The temperature dependence of χ/χ_N calculated from (7) is shown in Fig. 1 together with the experimental values by Reif[1] and Knight et al. It is very interesting to note that the experimental value obtained by Knight et al.[3] is very close to the theoretical curve. It seems likely that if a more refined theory were used to construct collective excitations with no energy gap, like spin waves in antiferromagnets, that the exponential decrease of χ with temperature would be replaced by a decrease like T^n where n is some positive power; but it seems very unlikely that such a refinement would give rise to a nonzero value for χ at zero temperature. We therefore conclude that the theory is in rough agreement with the experimental results of Knight et al. but in disagreement with those of Reif.

I am very much indebted to Professor C. Kittel, Professor M. Tinkham, and Dr. W. Marshall for their invaluable discussions.

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Acoustical Loss and Young's Modulus of Yttrium Iron Garnet

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YTTRIUM iron garnet and other rare earth garnets are important as a new class of magnetic oxides. The yttrium iron garnet crystal structure has cubic symmetry with the magnetic ions occupying octa- and tetrahedrally coordinated positions in the lattice, as is the case in ferrites (ferrites have similar but not identical crystal structure). Because of the variety of stress-induced relaxations which have been reported in ferrites[1,2] and the anomalous peak in the ferrimagnetic resonance line width between 20–65°K,[3] Young's modulus and acoustical attenuation of polycrystalline yttrium iron garnet were measured by a technique which has been described elsewhere.[4]

Two samples[5] were prepared by sintering the oxides at 1450°C in O_2. The first sample contained some alumina and silica as impurities, and the variation of Young's modulus and attenuation (Q^{-1}) with temperature is shown in Fig. 1. There is a typical stress-induced relaxation at 153°K for a frequency of 84.8 kc sec^{-1}.
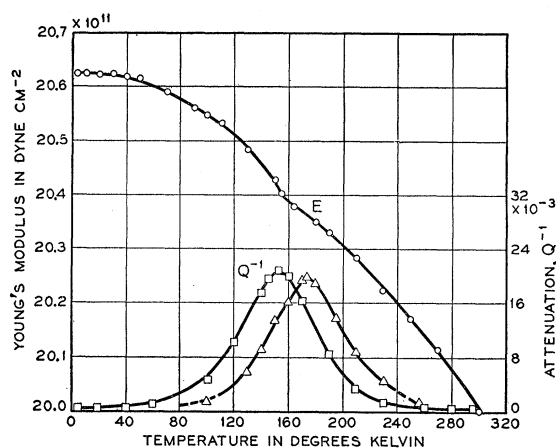

FIG. 1. Young's modulus and attenuation (Q^{-1}) for sample of yttrium iron garnet. □ attenuation at 84.8 kc sec^{-1}; △ attenuation at 249.2 kc sec^{-1}.

By exciting the specimen at its third harmonic, the maximum in the attenuation is shifted to 172°K. The shift corresponds to an activation energy of 0.12 ev/unit process. (A simple Arrhenius relation was used to calculate the activation energy even though the half-peak width is too broad for it to be strictly applicable.) A second specimen, prepared by a more refined technique, contained total impurities $<0.05\%$ and was within $\pm0.05\%$ of the stoichiometric composition $Y_3Fe_2(FeO_4)_3$. The stress-induced relaxation was only just resolvable with a maximum attenuation of 2.0 $\times10^{-4}$, an order of magnitude less than the first sample. The activation energy was the same as for the first sample.

Spheres of 0.010-in. diameter were made from each of the samples and the ferrimagnetic line width at 16 kMc sec^{-1} was measured at room temperature. The line width of the first sample was 150 oersteds while that of the second sample was only 47 oersteds. These observations lead us to believe that the stress-induced relaxation is not present in a homogeneous stoichiometric garnet structure. Localized departures from stoichiometry, however, allow the existence of a defect structure which is coherent (that is, not present as a second phase) with the parent garnet matrix. In this case, a stress-induced relaxation could occur by the stress-induced migration of electrons or ions. The value of the observed activation energy is lower than would be expected from an ion migration and is more in favor of an electron migration, indicating incomplete oxidation of the metal ions in the neighborhood of the defects. Because of the similarity between this relaxation peak and those reported in manganese ferrite crystals[1] and hausmannite[6] (i.e., the broad relaxation peak and variation of the peak with purity and homogeneity), it is felt that these relaxations are not a property of the stoichiometric defect-free composi-

tion, and as such could be used as a measure of the perfection of the material.

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Ferrimagnetic Fluoride—$Na_5Fe_3F_{14}$

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PRELIMINARY investigation of the $NaF-FeF_3$ phase diagram indicates that it is similar to that of $NaF-AlF_3$.[1] The iron analog of chiolite ($Na_5Al_3F_{14}$) is formed in the composition range 70 mole % $NaF-30$ mole % FeF_3 to 50% $NaF-50\%$ FeF_3. In this range there are at least three phases, two of which are high- and low-temperature forms of $Na_5Fe_3F_{14}$ with structures related to that of chiolite. X-ray powder diffraction patterns show similarities between $Na_5Fe_3F_{14}$ and chiolite, either as a mineral[2] or as the precipitate from aqueous solution made according to Cowley and Scott.[3] Single-crystal diffraction data confirm the relationship; in fact, the establishment of the formula $Na_5Fe_3F_{14}$ is based on this evidence.

Chiolite belongs to the tetragonal space group $D_{4h}(6)-P4/mnc$ with two formula units per unit cell which has dimensions $a=7.01$, $c=10.41\pm0.01$ A.[4] The high-temperature form of $Na_5Fe_3F_{14}$ in the form of a small crystal picked out of a quenched melt belongs to the tetragonal space group $D_4(6)-P4_22_12$, also with two formula units per unit cell with dimensions $a=7.34$, $c=10.38\pm0.02$ A. The single-crystal photographs of this phase bear a very close resemblance to the analogous ones of chiolite. Although the space group $P4_22_12$ is not a subgroup of $P4/mnc$, a reasonable trial structure for the high-temperature phase is obtained by comparison with the chiolite structure. It is interesting to note that $c/a=1.414\sim\sqrt{2}$; however, there is no doubt that the crystal is anisotropic, both from the x-ray data and optical examination of birefringence.

The low-temperature form is more complex. Though pseudotrigonal, a small crystal picked from a slow-cooled melt is actually monoclinic and belongs to one of the three space groups $C_{2h}(3)-A2/m$, $C_2(3)-C2$, or $C_s(3)-Cm$. The unit cell of dimensions $a=73.23$ ±0.10, $b=7.46\pm0.02$, $c=12.72\pm0.03$ A, and $\beta=90$ $\pm0.5°$ contains 24 formula units. The geometrical relationship of this cell to the more symmetric high-temperature one is

$$\mathbf{a}'=8\mathbf{a}+0\mathbf{b}+4\mathbf{c},$$
$$\mathbf{b}'=-\tfrac{1}{2}\mathbf{a}-\tfrac{1}{2}\mathbf{b}+\tfrac{1}{2}\mathbf{c},$$
$$\mathbf{c}'=\tfrac{1}{2}\mathbf{a}-\tfrac{3}{2}\mathbf{b}-\tfrac{1}{2}\mathbf{c},$$

where the primed axes refer to the monoclinic cell. The pseudotrigonal subcell contains 3 formula units. The x-ray densities of the high- and low-temperature modifications are 3.26 and 3.15 g/cc, respectively. That the low-temperature phase is less dense than the high is an indication perhaps of a change in coordination number for the sodium or iron ions.

All preparations probably contain more or less of both phases. It is difficult to ascertain the "phase composition" by means of powder photography.

Pellets of material which give mainly the x-ray powder lines of $Na_5Fe_3F_{14}$ have been prepared by sintering or barely fusing a 62.5 mole % $NaF-37.5$ mole % FeF_3 mixture at 700°C in an anhydrous HF atmosphere, then quenching. The material jumps to a small magnet at liquid nitrogen but not at liquid oxygen temperature. The resistivity of a sintered pellet is greater than 10^8 ohm-cm. Low-temperature magnetization measurements down to 1.7°K by R. M. Bozorth confirm that it is ferrimagnetic with a Curie temperature of about 80°K and a substantial magnetic moment. There is, however, an anomaly in the results at the lowest temperatures, which makes an accurate extrapolation to infinite field and 0°K impossible at the present time. The slow-cooled melts jump to a magnet from liquid nitrogen also.

The structure of chiolite[4] is one which could lead to ferrimagnetism if ions with permanent magnetic moments replaced the Al^{3+} ions. There are layers of AlF_6 octahedra, two-thirds of which share two corners and one-third of which share four corners. If, for example, Fe^{3+} ions in the two different sets of octahedra were antiferromagnetically ordered, a net moment of 5 Bohr magnetons per formula unit would result for $Na_5Fe_3F_{14}$. The high-temperature form of $Na_5Fe_3F_{14}$ probably resembles the chiolite very closely: the Fe^{3+} ions are in positions $2(a)$ and $4(d)$ of $P4_22_12$.

The origin of the magnetism in the low-temperature modification cannot now be discussed with any definiteness because of the large number of possibilities of interaction. Only a structure analysis and further magnetic and electrical investigations on single phase material can lead to this understanding. Because there are 72 Fe^{3+} ions in the unit cell, nine is the minimum number of nonequivalent sets of positions that may be occupied by these ions; these would be the $8(j)$ positions of $A2/m$. There are also many other possibilities too numerous to list.

Thus far, two trivalent metal ions of the many