for glasses; for vitreous silica the expansion coefficient remains negative to below 3°K ($T < \theta/100$),[10] and comparison of elastic and heat capacity data[14] suggests the existence of a low-lying transverse optical mode of frequency near 10^{11} sec^{-1}. Only at temperatures well below 3°K would this mode be frozen out, which may be a required condition for elastic and thermal data to agree and for the sign of the expansion coefficient to become positive. It is interesting to conjecture about possible physical models that may give rise to these changes in expansion coefficient.

We are grateful to Dr. J. G. Collins and to Dr. C. S. Smith for some interesting discussions.

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SODIUM IRON FLUORIDE, A TRANSPARENT FERRIMAGNET

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The purpose of this Letter is to report new optical and magnetic observations, including a new giant anisotropy in sodium iron fluoride, $Na_5Fe_3F_{14}$, the first example of a ferrimagnetic material which is highly transparent in the bulk. This is in distinction to magnetic oxides such as yttrium iron garnet and the ferrites, as well as to other ferromagnets, which are only partially transparent for very much shorter optical path lengths. The measurements include the magnetization, microwave resonance, optical absorption, and optical Faraday rotation.

Knox and Geller reported[1] the discovery of sodium iron fluoride in 1958 along with a detailed analysis of its crystal structure. They showed that there are at least two forms: a high-temperature tetragonal form belonging to space group $D_{4h}{}^6$-$P4_22_12$ and having a structure closely related to that of chiolite,[2] $Na_5Al_3F_{14}$; and a low-temperature, monoclinic, pseudotrigonal form belonging to one of the three space groups $C_{2h}{}^3$-$A2/m$, $C_2{}^3$-$C2$, or $C_s{}^3$-C_m. The monoclinic cell has a very long a axis, 73.23 Å, and is quite complicated in structure. It is probable that the low-temperature form is the stable one at room temperature[3] and that both forms are ferrimagnetic.[1]

Recently we have grown several small single crystals of sodium iron fluoride whose sizes preclude the carrying out of some desired experiments. Therefore, the data presented should be considered in some respects to be qualitative. The magnetization measurements were made using a polycrystalline sphere approximately 1 mm in diameter. The microwave measurements were made using an oriented, polished, single-crystal sphere of approximately 0.3-mm diameter. The optical measurements were made using a flat crystal with natural faces 1 mm across and 0.25 mm thick. The light beam was 0.3 mm in cross section and was in a direction of twofold crystal symmetry.

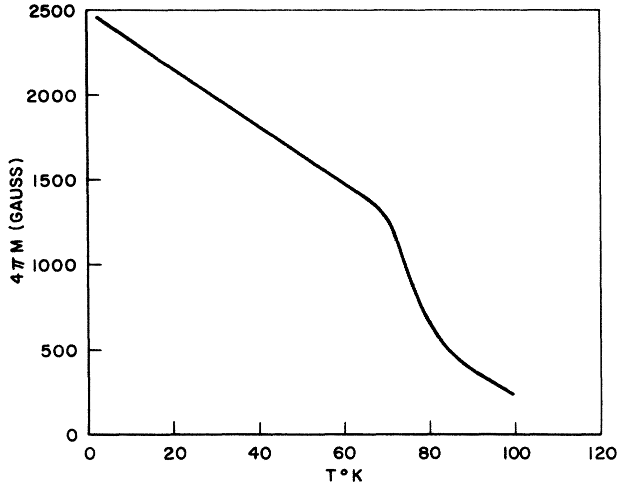

FIG. 1. Saturation magnetization, $4\pi M$ vs T for sodium iron fluoride, measured by H. J. Williams and R. C. Sherwood.

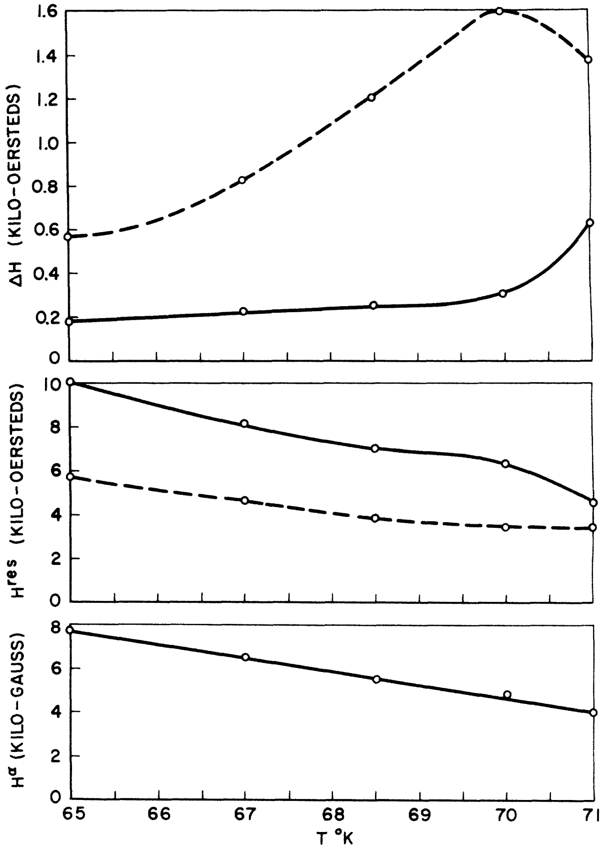

FIG. 2. Linewidth, ΔH (upper figure), and dc field for resonance, H^{res} (middle figure) vs T. The dc field is along a hard axis of magnetization which results in the two resonances at each temperature. From the two values of H^{res} an estimate of the anisotropy field, H^{a}, is obtained as shown in the lowest figure. The sample is a sphere 0.25-mm diameter, and the measurements were made at 11400 Mc/sec.

The magnetization, as a function of temperature, was measured by H. J. Williams and R. C. Sherwood using a pendulum balance magnetometer described elsewhere.[4] The results are shown in Fig. 1. Two essential points are noted. The first is that $4\pi M$ approaches 2500 gauss at 0°K which corresponds to 5 Bohr magnetons per formula weight. Since there are nine inequivalent sites for the Fe^{3+} ions in a unit cell of three formula weights, the ions must be ferrimagnetically ordered in the ratio of 6 to 3. Secondly, the slow decrease in $4\pi M$ with temperature in the vicinity of the Curie temperature, about 100°K, is indicative of other than the usual ferrimagnetic transition. It is probable that this slow decrease is associated with anisotropy in the magnetization, which is due in part to the large anisotropies found in this crystal.

Ferrimagnetic resonance absorption and the associated dc magnetic field, H^{res}, have been measured at low temperatures on the single-crystal sphere oriented along a twofold symmetry axis. The linewidth of the absorption is quite large near the Curie temperature and decreases almost linearly with temperature. From the H^{res} values it may be deduced that the magnetic anisotropy field, H^{a}, is likewise large. Figure 2 shows ΔH, H^{res}, and H^{a} over a small temperature range above 65°K. Below this temperature the anisotropy fields are so large that H^{res} could not be obtained with the magnetic fields available. At 65°K, H^{a} is approximately 8000 gauss and decreases linearly to a minimum of 4000 gauss at 71°K. Above this temperature the anisotropy field increases markedly before going to zero at the Curie temperature. This is an anomalous result and is consistent with the previous observation concerning the behavior of the saturation magnetization in this temperature range. A striking feature is noted when H_{dc} is within ±2° of the axis of hard magnetization, namely, the fields for resonance and the linewidths increase abruptly. This characteristic is observed over all of the temperature range studied. Figure 3 shows the data taken at 79°K. These observations indicate a new type of giant anisotropy which is similar in many respects to the giant anisotropy described in several papers[5] by Dillon, and Dillon and Nielsen. Their effect occurs in the liquid helium temperature range for rare-earth doped YIG and appears to be associated with the close approach of low-lying rare-earth energy levels as the crystal orientation of the magnetic field is varied.[6,7] The number and position of the peaks with respect to crystallographic orientation are then explained by the number and orientation of the dodechedral rare-earth ion sites.[7]

Since sodium iron fluoride is not doped with other magnetic ions and because the width of the anisotropy peak is narrow at such high temperatures, explanations based on the giant anisotropies in rare-earth doped YIG, at least, must be modified. One possible modification suggests that the ferric ions possess a mirror plane symmetry such that the energy levels of the two groups of ions are coincident for $H_{\rm dc}$ in the mirror plane. In the immediate neighborhood of this orientation, the anisotropy energy can vary almost discontinuously.

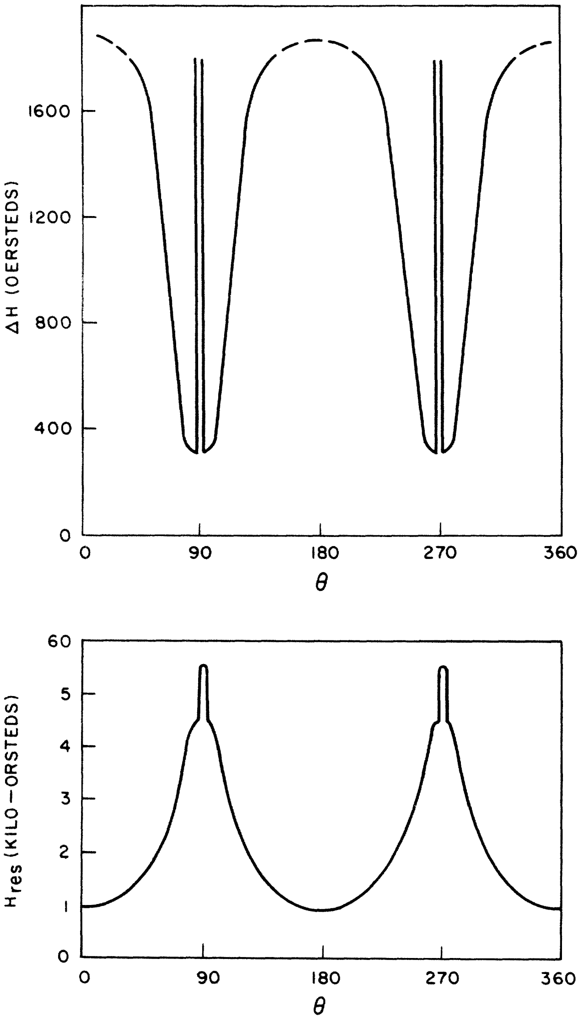

FIG. 3. ΔH and $H^{\rm res}$ as functions of crystal orientation, showing a discontinuity in each for $H_{\rm dc}$ within ±2° of the hard axis of magnetization.

The optical absorption of sodium iron fluoride given in Fig. 4 is characterized by a series of sharp peaks with weaker ones at approximately 15 000 and 20 000 cm^{-1} and with much stronger ones at 26 000 and 29 500 cm^{-1}. All Fe^{3+} ions are in one of two different kinds of FeF_6^3 octahedra, one third of them being of one type and two thirds of them another type.[2]

The optical absorption spectrum of the FeF_6^{3-} octahedron has been investigated previously by Jørgensen[8] using the reflection of crystalline (ethylendiamine H)$_3$FeF$_6$. The spectrum of Na$_5$Fe$_3$F$_6$ is almost identical to this in both frequency and magnitude. On this basis, an assignment is made for the transition energies of sodium iron fluoride. The absorptions at 15 000 cm^{-1}, 20 000 cm^{-1}, 26 000 cm^{-1}, and 29 500 cm^{-1} correspond to transitions from the ground state ${}^6A_1$ (${}^6S_{5/2}$) to ${}^4T_1$ (${}^4\Gamma_4$), ${}^4T_2$ (${}^4\Gamma_5$), ${}^4A_1$ (${}^4\Gamma_2$) and ${}^4E$ (${}^4\Gamma_1$), and ${}^4T_2$ (${}^4\Gamma_5$), respectively. An energy level diagram of Fe^{3+} in a cubic crystal field is given by Clogston.[9]

In YIG there is an intense, dominating, broad absorption band which is ascribed to a charge transfer process,[9,10] in which an electron is excited from an essentially oxygen bonding orbital into an essentially $3d$ ferric ion antibonding orbital. It is evident from Fig. 4 that the intensity of this absorption is at least greatly reduced for

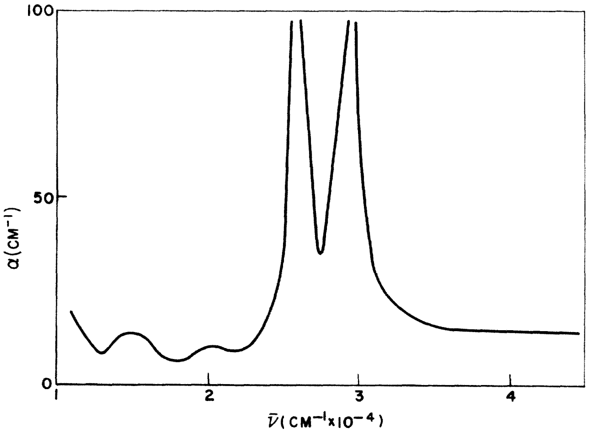

FIG. 4. Optical absorption α in cm^{-1} as a function of wave number $\bar{\nu}$. The sample is an unpolished, single-crystal plate, approximately 1 mm × 1 mm × 0.25 mm, and the light propagation is along a twofold axis of symmetry.

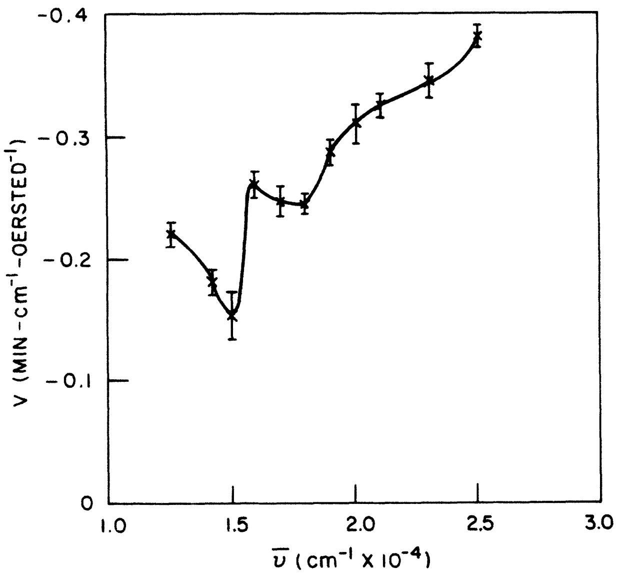

FIG. 5. Verdet constant for paramagnetic Faraday rotation vs wave number at $T = 300$°K.

sodium iron fluoride. This accounts for the greater transparency of sodium iron fluoride.

Finally, Fig. 5 shows the optical Faraday rotation at room temperature. The measured Verdet constant, V, is seen to range from -0.15 min-cm^{-1}-Oe^{-1} at $\bar{\nu} = 15\,000$ cm^{-1} to -0.38 min-cm^{-1}-Oe^{-1} at $\bar{\nu} = 25\,000$ cm^{-1}. These values are comparable to those of the strongest known transparent Faraday rotators. For sodium iron fluoride the rotation was found to be the same in the ferrimagnetic region (measured at 90°K) for the orientation investigated. The large Faraday rotation associated with the strong absorption in YIG is absent. This fact is consistent with the absence of that absorption in sodium iron fluoride.

We would like to express our appreciation to S. Geller for calling our attention to sodium iron fluoride. We are also indebted to S. Geller, K. Knox, L. G. Van Uitert, and H. Guggenheim for many discussions on the structure, properties, and crystal growth of this material; to H. J. Williams and R. C. Sherwood for making the measurements on the temperature dependence of magnetization; and to L. J. Varnerin for helpful suggestions on the presentation of the data.

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OBSERVATION OF "ANTICROSSINGS" IN OPTICAL RESONANCE FLUORESCENCE*

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The level-crossing technique of atomic spectroscopy[1] utilizes an interference effect in resonance fluorescence which can occur when two Zeeman levels of an excited state of an atom are tuned to the same energy ("crossed") by the application of an external magnetic field. When the two levels are within an energy separation comparable to their radiation widths, one can obtain in certain instances spatial interference in the resonant scattering from these two levels. Franken[2] and Rose and Carovillano[3] have analyzed this phenomenon in detail and discussed the magnitude and shape of the interference signal as a function of magnetic field strength for various experimental geometries.

During a level-crossing investigation of the $2P$ state of lithium, we observed substantial asymmetry of a crossing signal which we were unable to explain away as an instrumental effect. This asymmetry has been traced to the presence