

Low-Temperature Acoustic Relaxation in Ni-Fe Ferrites

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An acoustic relaxation effect occurs near 40°K in $\text{Ni}_{0.75}\text{Fe}_{2.25}\text{O}_4$ and is attributed to a stress-induced change in distribution of Fe^{++} and Fe^{+++} similar to that occurring in magnetite. The process involves electron diffusion. The activation energy is between 0.026 and 0.055 eV per electron jump.

IN magnetite¹ a low-temperature ordering transformation ($T_c \approx 115^\circ\text{K}$) occurs which involves the distribution of Fe^{++} and Fe^{+++} among the available octahedral sites in the structure. Only electron diffusion is involved since $\text{Fe}^{+++} + e \rightleftharpoons \text{Fe}^{++}$. An applied stress^{2,3} changes the local distribution of Fe^{++} and Fe^{+++} . For example, a tensile stress would induce more of the larger Fe^{++} ions to be distributed in the stress direction. This additional strain lowers Young's modulus for the $\langle 111 \rangle$ direction in magnetite³ at temperatures as high as 600°K. Considering the stress constant, the induced strain from change in distribution of Fe^{++} and Fe^{+++} and the decrease in modulus therefrom reach their maximum at the critical ordering temperature, 110°K in the sample of magnetite studied.³ The internal friction peaks at 95°K where the relaxation time for the electron diffusion process and the period of the impressed vibrations are approximately equal.

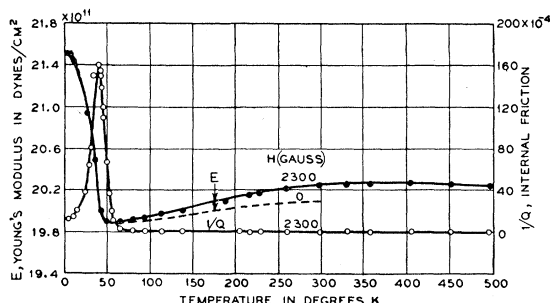


FIG. 1. Young's modulus and longitudinal internal friction of $\langle 111 \rangle$ in $\text{Ni}_{0.75}\text{Fe}_{2.25}\text{O}_4$. The frequency of measurement was approximately 83 kc/sec. The external magnetic field was applied in the $\langle 111 \rangle$ direction.

Recently, the elasticity and internal friction were investigated in a single crystal of approximately $\text{Ni}_{0.75}\text{Fe}_{2.25}\text{O}_4$ (that is, $\frac{3}{4}$ of the Fe^{++} is replaced by Ni^{++}) obtained from Linde Air Products Company through Dr. G. W. Clark. Galt, Yager, and Merritt have studied domain wall velocities⁴ and ferromagnetic resonance⁵

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¹ Verwey, Haayman, and Romeijn, *J. Chem. Phys.* **15**, 181 (1947).

² L. R. Bickford, *Revs. Modern Phys.* **25**, 75 (1953).

³ M. E. Fine and Nancy T. Kenney, *Phys. Rev.* **94**, 1573 (1954).

⁴ J. K. Galt, *Bell System Tech. J.* **33**, 1023 (1954).

⁵ Galt, Yager, and Merritt, *Phys. Rev.* **93**, 1119 (1954).

in similar crystals. The crystal was ground into a cylinder, 5 mm in diameter and 38.3 mm long, accurately oriented in a $[111]$ direction. Young's modulus, the torsional modulus, and the internal friction for longitudinal and torsional vibrations were measured from 2°K to above room temperature as shown in Figs. 1 and 2 using a resonant piezoelectric method. The equipment and procedure are described elsewhere.⁶

The measurements show the presence of a low-temperature relaxation effect in the $\text{Ni}_{0.75}\text{Fe}_{2.25}\text{O}_4$ crystal. The relaxation effect is presumably a stress-induced change in distribution of Fe^{++} and Fe^{+++} , that is a remnant of the magnetite effect is present. The internal friction peak occurs near 38°K as shown in Figs. 1 and 2. Near this temperature the observed Young's modulus, Fig. 1, abruptly increases, approaching the value for the unrelaxed modulus at very low temperatures, but there is no sharp minimum as in magnetite. If the difference between the relaxed and unrelaxed moduli were constant, the relaxed modulus would increase on cooling; however, the relaxed modulus decreases on cooling until near the temperature of the internal friction peak. Thus a given applied stress induces more configurational strain at low temperatures, but the effect is present at 500°K since even here the temperature coefficient of modulus is abnormally low. If vibrations of much lower frequency are used, the relaxed modulus can be observed below 50°K. There is a possibility that the relaxed modulus might have a sharp minimum below 50°K, but nothing

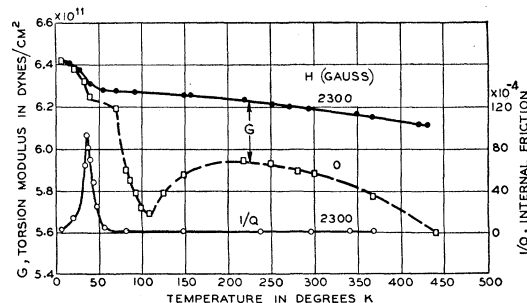


FIG. 2. Torsional modulus and torsional internal friction of $\langle 111 \rangle$ in $\text{Ni}_{0.75}\text{Fe}_{2.25}\text{O}_4$. Torsional waves were propagated in a $\langle 111 \rangle$ direction. The frequency was approximately 50 kc/sec. The external magnetic field was applied in the $\langle 111 \rangle$ that was the direction of wave propagation.

⁶ M. E. Fine (to be published).

indicative of a critical ordering temperature is observed above 50°K.

When no external magnetic field is present, the torsion modulus has a minimum near 105°K, Fig. 2, but this disappears when the sample is saturated. It is thus a domain wall motion effect and is associated with changes in magnetostriction and permeability.

The longitudinal internal friction was also measured near 275 kc/sec. The measurements, not shown, are less reliable than those for the lower frequency since

the experimental conditions were not as satisfactory, but the internal friction appeared to peak at a temperature 3 to 7° higher than the 83-kc/sec measurements. This corresponds to an activation energy of between 0.055 and 0.026 ev per electron jump. The value obtained from ferromagnetic resonance line widths⁵ is within this range.

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Theory of Donor and Acceptor States in Silicon and Germanium

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An exact theory of impurity states in crystals is developed, and an evaluation is given of the applicability of the Wannier equation to the donor states in Si and Ge in view of the multiple energy minima in the conduction band. The theory is extended to include degenerate bands, and it is shown by two different methods that the Wannier equation is to be replaced by a set of coupled wave equations. The theory is applied to acceptor states in Si and Ge. The agreement with experiment is fairly good for both donors and acceptors.

WE are concerned here with the calculation of the ionization energies of the shallow donor and acceptor impurity states in silicon and germanium. The ionization of these levels is largely responsible for the charge carrier concentrations observed at room temperature and below. The central experimental facts¹ are that the approximate ionization energies of electrons associated with pentavalent substitutional impurities are 0.04 ev in Si and 0.01 ev in Ge, and the ionization energies of holes associated with trivalent substitutional impurities are about 0.05 ev in Si and 0.01 ev in Ge. The general picture which one has of the donor and acceptor ground states is that their wave functions are spread out over a hydrogenic 1s orbital with a large effective radius, of the order of 20 Å or more. The loose binding is thought to be the result of the high dielectric constant of the crystals and the light effective masses of the carriers. We recall that the radius R_0 of the first Bohr orbit of an electron of mass m^* moving in a medium of dielectric constant ϵ around a fixed charge $|e|$ is

$$R_0 = \epsilon \hbar^2 / m^* e^2 = (\epsilon m / m^*) a_H, \quad (1)$$

where $a_H = \hbar^2 / m e^2$ is the usual Bohr radius. As an example, $R_0 \approx 50 a_H \approx 25$ Å if $\epsilon = 16$ and $m^* = 0.3m$. The effective nuclear charge is taken as $\pm e$ for pentavalent or trivalent substitutional impurities in silicon or germanium.

Our interest in the problem was heightened by the striking circumstance that in both Si and Ge the ionization energies of donors are approximately equal to the

ionization energies of acceptors. This is the more remarkable because the forms of the conduction and valence bands are known from cyclotron resonance experiments² to be entirely different from each other. The principal energy bands for silicon are shown in Fig. 1. The conduction band energy surfaces are spheroids in k space along $\langle 111 \rangle$ axes in Ge and along $\langle 100 \rangle$ axes in Si, of the form

$$E(\Delta k) = \hbar^2 \left[\frac{(\Delta k_{11})^2}{2m_1} + \frac{(\Delta k_{\perp})^2}{2m_2} \right], \quad (1)$$

where $\Delta k = k - k_i$, with k_i at one of the set of equivalent energy minima. The valence band energy surfaces for both crystals consist of two fluted or warped spheres³ degenerate at $k=0$:

$$E(k) = Ak^2 \pm [B^2 k^4 + C^2 (k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)]^{1/2}. \quad (2)$$

The numerical calculations given below suggest that the apparent equality of donor and acceptor energies is only accidental, without fundamental significance.

IMPURITY STATE THEORY

The unusual character of the energy surfaces in Si and Ge makes one hesitant about applying the Wannier theorem⁴ without further examination. We have

² For a review of this work, see papers by Kip, Lax, and Kittel, *Physica* (to be published).

³ Dresselhaus, Kip, and Kittel, *Phys. Rev.* **95**, 568 (1954).

⁴ G. H. Wannier, *Phys. Rev.* **52**, 191 (1937); J. C. Slater, *Phys. Rev.* **76**, 1592 (1949); G. F. Koster and J. C. Slater, *Phys. Rev.* **95**, 1167 (1954); for further references, see J. Friedel, *J. phys. et radium* **15**, 28 (1954).

¹ See, for example, J. A. Burton, *Physica* (to be published).