Ferromagnetic Resonance in the Single Crystals of some Ferrites.* I

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Synopsis

The ferromagnetic resonance absorptions in the single crystals of Mn-Zn ferrite were studied at the wavelength of 3.22 cm and Co-Zn ferrite at 3.22 and 1.27 cm at the temperatures from −195°C to the Curie point and the resonance phenomena in the polycrystalline specimens having the same composition were also studied.

The magnetic transition through which the first-order magnetocrystalline anisotropy constant K_1 changes its sign were found respectively, at ca. −100°C and +70°C for both ferrites and near these temperature two resonance peaks appeared on the resonance curves of polycrystalline specimens.

The half line widths were found to depend on the crystallographic directions; its temperature dependence was also observed.

g-factors and K_1 of Co-Zn ferrite were observed as functions of temperature. For Co-Zn ferrite, the temperature dependence of the line width showed a complicated behaviour at first by a rough measurement, but it was found to be monotonous by a further precise investigation.

g-value and the order of K_1 of Mn-Zn single crystal at the room temperature agreed with the results of Galt and co-workers, but the large descrepancies between our results and those of Galts' are found in the sign of K_1 and the value of the half line width at the room temperature, i. e., K_1 has a positive sign in our result, but negative in Galts', and the value of the half line widths by us is several times as large as that reported by Galt; the latter seems to be attributed to the "size effect".

I. Introduction

Ferromagnetic resonance in various ferrites have been studied in our laboratory(1-11) and many interesting results were obtained. As these experiments were carried out with the sintered polycrystalline specimens except the natural crystals of magnetite, experiments with the single crystals of these ferrites were most desirable for the study of the magnetic properties of ferrites.

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* A part of the present investigation, Phys. Rev. to appear in the Feburary 15, (1952).

(1) T. Okamura, Y. Torizuka and Y. Kojima, SCI. REP. RITU, A-Vol. 2, (1950) 663–672.

(2) T. Okamura and Y. Torizuka, SCI. REP. RITU, A-Vol. 2, (1950) 822–827.

(3) T. Okamura and Y. Torizuka, SCI. REP. RITU, A-Vol. 3, (1951) 214–218.

(4) T. Okamura, Nature, Vol. 168, (1951) 162.

(5) T. Okamura and Y. Torizuka, SCI. REP. RITU, A-Vol. 3, (1951) 219–222.

(6) T. Okamura and Y. Torizuka, Nature, June 16, Vol. 167, (1951) 986.

(7) T. Okamura and Y. Torizuka, Phys. Rev., Vol. 83, (1951) 847–848.

(8) T. Okamura and Y. Torizuka, Nature, November 17, (1951).

(9) T. Okamura, Y. Torizuka, and Y. Kojima, Phys. Rev., Vol. 84, (1951) 372.

(10) Y. Torizuka, SCI. REP. RITU, A-Vol. 3, (1951) 383.

(11) T. Okamura, Y. Kojima and Y Torizuka, SCI. REP. RITU, A-Vol. 3, (1951) 725–739.

The single crystals of nickel ferrite and manganese zinc ferrite were prepared by Galt and others,(12, 13) and the resonance phenomena were studied, especially on $NiOFe_2O_3$; many investigations have deen made by Yager and his co-workers(14) and recently by Healy(15).

We also succeeded in preparing the single crystals of manganese-zinc ferrite and cobalt-zinc ferrite by almost the same method, and the resonance phenomena of these single crystals were studied in the temperature range from −195°C to their Curie temperature at 9310 Mc; especially, the experiments were performed partly at a frequency of 23500 Mc by using the transmission type apparatus constructed recently in our institute.

In general, it is difficult to grind and obtain a spherical or disk form specimens from the single crystal, recently we succeeded to prepare the spherical specimen by means of the Bond's method,* and the resonance experiments on spherical specimens of single crystal are being planned. But the present experiments were carried out in the form of octahedra or half of octahedra, namely, the pyramid form specimens, to avoid the crystalline imperfection such as cracks or inner stresses that may grow during the grinding of crystals.

The sintered polycrystalline specimens were also used in forms of sphere, disk and pyramid, in order to obtain the value of saturation magnetization M_s and the demagnetizing factor N of single crystals.

We obtained the resonance field and the line widths as functions of the temperature for each crystallographic direction. The magnetic transition were found at the temperature of about −100°C and +70°C for Mn-Zn ferrite and Co-Zn ferrite, respectively, and intimately related with these transition, the double peak phenomena always appearing on the resonance curve were observed on polycrystalline specimens for both ferrites near the transition temperature.

The half line widths were found to depend on the crystallographic orientation and its temperature dependence was quite different for each crystal directions; these phenomena have not yet been shown in other reports.

The *g*-factor and first-order magnetocrystalline anisotropy constant K_1 of Co-Zn ferrite at various temperatures were calculated from the resononce field by using Kittel's formula.

II. Experimental Procedures

The single crystals of ferrites were prepared as follows: Mn-Zn ferrite; 6.4 gr Fe_2O_3, 1.6 gr ZnO, 2.3 gr $MnCO_3$ and 15 gr borax were ground and sufficiently mixed. The mixed powder was kept at 1320°C for five hours in a platinum crucible, and slowly cooled at a rate of 1°C/min till 1000°C, then the current to heat the

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(12) J. K. Galt, B. T. Matthias and J. P. Remeika, Phys. Rev, **79**, (1950) 391.

(13) J. K. Galt, W. A. Yager, J. P. Remeika and F. R. Merritt, Phys. Rev, **81**, (1951) 470.

(14) W. A. Yager, J. K. Galt, F. R. Merritt and E. A. Wood, Phys. Rev,. **80**, (1950) 744.

(15) D. W. Healy, Jr. Tch. Rep. No. 135 (1951). Cruft Lab. Harvard University Cambridge, Massachusetts,

* W. L. Bond, Rev. Scientific Inst, **22**, (1951) 344.

furnace was turned off and the sample was cooled to the room temperature in the furnace.

Co-Zn ferrite; 6.7 gr Fe_2O_3, 1.9 gr CoO, 1.4 gr ZnO and 12 gr borax were ground, mixed and heated at 1320°C for three hours in a platinum crucible; it was cooled at a rate of 1°C/min till 1150°C, then the sample was slowly cooled in the furnace to the room temperature.

Among from the resulting single crystals, two regular octahedral, large enough to be used in the present experiment, and mechanically strong crystals were selected. The dimension of one was 0.6 mm in the octahedral edge for Mn-Zn ferrite, and that of the other 1 mm in the edge for Co-Zn ferrite.

The Curie point of both crystals were observed by the resonance experiments at ca. 100°C and 340°C for Mn-Zn ferrite and Co-Zn ferrite, respectively; from these data, and referring to Guillaud's data(16) on the Curie temperature for various compositions of Mn-Zn and Co-Zn ferrites, the compositions of both crystals were found to be $Mn_{0.45}Zn_{0.55}Fe_2O_4$ and $Co_{0.7}Zn_{0.3}Fe_2O_4$.

The polycrystalline ferrites of the same composition as the single crystals were prepared by pressing and sintering method, and the specimens in the forms of disk, sphere and pyramid were polished out of the sintered blocks.

As the experimental method and the equipment for 3.2 cm wavelength were formerly reported,(1, 10, 17) they are neglected here.

Microwave components and an apparatus for 1.27 cm wavelength is shown in Photo. 1 and schematically in Fig. 1, respectively.

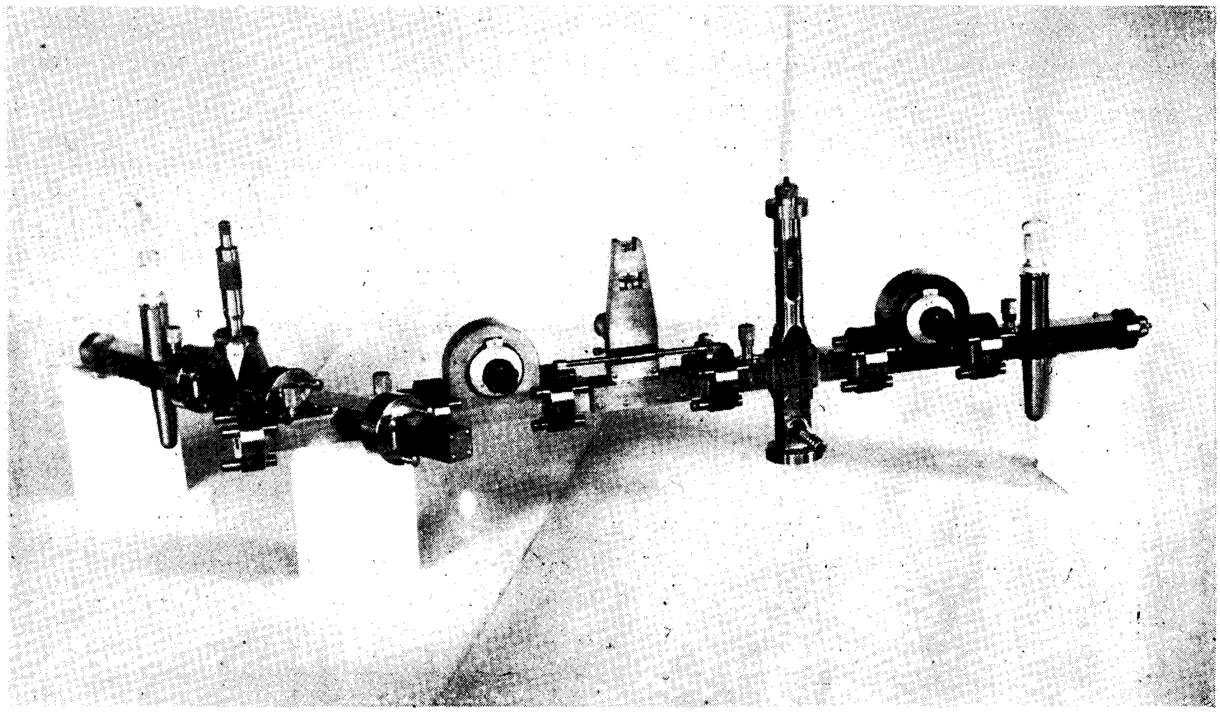

Photo. 1. Microwave components at a wave-length of 1.27 cm.

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(16) C. Guillaud and H. Crevaux, Compt. Rend, **230**, (1950) 1459.
(1) T. Okamura, Y. Torizuka and Y. Kojima, loc. cit.
(10) Y. Torizuka, loc. cit.
(17) T. Okamura, Y. Torizuka and Y. Kojima, SCI. REP. RITU, A-Vol. 3, (1951) 209.

As shown by Yager and his co-workers⁽¹⁴⁾, if the incident power kept constant during the experiment, the energy dissipated due to the ferromagnetic resonance could be observed by detecting the output power through the cavity, so by observing the galvanometer deflection versus steady field the resonance curve could be obtained.

Another galvanometer was connected to the crystal detector which would detect the power through the wavemeter, so it could be used not only to measure the microwave frequency but also to check the power and frequency stability during the experiment.

Fig. 2 is a sketch of the resonant cavity for the room and low temperature measurements at 1.27 cm wavelength. The sample was mounted on a tapered cylindrical post which was tightly fitted into a hole at the end plate of a rectangular cavity, the bakelite section of which covered with the thin silvered copper film was inserted in the middle of the cavity for thermal insulation.

Photo. 2 and 3 show an electromagnet used for 1.27 cm measurement and general view of 1.27 cm microwave spectroscope for the resonance experiment, respectively. As the magnetic flux of this Pit type magnet⁽¹⁸⁾ was completely closed, the disturbance for the galva-

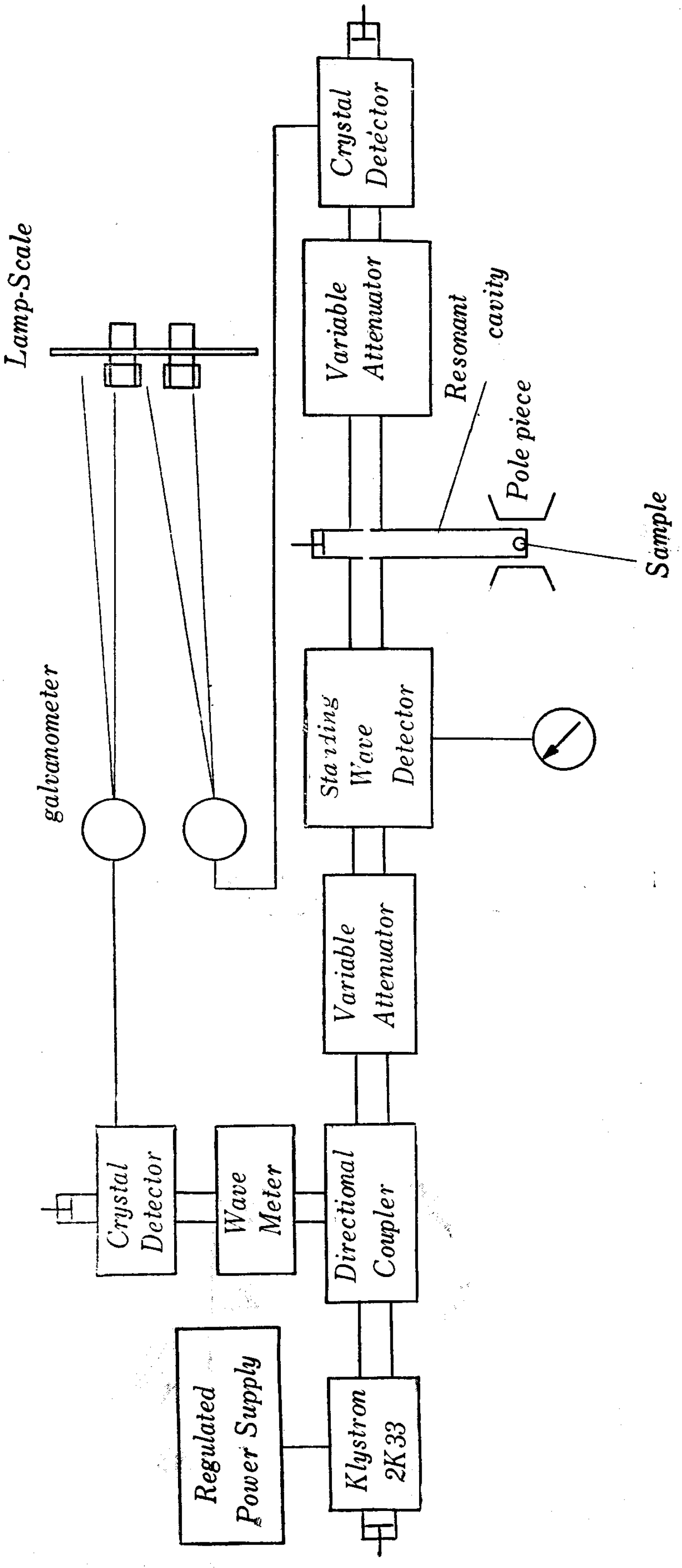

Fig. 1. Schematic diagram of experimental apparatus at a wave-length of 1.27 cm.

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(14) W. A. Yager, J. K. Galt, F. R. Merritt and E. A. Wood, loc, cit.
(18) F. Bitter and F. Everett Reed, Rev. Sci. Inst, 22, (1951) 171.

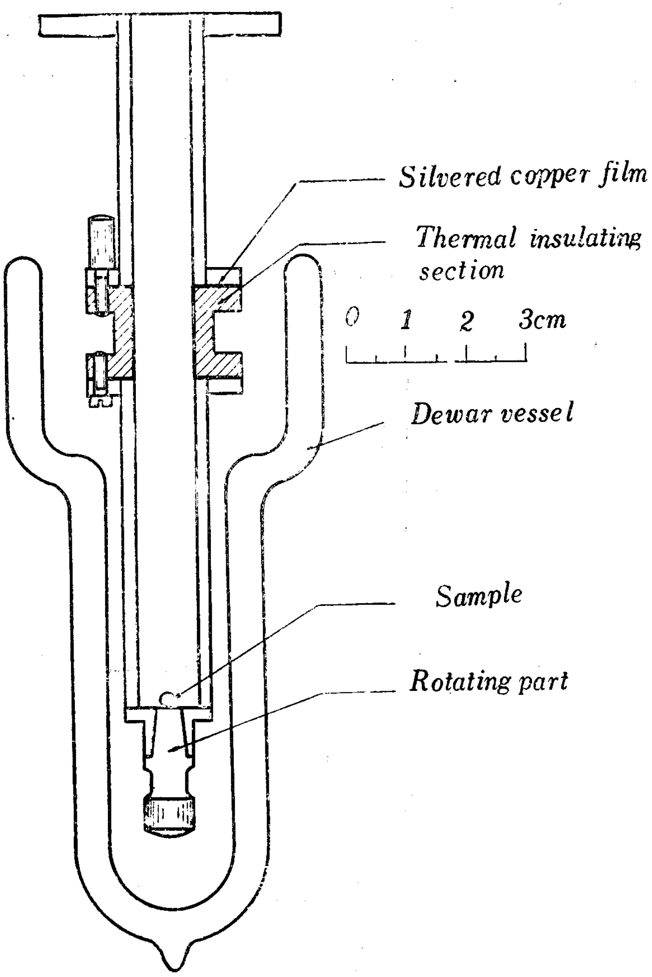

Fig. 2. Resonant cavity for low temperature at a wave-length of 1.27 cm.

nometer deflection or for the operation of a klystron due to the leakage of magnetic flux did not occur. The core of the magnet was 42 cm in diameter and 40 cm in length and the pole piece was 35 mm in diameter; the magnet could produce a magnetic field of 15,000 Oersted in a gap of 24 mm and a relation between the electric current and the magnetic field showed a complete linearity up to the field of 15,000 Oersted.

III. Results and Discussion

Mn-Zn Ferrite

The single crystal was mounted so as to make the (100) plane consistent with both direction of *r-f* magnetic field and *dc* magnetic field. Resonance phenomona were studied at a frequency of 9310 *Mc.* from liquid air temperature to *ca.* 100°C. The resonance

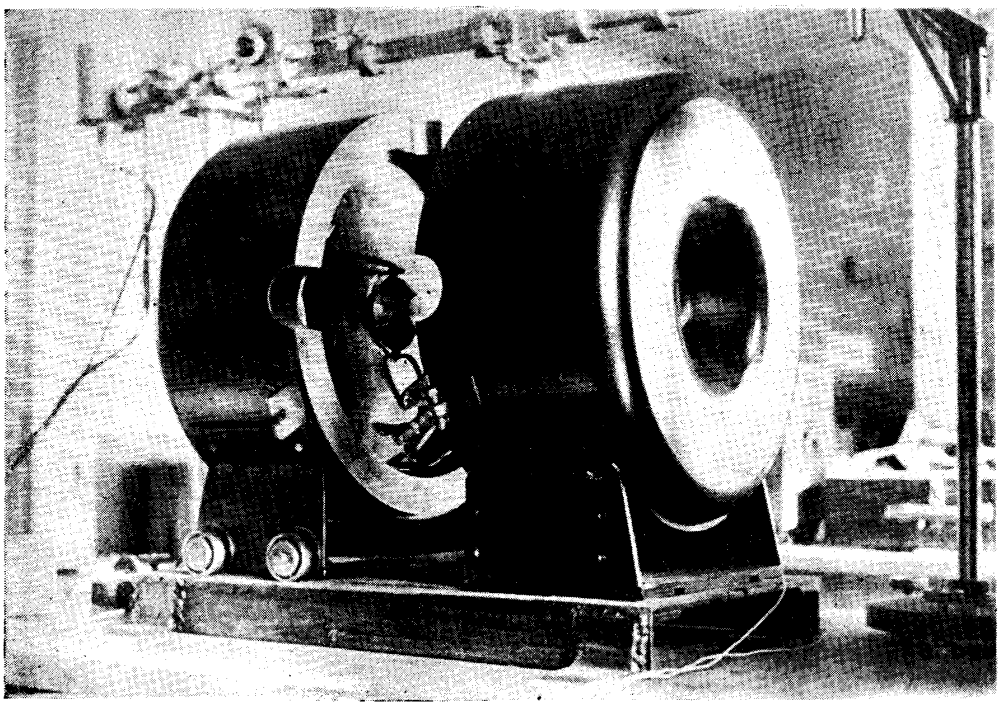

Photo. 2. Pit type electromagnet.

fields for the [110] and [100] directions parallel to the *dc* field are shown in Fig. 3 as function of temperature, both curves crossing at *ca.* −100°C; it shows that the axis of easy magnetization changes from [100] to [110] direction with the fall in temperature from the room temperature, that is, the first-order anisotropic constant K_1 changes its sign at *ca.* −100°C.

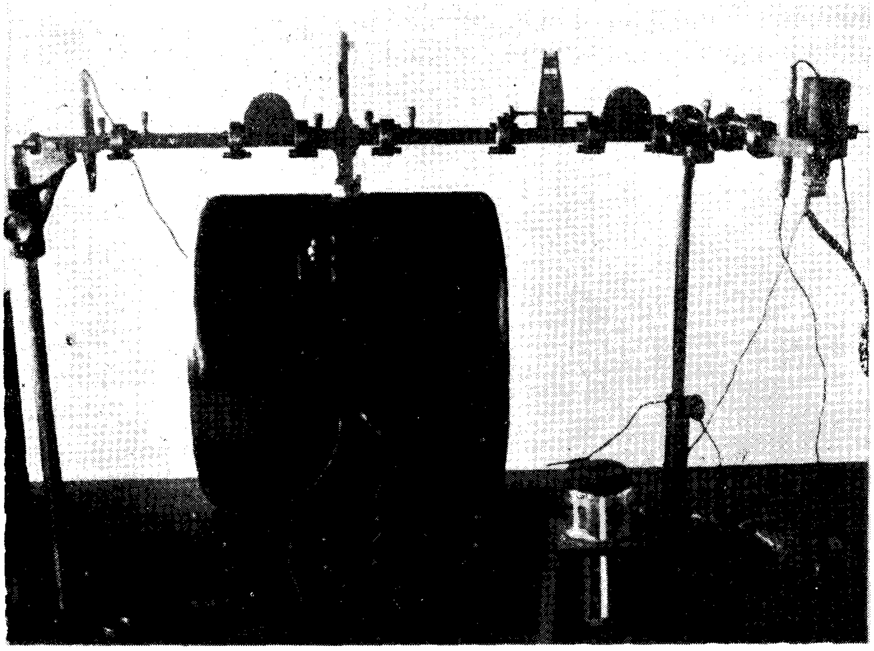

Photo. 3. General view of 1.27 cm microwave spectroscope for the resonance experiment.

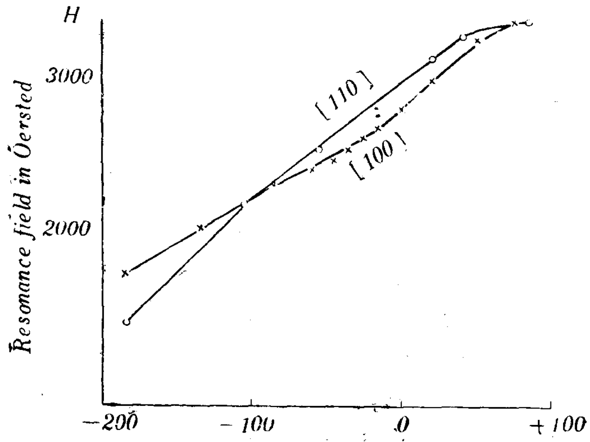

Fig. 3. Change of the resonance field with varying temperature for the single crystal of Mn–Zn ferrite:
⦿ [110] parallel to *dc* static field
× [100] parallel to *dc* static field

Fig. 4 shows the half line widths $\Delta H_{\frac{1}{2}}$ for both directions as functions of temperature. A considerable difference is found between both directions, that is, for the [110] direction, half line width $\Delta H_{\frac{1}{2}}$ always decreases continuously with rising temperature from the temperature of liquid nitrogen, on the otherhand, in the case of the [100] direction, $\Delta H_{\frac{1}{2}}$ decreases rapidly up to *ca.* −40°C and then increases rapidly and afterwards again slowly with rising temperature from −195°C. The curve shows a sharp minimum at *ca.* −40°C. The increase of $\Delta H_{\frac{1}{2}}$ at a low temperature might indicate the increase of the anisotropy energy, and the sharp minimum on the curve for the [100] direction should be explained in connection with the magnetic transition through which K_1 changed its sign.

The resonance in the polycrystalline disk specimens was also studied. The dimensions of the speimens were 2.65~4.55 mm in diameter, 0.25~0.50 mm in thickness. In the range of −95°C to −115°C in which the half line widths began to increase rapidly, two peaks were observed on the resonance curves, that is, in addition to the ordinally resonance peak, a small peak appeared at comparatively lower magnetic field.

These double peaks were quite similar to those of the polycrystal of manganese ferrite,(7, 11) nickel ferrite(4, 5) and cobalt-zinc ferrite(19), that had also been found recently by the authors. As the same phenomena was observed at the same temperature range with other specimens which had quite different dimensions from one another, it may have been a different phenomena from the cavity type resonance that was observed by Yager and the others(14) with the single crystal of nickel ferrite at the room temperature.

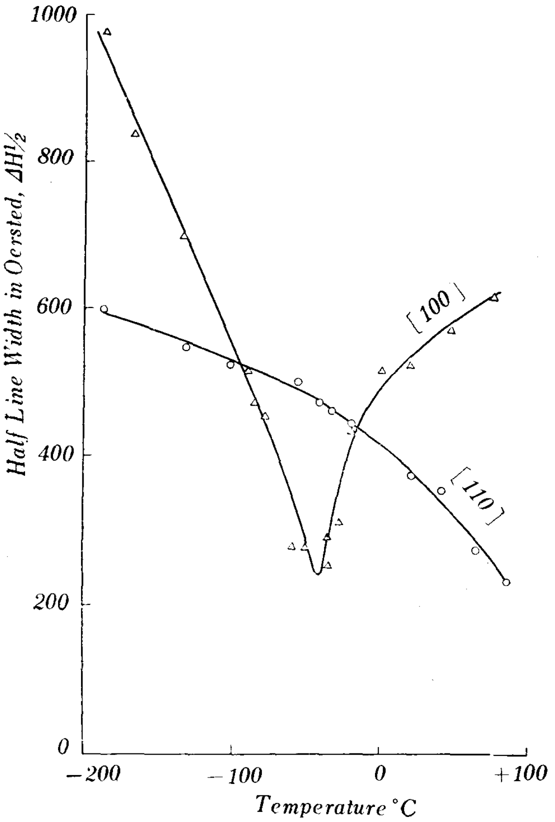

Fig. 4. Half line width versus temperature for the [110] and [100] directions in the (100) plane of Mn–Zn single crystal at a frequency of 9310 Mc.
○ [110] parallel to *dc* static field
△ [100] parallel to *dc* static field

The process of growth and disappearence of the double peaks are shown in Fig. 5. In the figure, the main resonance peak is neglected and only a part of the resonance curve on which a small peak appeared is shown. The resonance field of the small peak was about 300 Oersted at −115°C and moved towards the lower magnetic field with rising temperature up to about 200 Oersted at −95°C.

The accurate values of the *g*-factor and K_1 were not calculated, as the demagnetizing factor of the crystal was not known, but with roughly assumed values of demagnetizing factor and saturation magnetization, *g* value and the order of K_1 at the room temperature agreed with the results of Galt and others.(13) The large descrepancies between our results* and those of Galts' are found in the sign of K_1 and the amount of half line width at the room temperature, i. e., K_1 has a positive sign in our result, but negative in Galts', and the value of the half line widths

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(7) T. Okamura and Y. Torizuka, loc. cit.
(11) T.Okamura, loc. cit.
(4) T. Okamura, loc. cit.
(5) T. Okamura and Y. Torizuka, loc. cit.
(19) T. Okamura and Y. Kojima, Phys. Rev, to appear in the Feburary 15, (1952).
(14) W. A. Yager, J. K. Galt, F. R. Merritt and E. A. Wood, loc. cit.
(13) J. K. Galt, W. A. Yager, J. P. Remeika, and F. R. Merritt, loc. cit.; $K_1 = -3800$ ergs/cc, $g = 1.997$.
* According to our results, the value of K_1 and g was found to be +6500 ergs/cc and 2.00, respectively at room temperature.

observed by us is several times as large as that reported by Galt. The latter descrepancy might have been caused by the "size effect" namely the difference between the dimensions of our specimen and Galts', but the reason for the former difference is not known.

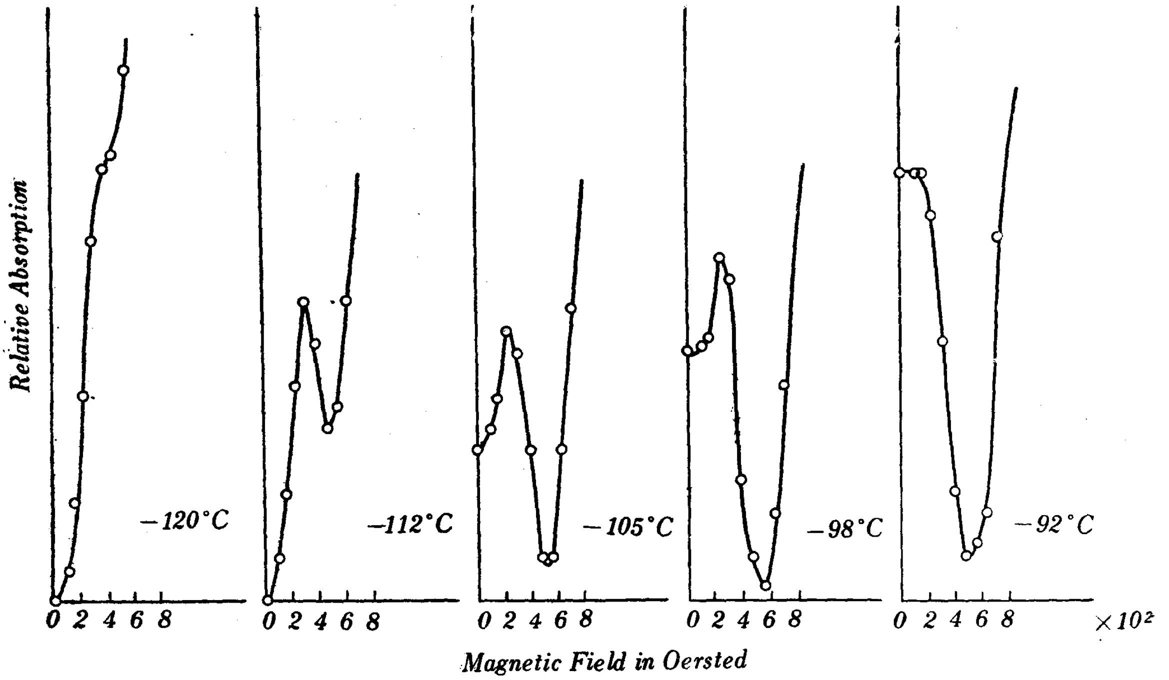

Fig. 5. Resonance curves at various temperatures in Mn–Zn ferrite showing the growth and disappearence of second peak.

The experiment on the polished crystals that have the suitable forms to know their demagnetizing factors, and the investigation at a higher frequency are being planned.

Co-Zn Ferrite

At 3.22 cm wavelength:

The single crystal was cut off to two pyramid forms at the (100) plane, one of which was mounted at the bottom of the cavity so as to make the dc applied field should always be in the (100) plane.

The resonance phenomena were studied from the room temperature to the Curie temperature for both cases in which the directions of the [110] and [100] were parallel to the static field. Fig. 6 shows the resonance fields and the half line widths for both directions as functions of temperature at 9310 Mc; the curves for resonance fields crossed at ca. +68°C, i. e, the [100] direction is the direction of easy magnetization from the room temperature to 68°C, but above 68°C to the Curie temperature, the direction of easy magnetization lies along the [110] direction, and the difference between the resonance field for both directions is especially larger at the room temperature as compared with other ferrites, because of the large anisotropic energy in the cobalt-zinc ferrite.

The double peaks were also observed on the resonance curve of polycrystalline specimen in the temperature range from 70° to 100°. It might be related to the change of the sign in K_1 as in the case of Mn-Zn ferrite.

At 1.27 cm wavelength:

The same crystal as described above was used for the measurement at 1,27 cm wavelength. The experiments were carried out in the range from the room temperature to the temperature of liquid nitrogen, but the resonance absorption was not detected below *ca.* −100°C for the [110] direction and *ca.* −60°C for the [100] direction.

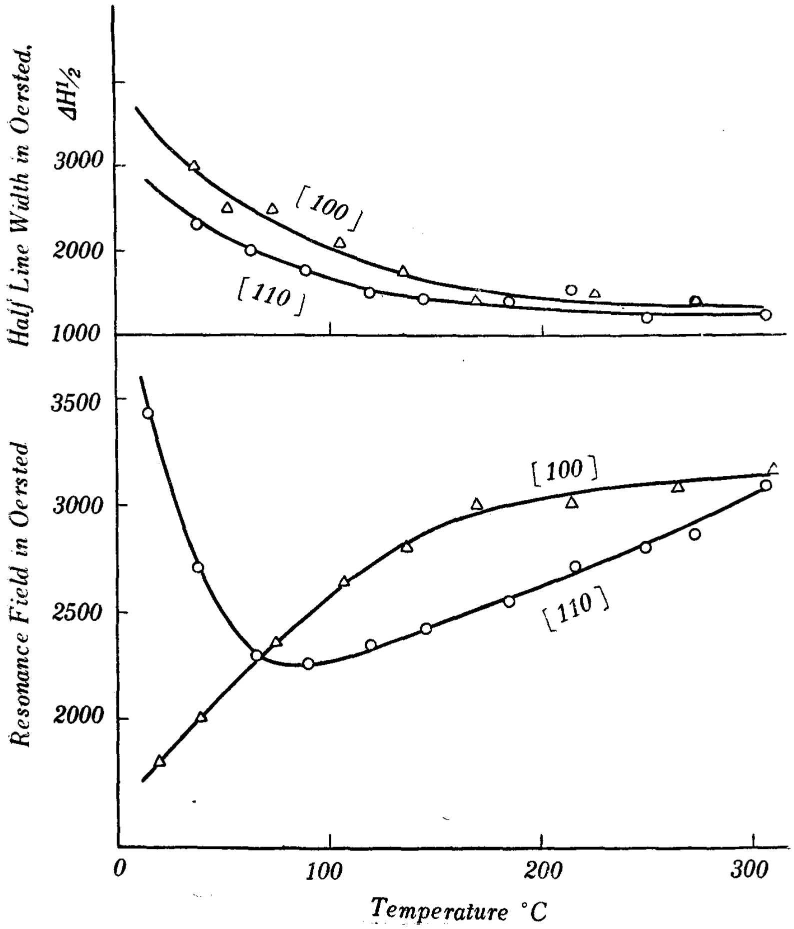

Fig. 6. Resonance field and half line width at various temperatures in the single crystal of Co-Zn ferrite at a frequency of 9310 *Mc* for the [110] and [100] directions in the (100) plane.
○ [110] parallel to *dc* static field
△ [100] parallel to *dc* static field

The typical resonance curves for both directions at the room temperature are shown in Fig. 7. The energy losses at lower magnetic field for the [110] direction were smaller than those at zero field; these phenomena were observed only for the direction of hard magnetization parallel to the *dc* magnetic field.

Fig. 8 shows the resonance field, relative absorption and the half line widths as functions of crystal orientation at the room temperature, all of them showed quite a periodic dependence on the angle between the crystal axis and *dc* magnetic field.

The resonance field for the [110] and [100] directions were also observed as functions of temperature as shown in Fig. 9.

The disappearence of the resonance phenomenon that occurred at −90°C in $Co_{0.8}Zn_{0.2}Fe_2O_4$ and at −40°C in $Co_{0.6}Zn_{0.4}Fe_2O_4$ as shown in our previous report(10) was also found on the single crystal; in the experiment that is, the resonance could not be observed below −100°C for the [110] direction and below −60°C for the [100] direction. It might be attributed to the large anisotropic energy at low temperature. The behaviour of the curves for both directions in Fig. 10 gives a sufficient explanation for the shape of the curves for resonance field versus temperature in polycrystalline specimens.

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(10) Y. Torizuka, loc. cit.

Calculation of g and K_1 of Co-Zn Ferrite

As Kittel has shown, the g-value and K_1 could be calculated from the results of

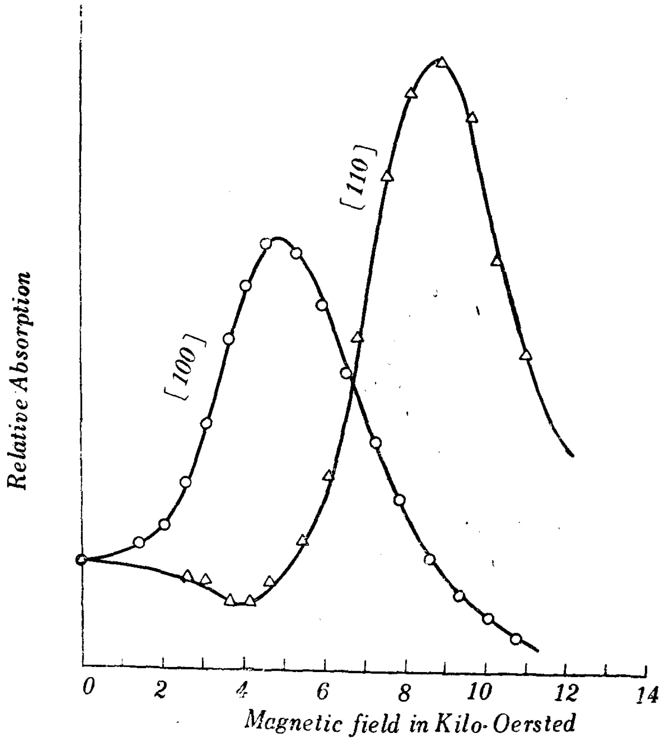

Fig. 7. Typical absorption curves for the [110] and [100] direction in the (100) plane of Co–Zn single crystal at a wave-length of 1.27 cm.

○ [100] parallel to *dc* static field

△ [110] parallel to *dc* static field

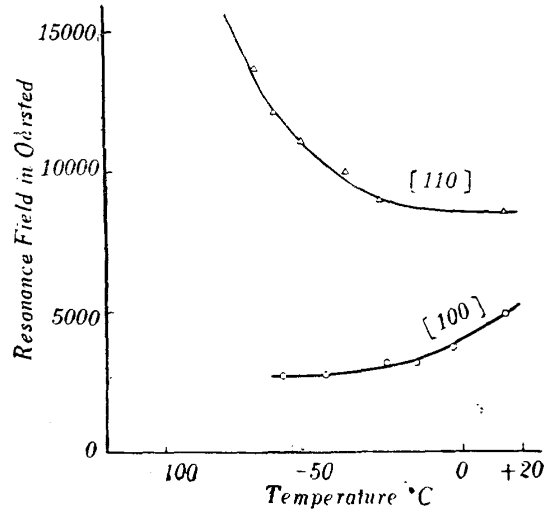

Fig. 9. Resonance field versus temperature for the [110] and [100] directions in the (100) plane of Co–Zn single crystal at a wave-length of 1.27 cm.

○ [100] parallel to *dc* static field

△ [110] parallel to *dc* static field

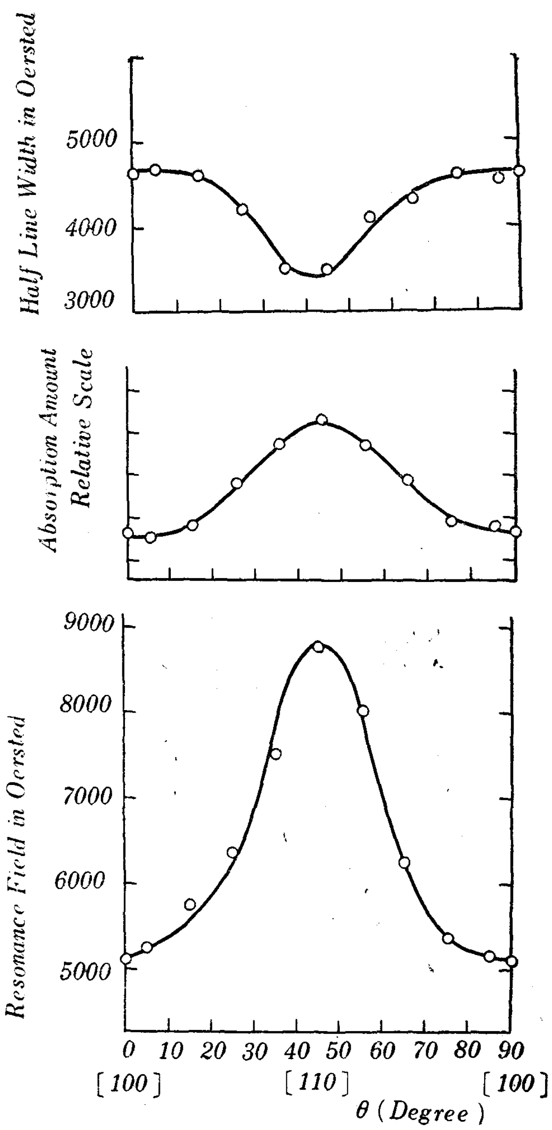

Fig. 8. Resonance field, relative absorption amount and half line width as functions of crystal orientation in the single crystal of Co–Zn ferrite at a wave-length of 1.27 cm, and at the room temperature in the (100) plane.

resonance experiment on single crystals if the values of demagnetizing factor and saturation magnetization are known. To obtain these values, the resonance experiment on the polycrystalline specimens in the forms of sphere, disk and pyramid were made in the range from the room temperature to the Curie temperature at 9310 Mc. The resonance conditions for these specimens are given as follows: for spherical specimen

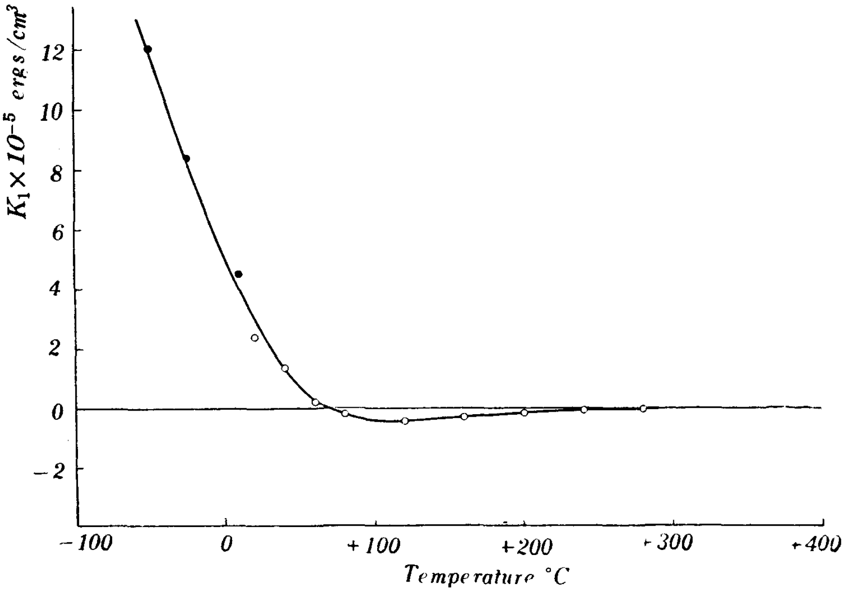

Fig. 10. K_1 as a function of temperature; cobalt-zinc ferrite.
● from the experimental result at a wave-length of 1.27 cm
○ from the experimental result at a wave-length of 3.22 cm

$$\omega=\gamma H$$

and for disk and pyramid form specimen

$$\omega=\gamma\{[H+(N_y-N_z)M][H+(N_x-N_z)M]\}^{1/2}.$$

The demagnetizing factor of disk specimen can be calculated from its dimension as shown by Osborne,(20) so the resonance fields on spherical and disk specimens will give the value of saturation magnetization M, and the resonance field on the polycrystalline pyramid form specimen will give the demagnetizng factor of a pyramid of single crystal.

The resonance formula for the (100) plane on the single crystal is

$$\omega=\gamma\{[H+(N_y+N_y^e-N_z)M][H+(N_x+N_x^e-N_z)M]\}^{1/2},$$

$$\text{where } N_x^e=2K_1/M_z^2 \cos 4\theta$$

$$N_y^e=(3/2+1/2 \cos 4\theta)K_1/M_z^2.$$

Substituting the value of the demagnetizing factors for a pyramid and M in the above formula, using the observed resonance field H at $\theta=0°$ and 45°, respectively, K_1 and g at various temperature were calculated.

Thus, demagnetizing factor N and saturation magnetization M at each temperature were calculated from the resonance fields of polycrystalline specimens, and substituting these values in Kittel's resonance formula, K_1 and g of the single crystal were determined for each temperatures as shown in Table 1 at forth and

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(20) J. A. Osborne, Phys. Rev. 67, (1945) 351.

the last column, respectively; the changes of K_1 with varying temperature are graphically shown in Fig. 10. The g_p-factor and Ms obtained by using the spherical and disk form polycrystalline specimens are also shown in the table; g-values satisfactorily coincide with one another, but some descrepancies are found near the room temperature. They seemed to come from the error in determining the g_p-factor which would be caused by the large anisotropic energy and partly by the "size effect" near the room temperature.

Table 1.

g-factor and K_1 of cobalt-zinc ferrite at various temperatures.
g_p : obtained from the experiment on a polycrystalline specimen.
g : obtained from the experiment on a single crystal.

Temp. °C	g_p	Ms. gauss	$K_1 \times 10^{-5}$ ergs/cm^3	g
−50	—	560*	12.03	1.90
−25	—	545*	8.41	1.90
10	—	500*	4.51	1.91
20	2.07	503	2.36	1.91
40	2.10	450	1.34	1.92
60	2.11	381	0.16	1.96
80	2.12	338	−0.21	2.06
120	2.15	269	−0.41	2.12
160	2.16	203	−0.34	2.12
200	2.17	134	−0.21	2.17
240	2.18	61	−0.07	2.16
280	2.19	8	−0.01	2.15

Then, the experiments below the room temperature were especially undertaken at a wave-length of 1.27 cm, for which K_1 were determined by using Ms^* assumed from Guilland's data.(16) Thus K_1 and g-value of cobalt-zinc ferrite over a range of −50°C to the Curie temperature were satisfactorily determined; the value of g is found to be 1.90 at −50°C and 2.15 near the Curie temperature.

The value of K_1 of cobalt-zinc ferrite is considerably larger than the other ferrites, that is at room temperature several times as large as that of nickel ferrite and several score times as large as that of manganese-zinc ferrite.

IV. Summary

The results of the present experimemt are summarized as follows:

1. K_1 and g-value of cobalt-zinc ferrite over a range of −50°C to the Curie temperature were determined satisfactorily.
2. Cobalt-zinc ferrite and manganese-zinc ferrite were found to have the transition point at +70°C and *ca.* −100°C, respectively, at which K_1 would change its sign.
3. The double peaks were observed always in the polycrystalline specimens in the temperature range of about 20~30°C near the transition point.
4. The half line width depends largely on the crystal orientation and the temperature dependence was quite different for each crystal direction.
5. g-value and the order of K_1 of Mn-Zn single crystal at the room tamperature agreed with the results of Galt and co-workers, but the large descrepancies between our results and those of Galts' are found in the sigh of K_1 and the

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(16) C. Guillaud and H. Crevaux, loc. cit.

value of the half line width at the room temperature, *i, e,* K_1 has a positive sign in our result, but negative in Galts', and the value of the half line widths by us is several times as large as that reported by Galt.

6. The energy dissipated by the resonance also depends upon the crystal orientation periodically.

The single crystals of other ferrites such as copper ferrite have been prepared by us and the resonance experiments are being planned.

In conclusion the authors express thanks to Mr. S. Sinozuka, K. Inagaki and others of our Institute for constructing the precise measuring apparatus and slso to Miss Koko Tskahasi for her earnest assistance during the course of the work.

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