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Anomalous Resonance Absorption in Cobalt Ferrite and Co-Zn Binary Ferrites

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Synopsis

Microwave resonance absorption in Co-ferrite and Co-Zn binary ferrites at 3.22 cm wave-length were observed at high temperature and from room temperature to -195°C, respectively. Resonance absorption in Co-ferrite could not be detected at the temperature below 40° C, because of a large anisotropic energy in Co-ferrite. Such phenomena had not been found in other ferrites, so the resonance experiment was undertaken at high temperatures ranging from 40° to Curie point.

In Co-Zn binary ferrites, the absorption disappeared below the temperature of -90°C and -140°C in $4CoO\cdot ZnO\cdot 5Fe_2O_3$ and $3CoO\cdot 2ZnO\cdot 5Fe_2O_3$, respectively, but the absorption in $CoO\cdot 4ZnO\cdot 5Fe_2O_3$ could be observed down to -186°C. The resonance fields corresponding to the maximum absorption were observed as a function of the temperature.

In the case of Co-ferrite, the resonance field corresponding to the maximum absorption gradually decreased with increasing temperature up to ca. 250° C and then rapidly increased to the Curie point.

On the other hand, the absorption amount at first increased linearly with increasing temperature, afterwards passed through a maximum and then decreased rapidly up to the Curie point.

The half line widths and *g*-factor were also obtained as functions of temperature up to the Curie point; the half line width monotonously decreased with increase of temperature up to the Curie temperature, at which the absorption disappeared.

The *g*-factor increased with the rise of temperature, afterwards passed through broad maximum and then decreased rapidly to the Curie point; the value of the reonance field just about at the Curie point was found to be within 3300 ± 100 Oe, for which *g*-factor was determined to be 2.02 ± 0.06 by using the paramagnetic resonance condition.

I. Introduction

The magnetic transformation in magnetite Fe_3O_4 at low temperature is a well known phenomenon and many intersting experiments(1) have been performed in connection with its transformation. Guillaud(2) and Crevaux reported that cobalt ferrite $CoOFe_2O_3$ also had a transition point at about -180°C.

Recently we have found that nickel ferrite $NiOFe_2O_3$(3) and manganese ferrite $MnOFe_2O_3$(4) also have the transition point at a low temperature.

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(1) T. Okamura, Sci. Rep. Tohoku University, 21, 231 (1932). L. R. Bickford, Phys. Rev., 78, 449 (1950).
C. A. Domenicalli, Phy. Rev., 78, 458 (1950).
T. Okamura and Y. Torizuka, Sci. Rep. RITU. A 3, 214 (1951).

(2) C. Guillaud and H. Crevaux, Compt. Rend., 236, 1256 (1950).

(3) T. Okamura, Nature, V 168 July, (1951).

(4) T. Okamura and J. Simoizaka, Phys. Rev., 23, 664 (1951).

We experimented on microwave resonace absorption in magnetite(5), nickel ferrite(6) and manganese ferrite(7) at low temperatures, and many interesting results were obtained in connection with their magnetic properties.

We also intended to observe the resonance in cobalt ferrite at low temperature especially near its transition point, but we could not observe the resonance in cobalt ferrite below room temperature at 3.2 cm wave-length. Since such phenomenon had never been observed in other ferrites, it should have been due to the anomolously large crystalline anisotropy in this ferrite as compared to other ferrites. Yager and his Co-workers(8) also reported that the extreme broadness of the absorption line in this ferrite was suggestive of the large anisotropic energy. We are now planning an experiment of cobalt ferrite at shorter wave length to avoid the effect of this extremely large anisotropy.

II. Resonance experiment on cobalt-zinc ferrites at low temperature

To observe the resonance in cobalt ferrite, zinc ferrite was added to cobalt ferrite in order to decrease the magnetic crystalline anisotropy in cobalt ferrite, and the binary ferrites of Co-Zn system were prepared for the present experiment so that the resonance could be detected even at low temperature.

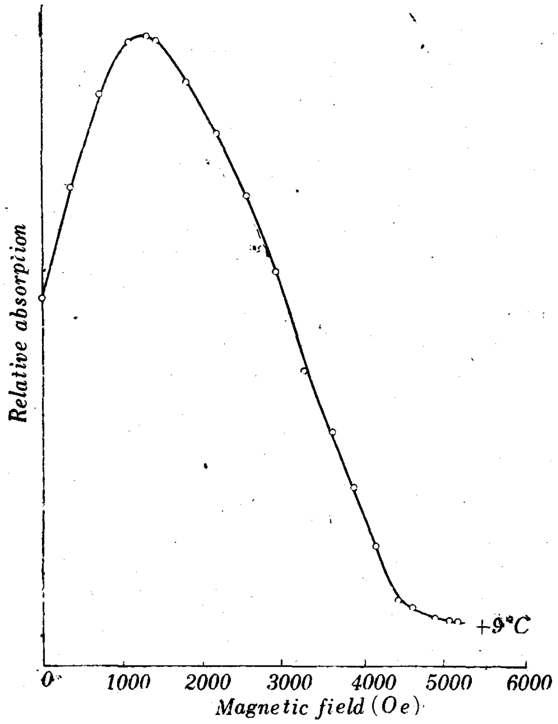

Fig. 1a. The curve of resonance absorption versus dc magnetic field in 4Co-OZnO5Fe_2O_3 at room temperature.

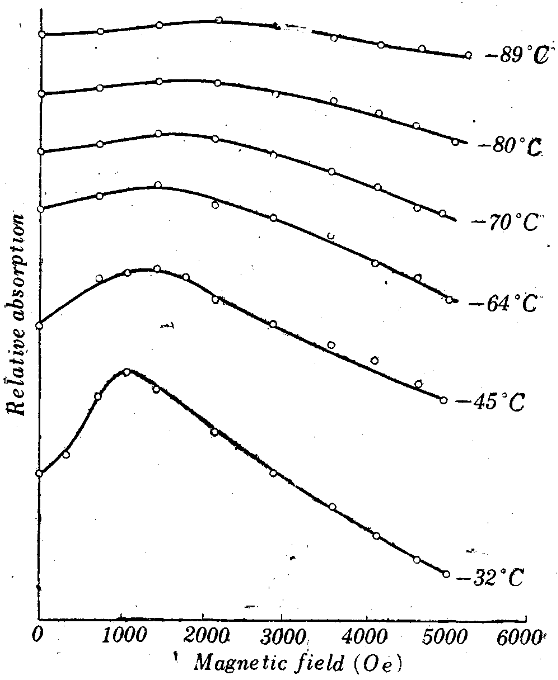

Fig. 1b. The curve of resonance absorption versus dc magnetic field in 4Co-OZnO5Fe_2O_3 at various low temperatures.

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(5) T. Okamura and Y. Torizuka, Sci. Rep. RITU. A 3, 215 (1951).

(6) T. Okamura and Y. Torizuka, Sci. Rep. RITU. A 3, 223 (1951).

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

(8) W. A. Yager, F. R. Merritt and C. Guillaud ; Phys. Rev., 81, 477 (1951).

The samples were sintered at 1300° C for 3 hours and the disk and spherical-specimens were prepared for the present experiments. The disk was 0.2 ~ 0.3 mm in thickness and the 3~5 mm in diameter, while the dimension of spherical specimens was all 2 mm in diameter.

The experimental method and procedure(9)(10) were the same as described previously, so are omitted here.

First, the results of experiment of the specimen in composition of $4CoOZnO5Fe_2O_3$ will be shown, namely, the Co-Zn ferrite having a composition of 80% cobalt ferrite and 20% zinc ferrite in mol ratio.

Figs. 1a and 1b show some resonance curves of $4CoOZnO5Fe_2O_3$ for disk specimen at various low temperatures, each curves representing the relative absorption versus dc static magnetic field strength at 9311 MC, at room temperature, an absorption maximum was found at about 1400 Oe, and as the temperature decreased, the intensity of absorption gradually decreased and the position of absorption maximum again shifted to about 1300 Oe at ca. −20° C, then removed towards the higher magnetic field at lower temperature. A broad resonance occurred at about 2500 Oe at ca. −90° C, and further below this temperature, the resonance could not be observed. The broadness of resonance line at low tem-

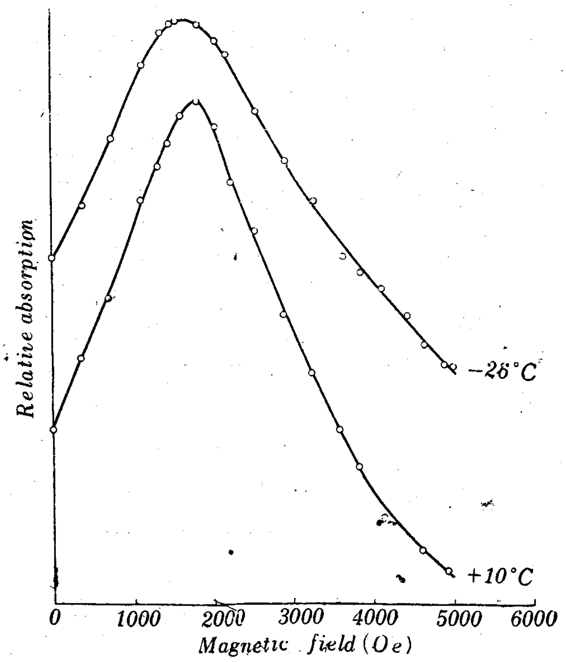

Fig. 2a. The curve of resonance absorption versus dc magnetic field in $3CoO2ZnO5Fe_2O_3$ at various low temperatures.

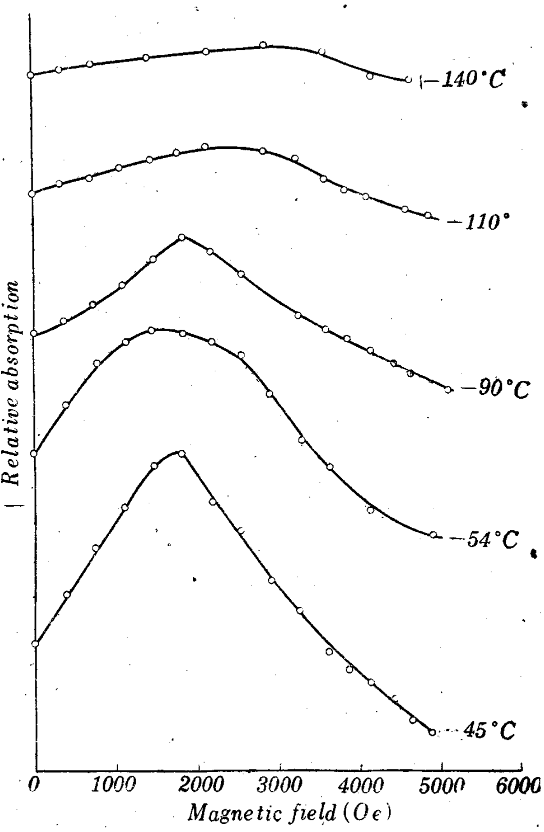

Fig. 2b. The curve of resonance absorption versus dc magnetic field in $3CoO2ZnO5Fe_2O_3$ at various low temperatures.

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(9) T. Okamura, Y. Torizuka and Y. Kojima, Sci. Rep. RITU. A 2, 663 (1950).

(10) T. Okamura and Y. Torizuka, Phys. Rev., 82, 285 (1951); Sci. Rep. RITU. A 3, 209 (1951).

perature must have been due to an unresolved double line corresponding to two different crystal forms, one being a cubic and the other a tetragonal one; that is, a mixed state of these crystal forms appeared in a process of transition of cobalt ferrite at low temperature.

The same experiments were performed on the sample of $3CoO2ZnO5Fe_2O_3$. Figs. 2a and 2b show resonance curves at various temperatures for the disk formed specimen; the same tendency as in the case of $4CoOZnO5Fe_2O_3$ was found, i. e., the resonance field first shifted towards the lower magnetic field with decreasing temperature ranging from room temperature down to ca. $-50°$ C, and below this temperature, it tended continuously toward higher magnetic field and a broad resonance was found at about 2500 Oe in the vicinity of $-110°$ C, and below $-140°$ C, the resonance gradually disappeared.

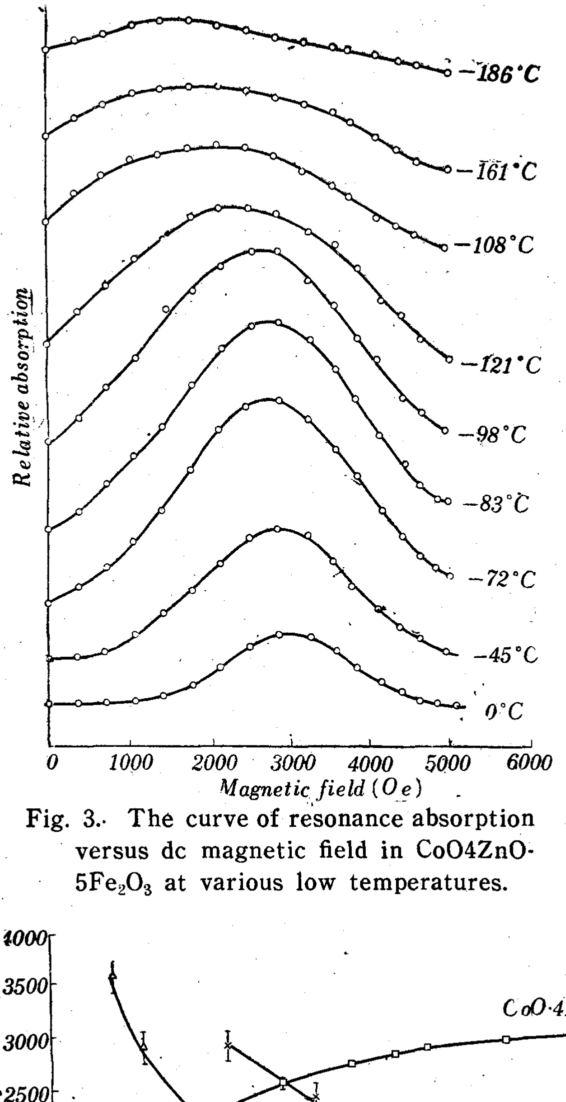

Fig. 3. The curve of resonance absorption versus dc magnetic field in $CoO4ZnO\cdot 5Fe_2O_3$ at various low temperatures.

$CoO4ZnO5Fe_2O_3$ shows the resonance similar to that of zinc ferrite, which shows a slightly ferromagnetic property; resonance curves are shown in Fig. 3; at room temperature the resonance occurred at about 3000 Oe, and as temperature decreased, the resonance field became to take gradually lowere value of 1600 Oe at $-186°$ C. On the other hand, the intensity of absorption became stronger near $-100°$ C; with further decreasing temperature, its amount gradually decreased.

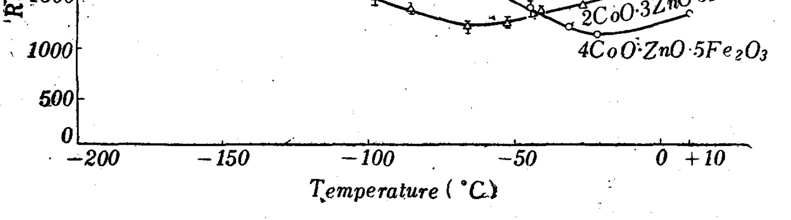

Fig. 4. Change of resonance field at the absorption maximum for Co-Zn ferrites with varying temperature; disk specimen.

The resonance fields for above-mentioned Co-Zn ferrites corresponding to the maximum absorption are graphically shown in Fig. 4 as the fuctions of temperature. The ordinate represents the resonance field in Oersted and the abscissa the temperature in Centigrades; the curves for $4CoOZnO5Fe_2O_3$, $3CoO2ZnO5Fe_2O_3$ and $2CoO3ZnO5Fe_2O_3$ have their minimum below room temperature; that is, the amount of resonance field first gradually decreases with decreasing temperature and afterwards tends to increase slowly. These tendencies should be explained as follows: as the saturation magnetizations of these specimens increase with decreasing temperature, the resonances are expected to occur at lower field as the result of Kittel's formula which assumes the frequency and g-value to be constant, while the increase in anisotropic energy in the specimen at low temperature tends to increase the resonance field, so the increase of resonance field that is found at low temperatures seems to be due to the increasing anisotropic energy in the specimens. Thus, the minimums found on the curve of the resonance field versus temperature are satisfactorily explained by the combined effect of increase of magnetization and anisotropic energy, accompanied by the change of temperature.

The resonance field of $CoO4ZnO5Fe_2O_3$ decraesed monotonously with decreasing temperature up to −186° C as shown in the same figure; the specimen containing high zinc ferrite had the Curie point at a comparatively low temperature, namely, near room temperature, and the intensity magnetization increased rapidly with decreasing temperature while the anisotropic energy was smaller than that of other Co-Zn ferrites, containing low zinc ferrite. Therefore, it seems that the curve for $CoO4ZnO5Fe_2O_3$ did not show any minimum which was found in the case of low zinc ferrites.

For each spherical specimen of various compositions, the resonance experiments similar to the case of disk specimens were carried out. The results show the same tendency as found for the disk specimens, and only two typical results are shown in Fig. 5, which gives the change of resonance field at the absorption maximum with varying temperature.

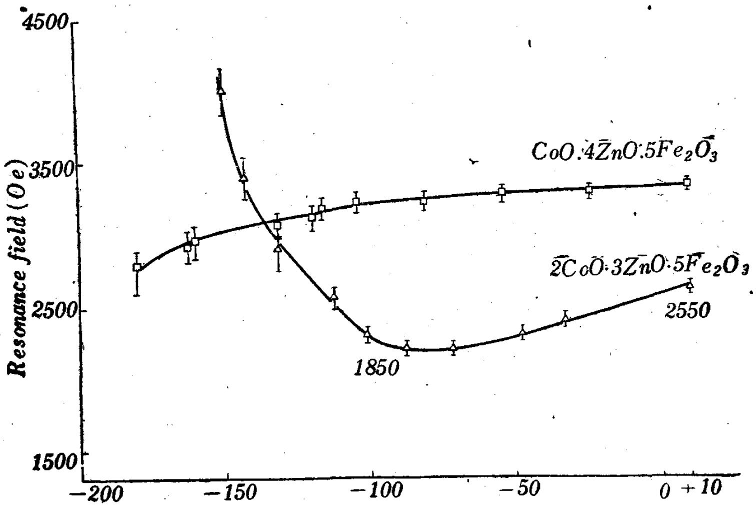

Fig. 5. Change of resonance field at the absorption maximum for Co–Zn ferrites with varying temperature; sphere specimen.

Generally speaking, in the case of Co-Zn ferrites, the temperatures below which the resonance absorptions cannot be detected, decrease with the increase of the content of zinc ferrite; that is an addition of zinc ferrite to cobalt ferrite causes the decrease of anisotropic energy as mentioned above. For the same reason, if the cobalt ferrite is heated at a high temperature, the resonance should become observable owing to the decrease in anisotropic energy.

III Resonance experiment of Cobalt ferrite at high temperature

Next, we performed a resonance experiment on a disk-formed polycrystalline specimen of cobalt ferrite, 3 mm in diameter and 0.22 mm in thickness, at 3.2 cm wave length and at high temperature. The specimen was fixed to the bottom of the resonant cavity with a drop of a special dental cement and the upper portion of the resonant cavity was protected by a double walled brass tube containing circulating water, and the lower part of the cavity was heated by an electric furnace, being wrapped with nickrom-wire 3.5 cm in length.

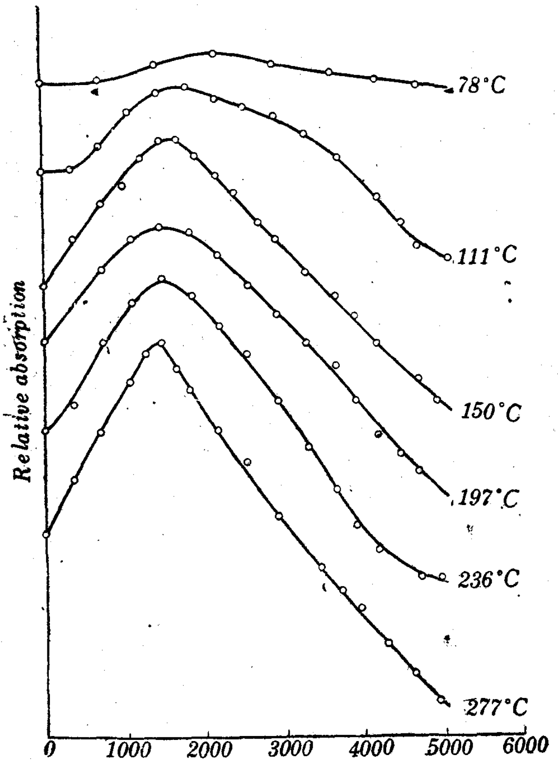

Fig. 6a. The curve of resonance absorption versus dc magnetic field in Co-OFe$_2$O$_3$ at various high temperatures.

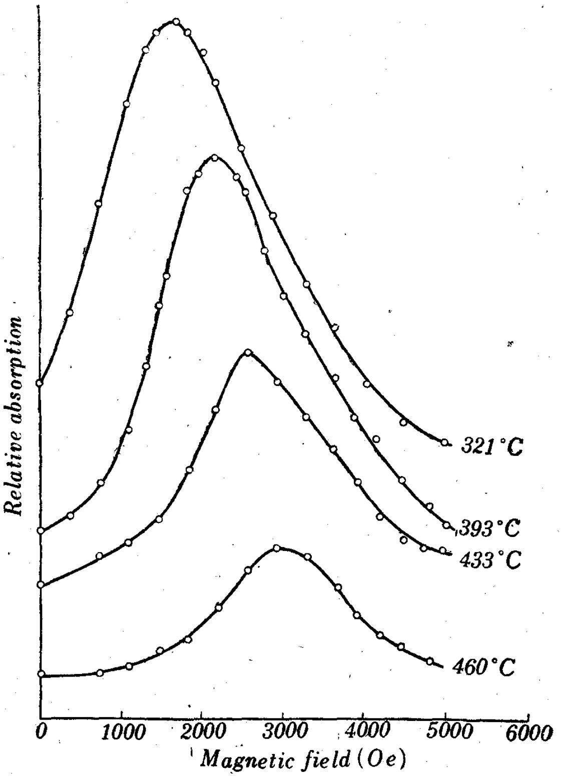

Fig. 6b. The curve of resonance absorption versus dc magnetic field in Co-OFe$_2$O$_3$ near the Curie temperature.

As was expected, the resonance could be observed from about 40° C, and the resonance curves at various high temperatures ranging from 100° to 490° C are shown in Figs. 6a and 6b. From these curves, the resonance fields, the amount of absorption and the apparent half line widths, disregarding so called "size effect(11)", were obtained as functions of temperature and are given in Fig. 7. From 78° C to 260° C, the resonance field decreased gradually with rising temperature because of the decrease in crystalline magnetic anisotropy K. With further rise in temperature, the resonance field increased rapidly up to the Curie temperature 495° C, because of the result of a rapid decrease of the saturation magnetization M 12) in this temperature range. It

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(11) W. A. Yager, F. R Merritt and C. Guillaud; Phys. Rev. 81, 477, (1951).

(12) R. Pauthonet, Compt. Rend, 230, 1843 (1950).

has already been pointed out (13) that the anisotropy energy will have an influence on the resonance condition. The shift in the resonance field of the order of K_1/Ms,

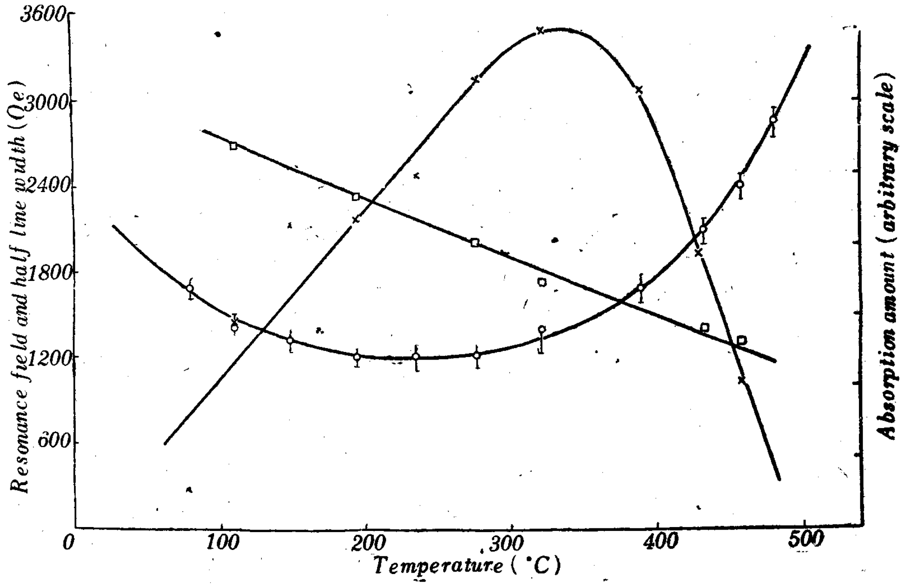

Fig. 7. The curves of resonance field, absorption amount and half line width with varying temperature. $CoOFe_2O_3$; ○ marked line denotes resonance field, × marked absorption amount and □ marked half line width.

where K_1 is the anisotropy constant and Ms saturation. Therefore, these facts were confirmed experimentally with the above mentioned experimental results. A maximum found on the curve of the amount of absorption versus temperature may also be explained qualitatively as being a combined effect of gradual decrease in the crystalline anisotropy and rapid change of the saturation magnetization at the temperature near the Curie point. The half line widths decreased linearly with rising temperature up to the Curie point, above which the resonance suddenly disappeared.* It may be due to a monotonous decrease in the value of K/M, in which the sudden decrease of magnetization near the Curie temperature is discontinuous and does not cover a range of temperatures.

The results were quite contrary to the case of ferromagnetic metals found by N. Bloembergen(14) near the Curie point on nickel and Supe rpermalloy.

Moreover, the apparent *g*-factors at various high temperatures were determined from the resonance fields H corresponding to the maximum absorption and M, and are given in Table I.

Table I.

Temp. °C	H(Oe)	g
100°	1550	2.22
200°	1200	2.81
300°	1250	2.91
400°	1770	2.26
480°	2850	2.08

From this table, it is seen that *g*-factor shows a broad maximum in the temperature range from 200° C to 300° C.

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(13) C. Kittel, Phys. Rev. 73, 155 (1948). J. H. Van Vleck, Phys. Rev. 78, 266 (1951).

* The same results were also obtained for $CuOFe_2O_3$, $MgOFe_2O_3$ and $MnOFe_2O_3$. Details will be published in Sci. Rep RITU.

(14) N. Bloembergen, Phys Rev., 78, 572 (1950).

Considering the error of observation for temperature and magnetic field strength, the value of the resonance field just at the Curie point was found to be within 3300±100 Oe, for which *g*-factor was determined to be 2.02 ± 0.05 by using the paramagnetic resonance condition.

IV. Double peaks in correlation with magnetic transition

It is very noticeable that the minimum points on the curve of the resonance field versus temperature for Co-Zn ferrites containing low Zn-ferrite agree with the beginning temperatures of their magnetic transition. And the high Zn-ferrite, namely, $\mathrm{CoO4ZnO5Fe_2O_3}$ does not exhibit any transition in the temperature range from room to liquid nitrogen temperatures.

As an example, only the results of magnetic measurement on $\mathrm{2CoO3ZnO\ 5Fe_2O_3}$ at low temperatures are presented. The, temperature changes in magnetization at three constant applied fields were observed with Ballistic method by using a specimen of "powder-compact", and are shown in Fig. 8. The ordinate gives deflection of galvanometer, and the abscissa the temperature. At first, intensity magnetizations at such low magnetic field as 180 Oe and 370 Oe., show a constant value from room temperature to Ca. −70° C with the fall of temperature, below which it begins to decrease slowly up to −140° C, and with further fall of temperature, its amounts increases and after-wards again decreases gradually.

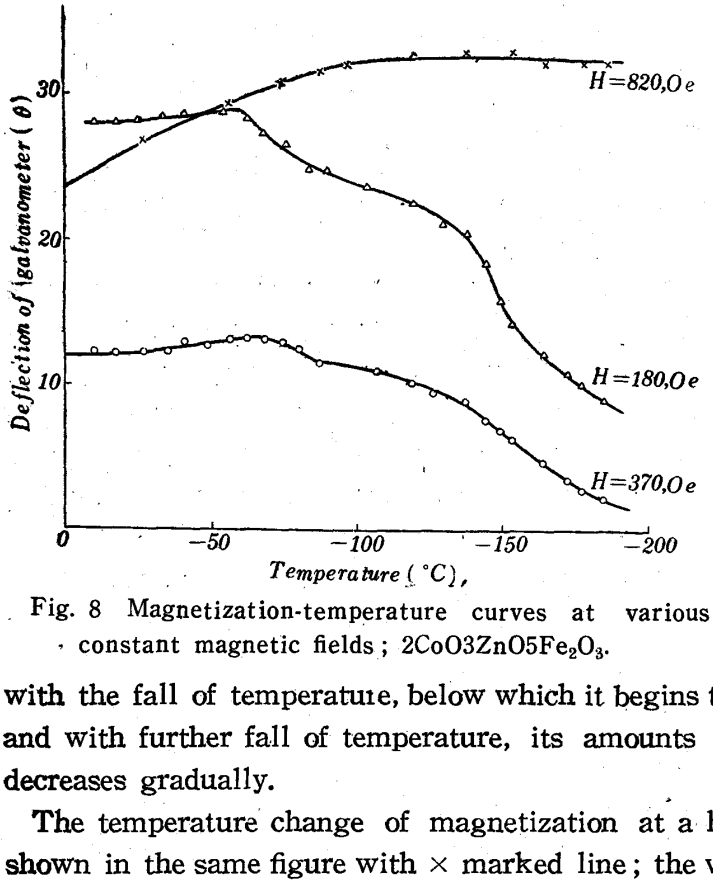

Fig. 8 Magnetization-temperature curves at various constant magnetic fields; $\mathrm{2CoO3ZnO5Fe_2O_3}$.

The temperature change of magnetization at a high magnetic field of 820 Oe. is shown in the same figure with × marked line; the value increases with the decrease of temperature and is found to be almost constant in the neighbourhood of −130° C.

Comapring this figure with the foregoing Fig. 4, we find a satisfactory agreement between the beginning temperature of the transition and the minimum point observed on the curve of resonance field at absorption maximum against the temperature.

In the present experiment, we could not observed double peaks similar to those found in the range of transition temperature for magnetite, nickel-ferrite and magnese-ferrite, but they seem also to be separated in the case of cobalt- and Co-Zn ferrites by means of resonance experiments using milimeter wave-length, which are being planned.

V. Problem on the intensity of absorption line

The problem on the intensity of absorption in the ferromagnetic microwave resonance has scarely been discussed, as far as we know, but the results obtained from the present experiments seem to offer some suggestions. For example, the absorptions in $4CoOZnO5Fe_2O_3$, $3CoO2ZnO5Fe_2O_3$ and $2CoO3ZnO5Fe_2O_3$ decrease at low temperature, and may be due to the increase in anisotropic energy with falling temperature in these specimens, while the intensity of absorption in $CoO4ZnO5Fe_2O_3$ at first increases from room temperature to about $-100°C$; the fact suggests the effect of increasing intensity magnetization in these temperature-ranges; and as mentioned above, the similar effect of decreasing anisotropic energy and of decreasing saturation magnetization accompanied by the change of temperature was also found in the absorption of cobalt ferrite at the temperature ranging from 100° C to 400° C and from 400° C to Curie point, respectively. Therefore, it can be concluded that the intensity of absorption line in ferromagnetic resonance at a given frequency must be influenced considerably both by the intensity magnetization and by the magetic crystalline anisotropy of tne specimen.

Summary

The results of the present experiment were summarized as follows:

1) In Co-Zn binary ferrites, the absorption disappeared below the temperature of $-90°C$ and $-140°C$ in $4CoOZnO5Fe_2O_3$ and $3CoO2ZnO5Fe_2O_3$, respectively, but the absorption in $CoO4ZnO5Fe_2O_3$, could be observed down to $-186°C$.

2) The minimum found on the curve of the resonance field versus temperature in Co-Zn ferrites, containing low Zinc ferrite are satisfactorily explained by the combined effect of increase of magnetization and anisotropic energy, accompanied by the change of temperature.

3) A good agreement between the beginning temperature of the transition and the minimum point observed on the curve of resonance field at absorption maximum against temperature was found in the case of Co-Zn ferrites.

4) Double peaks similar to those found in the range of transition. temperature for magnetite, Ni-ferrite and Mn-ferrite could not be observed in the case of Co-Zn ferrites at the wavelength of 3.2 cm.

5) Resonance absorption in Co-ferrite could not be detected at the temperature below 40° C, by using the wave length of 3.22 cm.

6) From the experimental results of Co-ferrite at various high temperatures, the resonance fields, the amount of absorption, the appaient half line widths and *g*-factor were obtained as functions of temperature up to the Curie point.

7) It was confirmed experimentally that the anisotropy energy has an influence on the resonance condition and the shift in the resonance field is of the order of K_1/Ms, where K_1 is the anisotropy constant and Ms the saturation magnetization.

8) It was concluded that the intensity of abosrption line in ferromagnetic resonance at a given frequency must be influenced both by the intensity magnetization and by the magnetic crystalline anisotropy of the specimen.

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