Maki and to Dr. A. Baratoff for informing us of errors in an earlier version of this work.

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MAGNETIC, ELECTRIC, AND CRYSTALLOGRAPHIC PROPERTIES OF GALLIUM IRON OXIDE

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Gallium iron oxide, $Ga_{2-x}Fe_xO_3$ with $0.7 \leqslant x \leqslant 1.4$, was first prepared by Remeika and shown to be ferromagnetic and piezoelectric.[1] This is the only crystal known to possess both properties. Recently, Rado[2] has observed a magnetoelectric effect in $Ga_{2-x}Fe_xO_3$. He showed this effect to be larger by an order of magnitude than that in any previously measured material, and also that the induced polarization is normal to the applied field. On the basis of a complete determination[3] of the crystal structure and of new magnetization measurements, we propose a magnetic-structure model that clarifies the results of previous studies.[2,4,5] We also suggest that the piezoelectricity originates in the oxygen-atom arrangement, in contrast to the ferromagnetism which is primarily due to the cations.

The unit cell and space group of $Ga_{2-x}Fe_xO_3$ have been reported by Wood.[6] The space group is $C_{2v}{}^9-Pc2_1n$, with eight formula weights per unit cell. The arrangement of cations is shown in Fig. 1, the oxygens being omitted from the figure for clarity. Each of the four cations in the asymmetric unit (e.g., within the area bounded by $a/4$ and b), at site positions with point symmetry C_1-1, are related to three other equivalent cations in the unit cell by the space-group symmetry. The ferromagnetic axis is c, and the polar axis is b (i.e., $\perp c$). If we assume no integral change in cell size and no loss of symmetry between the chemical and magnetic cells, the most probable Shubnikov groups for the magnetic unit cell are then $Pc2_1n$, $Pc2_1'n'$, $Pc'2_1n'$, and $Pc'2_1'n$. The first of these is antiferromagnetic; the other three are ferromagnetic, with a spontaneous mo-

ment allowed along the a, b, and c axes, respectively. Hence, the most likely Shubnikov group is $Pc'2_1'n$. Rado[2] has independently arrived at the similar conclusion that the magnetic point group is $2'm'm$. This should be written $m'2'm$ in terms of Wood's assignment[6] of axes, which we have retained. The magnetic space group $Pc'2_1'n$ requires the spin components in the ab plane to be antiparallel, with all the c-axis components parallel (for a given set of symmetry-related sites).

The magnetic moment per ferric ion, for stoichiometric $GaFeO_3$, is reported[5] to be $0.76\ \mu_B$. Assuming an S-state ion, with the spin at Fe(1) making an angle θ_1, and that at Fe(2) an angle θ_2 with the c axis, then

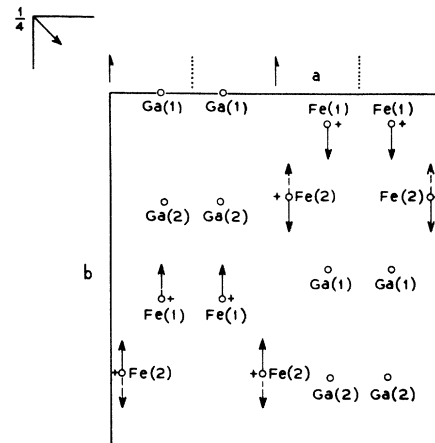$$\tfrac{5}{2}(\cos\theta_1 + \cos\theta_2) = 0.76.$$

FIG. 1. Schematic arrangement of cations and magnetic spins in $Ga_{2-x}Fe_xO_3$. Spin components in the ab plane are represented by arrows, along c by plus signs.

For the simple case of $\theta_1 = \theta_2 = \theta_C$, then $\theta_C = 81°$, i.e., the spins at each Fe(1) and Fe(2) site lie 9° out of the ab plane. The magnetoelectric effect in $Ga_{2-x}Fe_xO_3$ has recently been interpreted[2] based on a model of such a weak ferromagnet.

The magnetization of $Ga_{2-x}Fe_xO_3$ has been measured[7] at room temperature[8] with a vibrating-sample magnetometer. The variation in magnetic moment in the ab plane, for $H = 11.3$ kG, is shown in Fig. 2. The minima clearly lie very closely along the b-axis direction, in agreement with Nowlin's results.[5] The crystal symmetry does not require the minima in magnetic susceptibility to occupy any particular direction. The b axis must, hence, be very nearly parallel to the spin-axis component in the ab plane. Rado's model[2] also requires a small angle between the sublattice magnetizations and the b axis. For generality, consider the spin component at Fe(1) (xyz) to make a small angle, say θ_b, with the b axis. Then the c' symmetry operator requires the corresponding component at Fe(1) $(\frac{1}{2}-x, y, \frac{1}{2}+z)$ to make an angle $-\theta_b$ with the b axis; similarly, the $2_1'$ (and the n) operator makes the ab spin component for Fe(1) $(\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z)$ antiparallel to that at Fe(1) (xyz), and that at Fe(1) $(\bar{x}, \frac{1}{2}+y, \bar{z})$ antiparallel to that at Fe(1) $(\frac{1}{2}-x, y, \frac{1}{2}+z)$. The complete spin array follows if it is further assumed that the ab component of spin at Fe(2) is approximately parallel (or antiparallel) to its nearest Fe(1) neighbor. Figure 1 shows a spin array based on these assumptions, with all the c-axis spin components parallel.

In the crystal-structure study,[3] it was found that the Ga(2) site in $Ga_{2-x}Fe_xO_3$ (for $x \approx 1.3$) was partially occupied by the excess iron. The magnetic behavior of iron-rich $Ga_{2-x}Fe_xO_3$ can be accounted for by a spin array at the Ga(2) site similar to that at the Fe(1) and Fe(2) magnetic sublattices. In this case, $\theta_3 = 61°$ is obtained from Nowlin's observation[5] that each additional iron atom in excess of $x = 1$ has a magnetic moment of about 2.4 μ_B. On the basis of $S = \frac{5}{2}$ and no substantial rearrangement of the spins at Fe(1) and Fe(2) on occupancy of the Ga(2) site, the spin at Ga(2) thus appears to be 29° out of the ab plane.

The necessary condition for piezoelectricity is membership in one of the 21 acentric crystal classes. The cation arrangement shown in Fig. 1 approaches a violation of this condition.
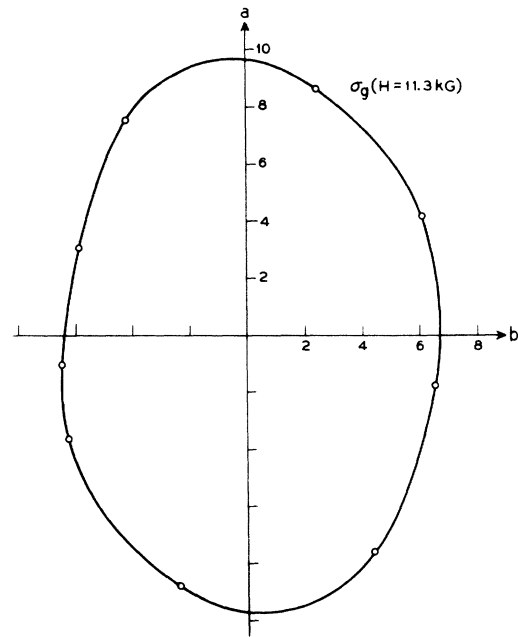

FIG. 2. Room-temperature magnetization of $Ga_{2-x}Fe_xO_3$ in the ab plane.

A fairly good approximation to inversion centers are located midway between pairs of Ga(2) cations, and also between pairs of Fe(2) cations, with the same y values. Any piezoelectric effect due to such a small departure from centrosymmetry would probably be negligible compared to the large effect found.[9] The piezoelectric effect is therefore most likely due primarily to the oxygen-atom array. These atoms form distorted octahedra around Ga(2), Fe(1), and Fe(2), with cation-oxygen distances that vary from 1.94 to 2.07 Å for Ga(2), and from 1.85 to 2.36 Å for Fe(1) and Fe(2). By contrast, the environment of Ga(1) is almost a regular tetrahedron, with a mean Ga(1)-O distance of 1.85 Å. One Ga(1)-O bond of each tetrahedron is approximately parallel to the polar axis. The four tetrahedra in the unit cell have the same sense. Although the entire oxygen array lacks an inversion center, and hence contributes to the piezoelectricity, the tetrahedron around Ga(1) is the outstandingly asymmetric object in the structure. It is therefore suggested that the piezoelectric effect originates in the Ga(1) oxygen tetrahedra.

It should be emphasized that the orientation of the spin array proposed in this Letter is predicated on several simplifying assumptions. Confirmation will be sought by neutron-diffraction experiments.

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IONIZED F-AGGREGATE COLOR CENTERS IN KCl

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(Received 29 October 1964)

The existence of ionized F-aggregate color centers in alkali-halide crystals has never been established.[1] This note reports new evidence for the existence of such ionized centers in KCl, specifically the F_2^+ and F_3^+ centers, which are ionized M and R centers, respectively.[2] A new absorption band occurring at 1.4 μ is believed to be due to a transition of the F_2^+ center,[3] and it appears very likely that a band at about 960 mμ arises from a transition of the F_3^+ center.

The technique employed for the production of ionized centers was the following. KCl crystals, additively colored in potassium vapor by the van Doorn method,[4] were exposed to light in the high-energy tail of the F band at room temperature to produce relatively large concentrations of F-aggregate centers. These crystals were subsequently cooled to liquid-helium temperature and exposed to x rays in order to introduce trapped-hole defects which could lead to the ionization of F aggregates. Without warming the crystal, bleaching of trapped-hole centers was then induced with 335-mμ light corresponding to the spectral region of the V_K and H bands; this light also produced bleaching of the F-aggregate centers.

The formation of the 1.4-μ band is most easily observed in a crystal which contains F and M centers predominantly. After the liquid-helium-temperature x irradiation, the 1.4-μ band grows in constant proportion to the decrease of the M band during the exposure of the crystal to 335-mμ light. The ratio of the change of absorption coefficients at the peak of the respective bands, $|\Delta\alpha_M/\Delta\alpha_{1.4\ \mu}|$, is

4.2. It is found that this ratio is also maintained during the reverse process, 1.4 $\mu \rightarrow M$ band, which is stimulated by F-light excitation near the F-band maximum. This reverse conversion is interpreted as resulting from the capture of F electrons by F_2^+ centers.

Since the M center has a $\langle 110 \rangle$ axis of symmetry, it is expected that the F_2^+ center should be characterized by this same axis. Figure 1 shows that the 1.4-μ band exhibits $\langle 110 \rangle$ dichroism when produced from an M band with the same dichroism. Similar data have shown that $\langle 100 \rangle$ dichroism is induced in the 1.4-μ band, if the M band is initially oriented at room temperature with $\langle 100 \rangle$ M light. These data are consistent with the expected $\langle 110 \rangle$ symmetry axis for the F_2^+ center; they further indicate that the $F_2 \rightarrow F_2^+$ conversion under 335-mμ light occurs largely without a reorientation of the axes of the centers. However, as seen in Fig. 1, the reverse process $F_2^+ \rightarrow F_2$ under F light occurs with some loss of orientation of both the F_2^+ and F_2 centers. A further interesting observation regarding the 1.4-μ band is that it can result from x-ray exposure alone (cf. curves 2a and 2b, Fig. 1). This would be expected, for example, if a free hole is captured by a M center, or if the M center is directly photoionized by the x ray itself.

We believe the foregoing results are most easily interpreted by assuming that the 1.4-μ band is due to a transition of the F_2^+ center. The possible centers which might form from M-center bleaching are severely limited. At the low temperatures employed, ionic processes are improbable. Considering the other