequency approximately 50 kc sec^{-1}.

At temperatures considerably above the critical ordering temperature a longitudinal stress applied along a ⟨110⟩, AC or DB in Fig. 6 changes the distribution of Fe^{++} and Fe^{+++} to give an additional strain component ϵ_3. Compression along AC, for example, would cause more of the smaller Fe^{+++} ions to populate the sites whose rows are parallel to AC, that is the second and fourth layers in Fig. 6(a). The larger Fe^{++} ions prefer rows parallel to DB, that is the first and third layers. Tension along AC or compression along DB reverse the preferred arrangement.

Tension-compression stresses applied in a ⟨100⟩ direction would not deform the structure in the manner shown in Fig. 6.[22] Consequently, no evidence for stress-induced ordering is expected in Young's modulus of ⟨100⟩ and none is observed, Fig. 1.

Consider a stress system causing torsion of the ⟨100⟩ rod with the long dimension of the rod as the stress axis. In this case stress-induced ordering is large, Fig. 2, because the stress induces atomic motions in ⟨110⟩ directions in certain areas of the rod. The effect of applying a magnetic field parallel to the ⟨100⟩ that is the long direction of the rod is shown in Fig. 7 and will be discussed later.

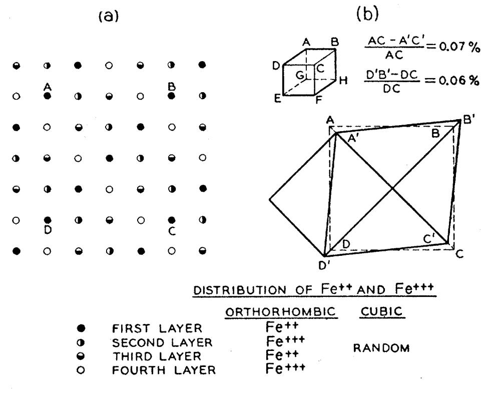

FIG. 6. (a) Stacking of successive {100} layers of octahedral sites in the spinel structure. (b) The relation between the cubic and orthorhombic phases in magnetite.

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[22] Near T_c a normal stress applied in ⟨100⟩ may determine the c axis of the orthorhombic phase (see reference 13), with a strain component resulting. This is essentially a domain motion effect and would be absent if an external magnetic field determines the c axis of the orthorhombic phase.

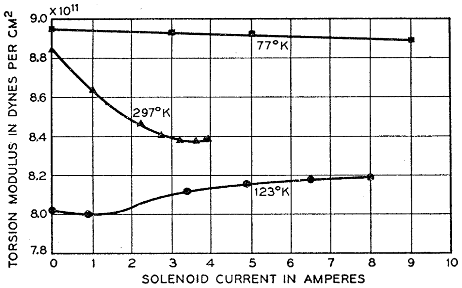

FIG. 7. Torsion modulus of ⟨100⟩ as function of external magnetic field. *H* at center of solenoid = 288 I gauss. Solenoid is 10.5 cm long, 12.5-cm o.d., and has 325 turns per cm.

The decrease in E_{111} on cooling and the minimum near 108°K, Fig. 3, probably also derive from stress-induced ordering. A normal stress applied in a ⟨111⟩ direction probably transforms the structure to orthorhombic. The resulting orientation of the orthorhombic cell is determined by the relative change in lengths of the body diagonals upon transforming. For example compression applied in the direction of *AF*, Fig. 6(b) would tend to make *AF* and *CG* the short diagonals and favors the ordered arrangement shown in Fig. 6. A strain component results, lowering the modulus.

The change in degree of order caused by a constant applied stress increases as the temperature is lowered toward T_c the critical ordering temperature and is maximum at T_c, where the free energy would be most sensitive to state of stress. G_{100} and E_{111} have their lowest values at 108°K. The relaxation time for the ordering process is also an important consideration. Above T_c where local order is involved, diffusion of electrons takes place very rapidly compared to the periods of the vibrations used in this investigation. The relaxed modulus is measured; the internal friction is low. Below the critical temperature long range order is involved; consequently, the relaxation time for the ordering process rapidly becomes longer on cooling and becomes approximately equal to the period of the vibrations at 95°K where the internal friction peak is observed, Figs. 4 and 5. In E_{100} there is no stress-induced ordering involved; no internal friction peak is observed.

The effect on E_{111} and G_{100} of a magnetic field applied along the rod will be discussed next. Above 130°K the directions of easy magnetization are the ⟨111⟩'s. If a normal stress is applied in a ⟨111⟩, domain motion occurs; consequently, applying a field in ⟨111⟩ causes E_{111} to increase, Fig. 3. Below 130°K when ⟨100⟩ is the magnetic axis, the domain motion component of E_{111} is small. In the case of torsional vibrations of the ⟨100⟩ rod the effects of applying an external magnetic field along the rod, Fig. 7, are difficult to explain. At 297°K the torsion modulus decreases 5.5 percent when a field[23] of 980 gauss is applied; further increase of the field to 1130 gauss increases the modulus slightly. Ordinarily one expects application of a magnetic field to increase the torsion modulus since the external field impedes domain motion.[24] The observed decrease in modulus seems to imply that the field aids stress-induced ordering.

Ordinarily in cubic substances the elastic constants (c_{11}, c_{12}, c_{44}) could be calculated from E_{100}, E_{111}, and G_{100}, but this is not the case for magnetite since the observed moduli are determined to such a large extent by nonelastic strains.

It is of interest to estimate how much change in atomic order is required to account for the lowering of modulus in the ⟨111⟩ rod. At the temperature of minimum in the modulus-temperature curve, Young's modulus of the ⟨111⟩ rod, Fig. 2, is roughly 30 percent lower than the value of modulus established by extrapolating from higher temperatures, assuming the usual sort of temperature dependence. If a stress of 1000 grams cm^{-2} is applied, approximately the maximum stress in the measurements, the total strain is 7.4×10^{-7} of which we estimate 5.3 is true elastic strain and 2.1×10^{-7} is due to stress-induced change in order. According to Bickford,[13] transformation of the cubic phase to orthorhombic causes a change of 0.06 percent in one of the ⟨111⟩ directions. Assuming for purposes of calculation that this change occurs linearly from 0 to complete order, a strain of 2×10^{-7} would come from a change in degree of order of 0.03 percent; consequently, the dimensional changes in the ordering process are ample to account for the observed moduli.

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