Division 6 - Lincoln Laboratory
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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 under-
            taken 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 relax-
            ation 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 produc-
tion and procurement of single crystals. An outline of some of the
information received follows.

        1.) J. K. Galt is continuing work on picture-frame experi-
ments. 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 varia-
tion of external field necessary to pass through the maximum absorption
from its half-amplitude value on one side to that on the other. His
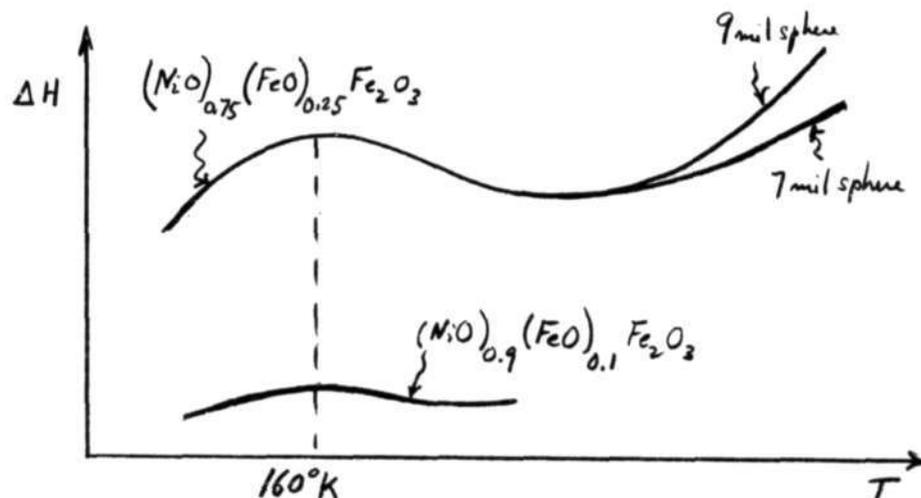results are sketched in Figure 1. The rise in ΔH with T at high

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 maxi-
mum occurs for two different frequencies. For atomic diffusion processes,

C. Zener has shown that the relaxation time τ varies with the temperature of measurement $\dot{T}$ (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

$$\tau = 1/2\pi\nu. \tag{1}$$

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

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

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

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

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

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

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

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).
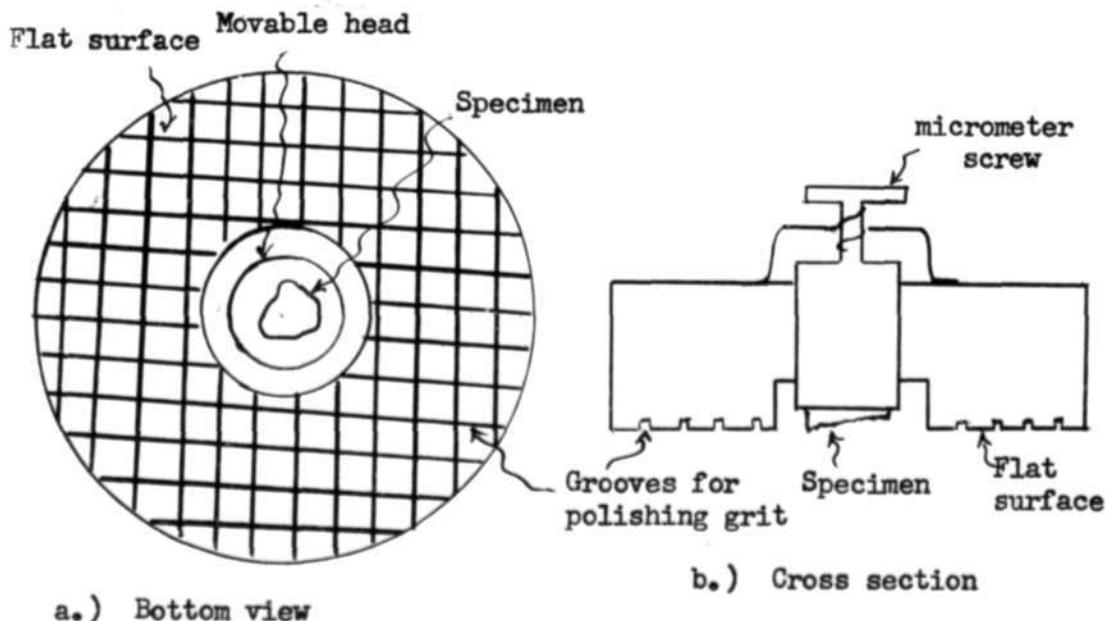

a.) Bottom view

b.) Cross section

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).
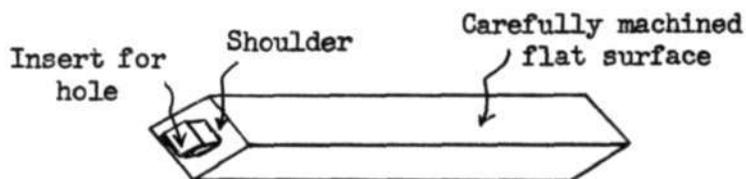

Figure 3 - Tool used for aligning and polishing outer edges of picture frame.

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