Division 6 - Lincoln Laboratory
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

SUBJECT: TRIP REPORT TO BELL TELEPHONE LABORATORIES, MURRAY HILL, N.J. January 6, 1954

To: David R. Brown

From: J. B. Goodenough

Date: January 14, 1954

Abstract: The ferrite single-crystal-synthesis program of the Bell Telephone Laboratory was investigated. Information on some experimental techniques for measurements about to be undertaken in this laboratory were also obtained. Galt reported some recent work on microwave resonance in nickel ferrite which suggests a general technique for the measurement of the heat of activation for various electron-transfer relaxation phenomena. A brief outline is given to indicate an immediate extension and application of these measurements.

D. R. Brown, F. E. Vinal and J. B. Goodenough spent Wednesday, January 6, at the Bell Telephone Laboratories. The purpose of the trip was a mutual exchange of information with special emphasis on the production and procurement of single crystals. An outline of some of the information received follows.

1.) J. K. Galt is continuing work on picture-frame experiments. He is also conducting microwave-frequency experiments as a function of temperature. He is using single crystals supplied by Linde Air Products. The physical quality of these crystals is sufficiently good for his purposes. Although these crystals are not chemically controlled, he is satisfied with a knowledge of their content from chemical analysis. (From our point of view, if an entire set of experiments can be accomplished on one crystal to establish a self-consistent set of parameters, these crystals will be satisfactory. It is useless, however, to hope to compare parameters which have been measured on one crystal with those on another. Such a set of self-consistent measurements has been proposed for some time). Aside from the statement that the viscous damping rises sharply at low temperatures in nickel ferrite, Galt had no new experimental results to report from window-frame experiments. He encouraged us to go ahead with our planned investigation of Bloch-wall motion as a function of temperature. His ferromagnetic resonance work, on the other hand, was quite significant.

The resonance line width of energy absorption in a wave-guide cavity in which a small, spherical sample of $(NiO)_{0.75}$ $(FeO)_{0.25}(Fe_2O_3)$

was placed and subjected to a strong uniform, external magnetic field was measured as a function of the temperature. The frequency used was 2.4×10^{10} cycles/sec, and the half width was measured as ΔH, the variation of external field necessary to pass through the maximum absorption from its half-amplitude value on one side to that on the other. His results are sketched in Figure 1. The rise in ΔH with T at high

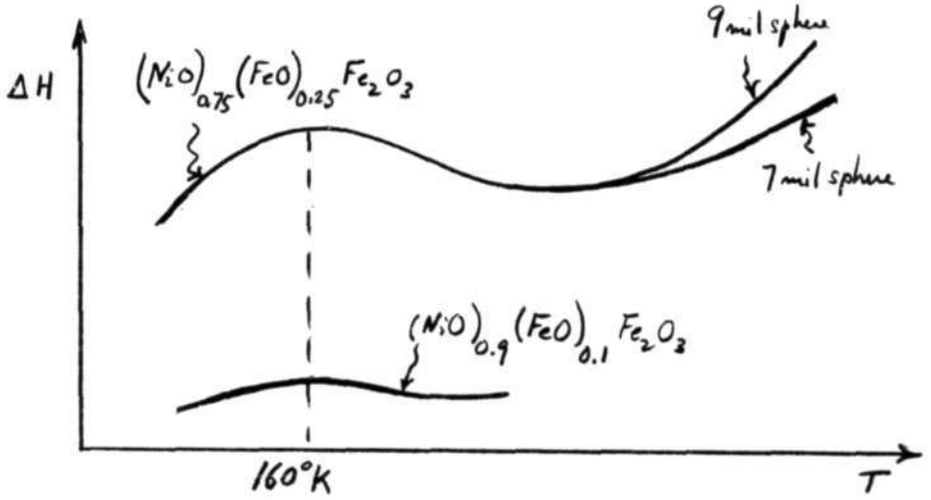

Figure 1 - Line width vs. temperature in nickel ferrite at 2.4×10^{10} cycles/sec.

temperatures is attributed to electrical conductivity, or eddy-current losses. Reduction in sphere size markedly reduced this effect. The purpose of the experiment was to investigate the physical mechanism which accounts for the relaxation frequency Λ which, until now, is introduced into the theory in a purely phenomenological way. The line width ΔH is a measure of this frequency Λ. The results of Figure 1 indicate there is a relaxation phenomenon present. Wein suggested at the College Park Conference that there might be such a relaxation due to electron transfer from an Fe^{2+} ion to an Fe^{3+} ion. Since the temperature at which the maximum occurred was the same, but the amplitude reduced, for a $(NiO)_{0.9}(FeO)_{0.1}Fe_2O_3$ sample, this explanation appears most attractive.

[It is recommended that Group 37 try some experiments along these lines. It should be realized that the activation energy for electron transfer can be obtained by obtaining the temperature at which the maximum occurs for two different frequencies. For atomic diffusion processes,

C. Zener has shown that the relaxation time τ varies with the temperature of measurement T (in °K) as

$$\tau = \tau_o e^{\mathcal{H}/RT}$$

where τ_o is a constant, R is the universal gas constant, and $\mathcal{H}$ is the heat of activation. A similar expression will hold for electron diffusion. It can be shown that the dimensionless line width ($\Delta H/H$) will reach its maximum value when

$$\tau\omega \cong 1$$

where ω is the angular frequency of the a-c field. The time of relaxation is therefore given by

$$\tau = 1/2\pi\nu. \qquad (1)$$

Since ($\Delta H/H$) is dimensionless, it is a function of the parameter ($\tau\nu$), or

$$(\Delta H/H) = A \cdot \text{fcn}\,(\nu e^{\mathcal{H}/RT}) \qquad (2)$$

where A is independent of ν but may be a function of T. However, if there is a heat of activation associated with the relaxation process concerned, the factor A can only be a slowly varying function of T. This means that the necessary condition for the existence of a unique heat of activation is that the internal friction is determined primarily by the parameter $\nu e^{\mathcal{H}/RT}$. Under such a condition, an increase in ν would shift the ($\Delta H/H$) curve to higher temperatures without changing the shape of the curve when plotted with ($\Delta H/H$) vs 1/T. If both sides of Equation 2 are differentiated with respect to 1/T and the term containing dA/d(1/T) is neglected, then

$$\frac{d(\Delta H/H)}{d(1/T)} = 0 = A\,\text{fcn}'\,(\nu e^{\mathcal{H}/RT}) \cdot e^{\mathcal{H}/RT}\left(\frac{d\nu}{d(1/T)} + \frac{\nu\mathcal{H}}{R}\right)$$

where the prime indicates the first derivative of the function with respect to its argument. Thus

$$\frac{d\nu}{d(1/T)} = -\nu\mathcal{H}/R$$

$$\mathcal{H} = -R\,\frac{d(\ln\nu)}{d(1/T)}\,.$$

If two frequencies of excitation are used, the heat of activation is given by

$$\mathcal{H} = 2.3\ R \frac{\log_{10} (\nu_2/\nu_1)}{1/T_1 - 1/T_2} . \qquad (3)$$

This may prove to be a most successful tool for determining electronic activation energies within the spinel and perovskite systems of current interest.]

Galt also explained in detail their method of preparing single-crystal window frames. a.) The crystal is mounted in wax on a flat head which can rotate 8° from the perpendicular to a cylindrical holder. The crystal is oriented by moving it manually until the proper Laue spots of an X-ray photograph overlap. b.) The crystal is then fastened to the head firmly in plaster-of-paris. The fine orientation adjustment is made in a spectrometer. c.) The crystal is brought against a sanding belt at the proper angle, and a flat surface is made. Carefully machined tools to give good right angles make this operation easy. d.) A second surface is similarly located and ground flat. For a diamond window frame these surfaces are the (110) and a perpendicular (112). e.) A series of cuts are made parallel to the (110) surface. Before each succeeding cut, however, the (110) sawed surface left on the crystal is reoriented in the spectrometer and ground true. There results a series of discs with flat surfaces ground true to a (110) and a perpendicular (112) and a sawed edge nearly parallel to the (110). f.) The sawed edge is ground true by mounting the specimen in a polishing block (cf. Figure 2).

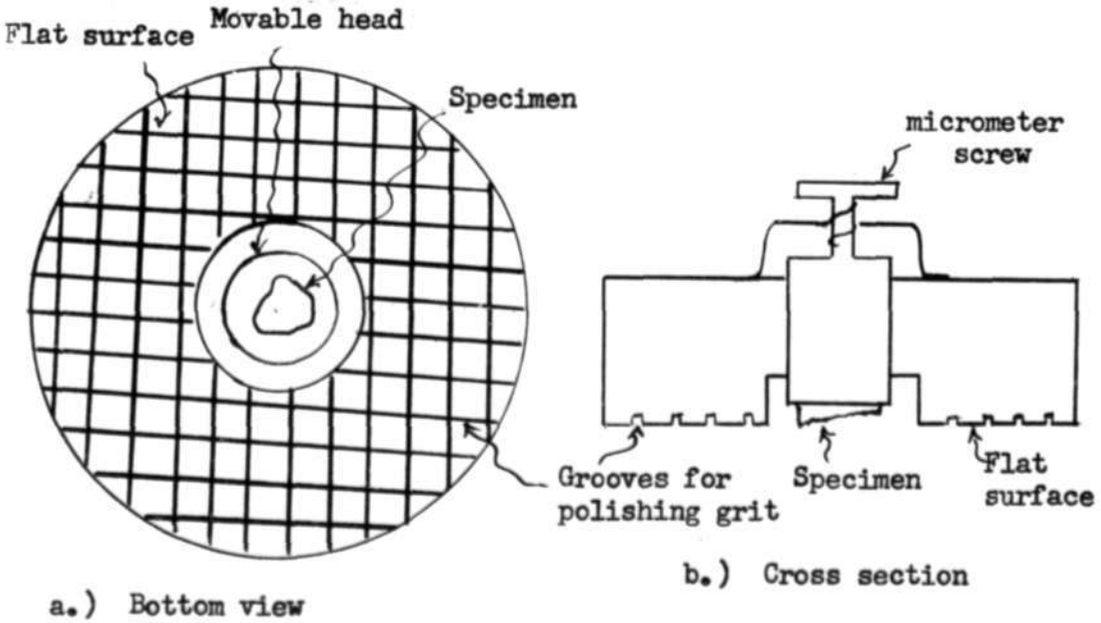

Figure 2 - Polishing Block

The true (110) face is waxed to the base of a carefully machined micrometer screw which pushes the sample gradually flush with the flat surface of the block. With careful adjustment of the screw, the entire face will gradually be ground truly parallel to the original (110) surface. The whole trick here is to obtain an accurately machined block. After grinding, the surface is polished with 1 micron grit or smooth, dry paper. g.) The polished surface is inspected under the microscope for blow holes. If such holes are visible, the crystal is discarded as imperfect. h.) Then the sample is turned around and the originally ground (110) surface is polished. i.) The sample is then boiled for 30 min. in H_2SO_4 under a compression hood. If there are chemical inhomogeneities in the sample, these will etch preferentially, and the polish will be destroyed. If this happens, the crystal is discarded as imperfect. j.) If the crystal has withstood these tests, the flat disc is now placed in a "cookie cutter." The center hole of the window frame is alone cut out by the cutter. It is feared that if, in cutting the whole frame out at once, both the inside and the outside of the frame were not struck at once by the cutter, shearing stresses across the crystal would easily crack it. The carefully machined head for cutting out the center is aligned by aligning a flat edge parallel to the ground (112) surface. k.) After the center hole is cut, another carefully machined head with shoulders the desired width of the picture frame is inserted into the center. (cf. Figure 3).

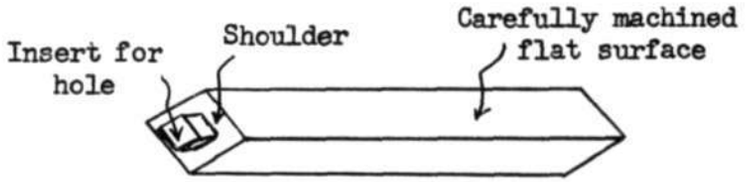

Figure 3 - Tool used for aligning and polishing outer edges of picture frame.

The edge of the disc is ground down to the shoulder of the center tool. (Again a polishing block would be advantageously used.) After the surface is ground, it is polished. The three succeeding surfaces are similarly ground and polished. l.) The specimen is again etched in boiling H_2SO_4 for 30 min. to remove the surface strains put in by the polishing process. The sample is now ready for experimentation.

2.) H. J. Williams and R. M. Bozorth reported that they have been able to influence the magnetization direction in cobalt ferrite with a magnetic anneal. The easy-magnetization direction is along the (100) direction instead of along the (111) as in other ferrites. They have cut rectangular window frames for this material and observed the domain walls with colloidal magnetite. A perpendicular magnetic field is necessary if the walls are to be distinct. All the walls they have

observed are straight whereas Galt observed wavy domain walls. Galt observed a single domain wall by first saturating the core and then reversing the magnetic field until the Cioffi flux meter showed the frame was beginning to switch. The driving field was immediately shut off so as to capture the wall midway across the specimen. The arrest of the dynamic motion resulted in a wavy line; the wall appeared to be hung up on imperfections at various points. Williams and Bozorth showed us walls which were observed in a demagnetized sample. [A more important difference, however, is probably due to the fact that Galt's walls were observed on an outside edge, whereas theirs were observed on a (110) face. The opposite end of Galt's wall was anchored on the unpolished inner surface, whereas both edges of the Williams-Bozorth walls terminated on polished surfaces. The imperfections at which Galt's walls stuck may well have been inner-surface rather than bulk defects. This suggests that it may be important to polish the inner surfaces in some way. For the measurements intended, it is important to make the dimensions of the frame in such a way that the Bloch wall will move from bottom to top (rather than from inside to outside) so that the area of the wall will remain constant during its motion.]

Bozorth also showed us the torsion equipment used for anisotropy measurements and the strain-gauge method they use for measuring magnetostriction. The strain-gauge method is relatively quick, simple, and inexpensive. It is much preferred to any other method now in use.

3.) H. J. Williams was asked how difficult he thought it would be to locate a grain in a polycrystalline sample which was oriented parallel to an axis of easy magnetization. He agreed that one should be able to locate those grains which were nearly so oriented by the "tree patterns" on the surface. Proper polishing could then be used to align these grains. It is hoped to employ this technique in this laboratory with samples of Si-Fe and 68 Permalloy. It is hoped that direct observations of the nucleation process at grain boundaries can be made.

4.) Dr. Scaff of the chemistry department has started a program to prepare single crystals of ferrite from a Borax flux. Galt has cooled a flux saturated with ferrite ions at high temperatures to obtain single crystals which were large enough to give the small spheres used in microwave resonance work. Dr. Scaff, however, is using the flux to transport ions continuously across a temperature gradient. A vertical furnace is used to provide the gradient. A seed crystal is planted at the bottom of a cylinder. Above this is the flux, and above this is a polycrystalline sample. A temperature drop of about 20°C is maintained across the flux which is kept at about 1180°C. Ions from the polycrystalline sample are dissolved in the flux and deposited on the seed crystal. This method is just being developed. A $(NiO)_x(ZnO)_{1-x}Fe_2O_3$ crystal of 1 mm^2 cross section and 4 to 5 mm length was been grown by this process. It seems to be the most promising attempt yet to obtain single crystals of ferrite with controlled chemical composition.

JBG/jk

cc: Group 63 Staff
Earl Thomas (2 Copies)
Ben Lax (4 copies)
S. Foner

Signed John B. Goodenough
John B. Goodenough

Approved DRB
David R. Brown