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Powder ferromagnetic resonance spectra of some mixed ferrites

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The powder FMR of six ferrites at 9.1 GHz in the temperature range 25 to 290° C is reported in this paper. The effect of the internal fields on the linewidths and the resonance fields are studied. Curie temperatures obtained for some of the ferrites from FMR are compared with the values obtained from an oscillator technique. The line shapes are found to be of Lorenzian shape. Effective *g* values were calculated and a brief discussion is made about the various contributions to the total field.

1. Introduction

The ferromagnetic resonance phenomena (FMR) in ferrites can be described in terms of the solutions of the equations of motion for the precessing magnetic vector. The phenomenological description requires the use of the appropriate effective magnetic field acting on the magnetization and of relaxation parameters which determine the linewidth. Contributions to the linewidth come from anisotropy, porosity, eddy currents within the cavity wall, inhomogeneous demagnetization and intrinsic properties.

In the present paper, the powder FMR spectra of $Co_xZn_{1-x}Fe_2O_4$, ($x = 0.14$, 0.32, 0.49, 0.74), $Mg_{0.25}Zn_{0.75}Fe_2O_4$ and $BaFe_{12}O_{19}$ are reported at 9.1 GHz in the temperature range 25 to 290° C and in the magnetic field 0 to 6000 Gauss. The line shapes are found to be of Lorenzian shape from the theoretical curve fitting using an IBM 370/155 computer. The linewidths, resonance fields and absorption are presented. Transition points from the ferromagnetic state to the paramagnetic state are observed for some of these ferrites. The Curie temperatures are compared with the temperatures obtained from the oscillator technique. The resonance field variation with cobalt concentration at 25° C showed a similar type of behaviour to that observed in the susceptibility measurements.

2. Experimental apparatus

The FMR spectra were recorded at 9.1 GHz using a rectangular cavity resonator and a field-modulated Varian E4 spectrometer. The sample was placed at the maximum magnetic field in the cavity but not near the walls. A cylindrical quartz tube was used to mount the sample in the cavity. The sample was used in minute quantities in powder form of weight around 1 mg. The quantity of the sample was kept to a minimum so that the resonance absorption did not depend significantly on the amount of the sample and also to avoid loading of the cavity. At these amounts of sample, the linewidth was found to be invariable with the amount and porosity of the sample. The temperature was maintained to an accuracy of ± 1° C. The error in the magnetic field measurement was ± 10 G. Since the spectra are broad at room temperature (25° C), the error in the magnetic field can be neglected. The preparation and some of the electrical and magnetic properties of these ferrites were published in our earlier publications [1–3].

A CW oscillator working in the frequency range 40 to 50 MHz was employed to determine the Curie temperatures [4]. The principle of this oscillator technique measurement is explained below. The oscillator has a tank coil (LC) tuned to a resonant frequency equal to $1/2\pi(LC)^{1/2}$. When a

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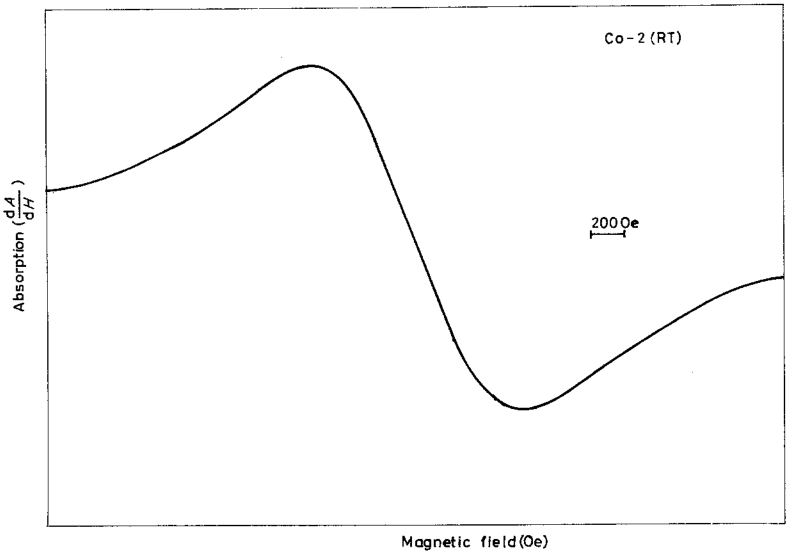

Figure 1 Recorded FMR spectrum of Co-2 at room temperature.

magnetic material is introduced into the tank coil, the inductance of the tank coil will be changed with the magnetization value of the sample, so there will be a shift in the frequency of the oscillator. When the sample is heated, the magnetization value is reduced and the frequency of the oscillator also begins to fall. This frequency decrease continues until the Curie temperature of the sample is reached. At this point, the material becomes paramagnetic and the frequency of the oscillator returns to its original value with a steep rise, as there will be no contribution to the total inductance of the coil due to the sample. A plot of frequency against temperature will give the Curie temperature of the sample. The accuracy in the Curie temperature measurement is ± 2° C.

3. Results

The FMR spectra were recorded as a first derivative of the absorption spectra. One of the recorded spectra of cobalt zinc ferrites is shown in Fig. 1. The linewidths were calculated from the spectra for all these ferrites and the values at 25° C are given in Table I together with the resonance fields and the area under the curve. The resonance field values and the magnetic moments are shown in Fig. 2 as a function of cobalt concentration. From Fig. 2, it can be seen that the value of H_R decreases with cobalt concentration up to $x = 0.49$, and above $x = 0.49$ it increases once again. This type of behaviour is expected, since the total field is a combination of the external field and the various contributions discussed below [5].

TABLE II Variation of *g* with temperature

Temperature	Co-1	Co-2	Co-3	MgZn	BaFe
RT	2.131	2.485	4.714	3.182	2.997
50	2.128	2.227*	4.258	2.912	2.955
90	2.093	2.395	3.866	2.614	2.845
130	2.052	2.398	3.399	2.399	2.701
170	2.044	–	3.074	2.101	2.633
190	2.046*	–	2.921	2.032*	2.567
230	2.468	–	2.642	2.032	2.455
250	2.458	–	2.362	–	2.421

The variation of linewidth with cobalt concentration is shown in Fig. 3. This variation is found to be different with the observed linewidth variations in other spinel ferrites. The first derivative spectra were converted into the absorption spectra

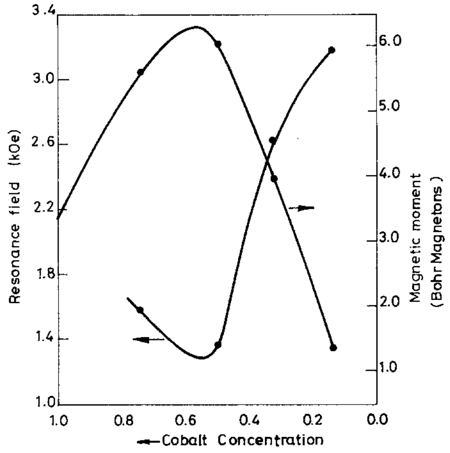

Figure 2 Variation of the resonance fields and the magnetic moments with cobalt concentration.

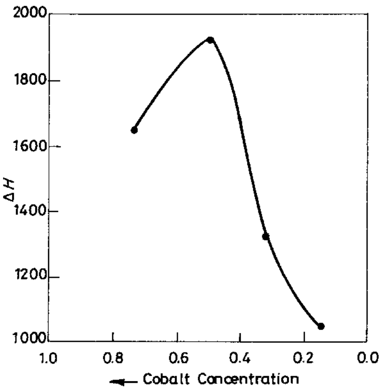

Figure 3 Variation of line widths with cobalt concentration.

and these were used to estimate the susceptibility parameters. The variations of absorption with temperature are shown in Figs. 4 and 5 for Co-3 and barium ferrites. In these ferrites the linewidth decreased sharply near the Curie temperature suggesting a change in the magnetic state of the ferrites. Above the Curie temperature, the resonance line is a combination of both parallel and perpendicular components. The Curie temperatures thus obtained are given in Table I together with the values obtained from the oscillator technique. For some of the ferrites the Curie temperatures are well beyond the present temperature range studied. The variation of linewidths with temperature is shown in Fig. 6. Absorption of microwave power by the ferrites in arbitrary units is shown in Fig. 7: the absorption reduces from a high value at 25°C to a lower value at the Curie temperature.

4. Discussion

In polycrystalline magnetic materials, the field contributions to the FMR arise from anisotropy, porosity, eddy currents, inhomogeneous demagnetizations and intrinsic parameters. Sparks [6], Srivastava *et al.* [7], Scholamann [8] and others derived the equations for the various contributions. The total field for a spherical sample is a combination of [5, 7]

$$H_\mathrm{R} = H_0 + \frac{4\pi M}{3}\frac{v}{V} - \frac{K_1}{2M} - 0.321[1 + (\epsilon\mu_\mathrm{e})^{1/2}].$$

$$4\pi M\frac{d}{\lambda} + \left(\xi_1\frac{d}{\lambda} + \xi_2\frac{d^2}{\lambda^2}\right)4\pi M.$$

where $4\pi M$ is the saturation magnetization, K_1 the anisotropy constant, v/V is the pore sample volume ratio, d is the diameter of sample, H_0 is the value of the d.c. resonant field, ϵ is the dielectric constant, and ξ_1 and ξ_2 are functions of the effective permeability μ_e.

Similarly, the linewidth contributions were also calculated showing the effect of saturation magnetization on linewidths. From the above equations, it can be seen that the magnetization value plays a dominant role in the evaluation of the resonance fields and the linewidths.

In polycrystalline samples, the random orientation of crystallites and the presence of pores causes the resonance fields to vary from point to point within the material. This broadens and shifts the resonance line. The recorded spectra of magnesium zinc ferrite is shown in Fig. 8. This shows a steep rise on the low field side and a slow

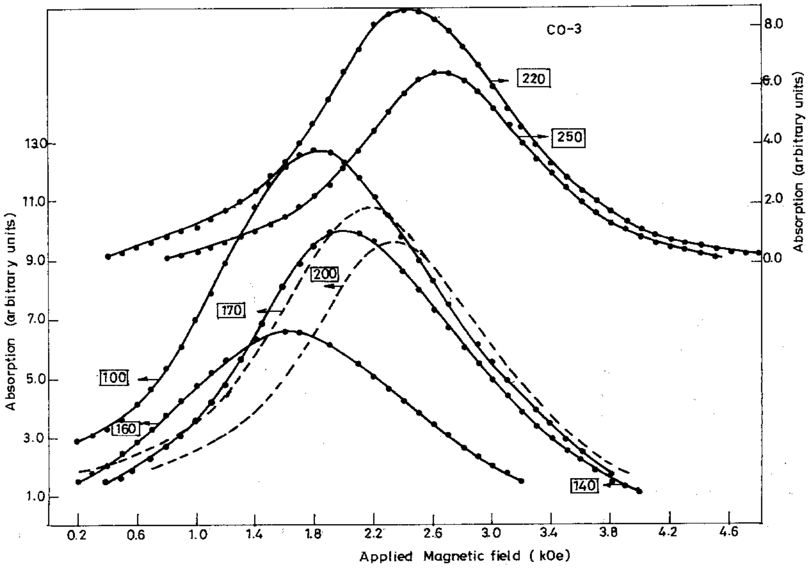

Figure 4 Variation of FMR absorption curves with temperature of Co-3.

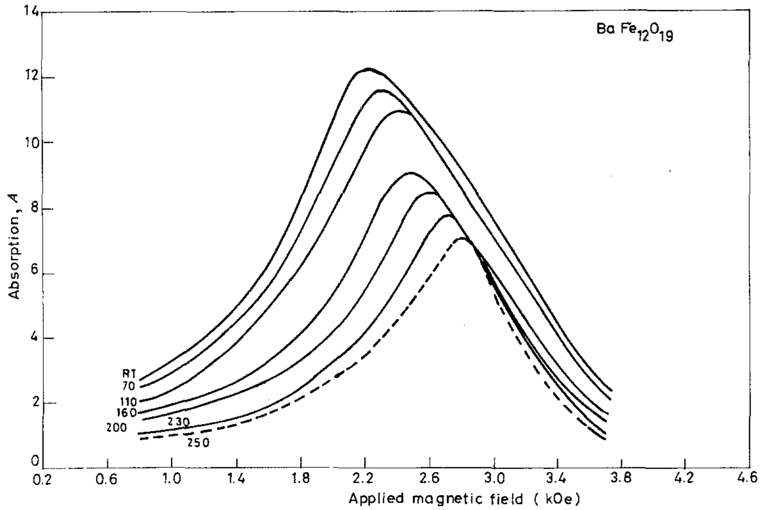

Figure 5 Variation of FMR absorption curves with temperature of $BaFe_{12}O_{19}$.

variation on the high field side. This type of behaviour is expected for materials with negative anisotropy constant. The negative anisotropy indicates an easy axis of magnetization along the body diagonal (there are three in a cubic crystal) and the hard axis along the cube edge (there are four in a cubic crystal). So the absorption curve should be asymmetrical and also steep on the low field side [9].

As seen from Fig. 3, a maximum in ΔH is observed for a certain concentration of cobalt in cobalt zinc ferrites. Cobalt ferrite has a positive anisotropy constant and the anisotropy value changes with the addition of zinc. At lower concentration of cobalt, the anisotropy constant and magnetization becomes small and due to these contributions to the linewidth, the total linewidth is expected to increase until these parameters

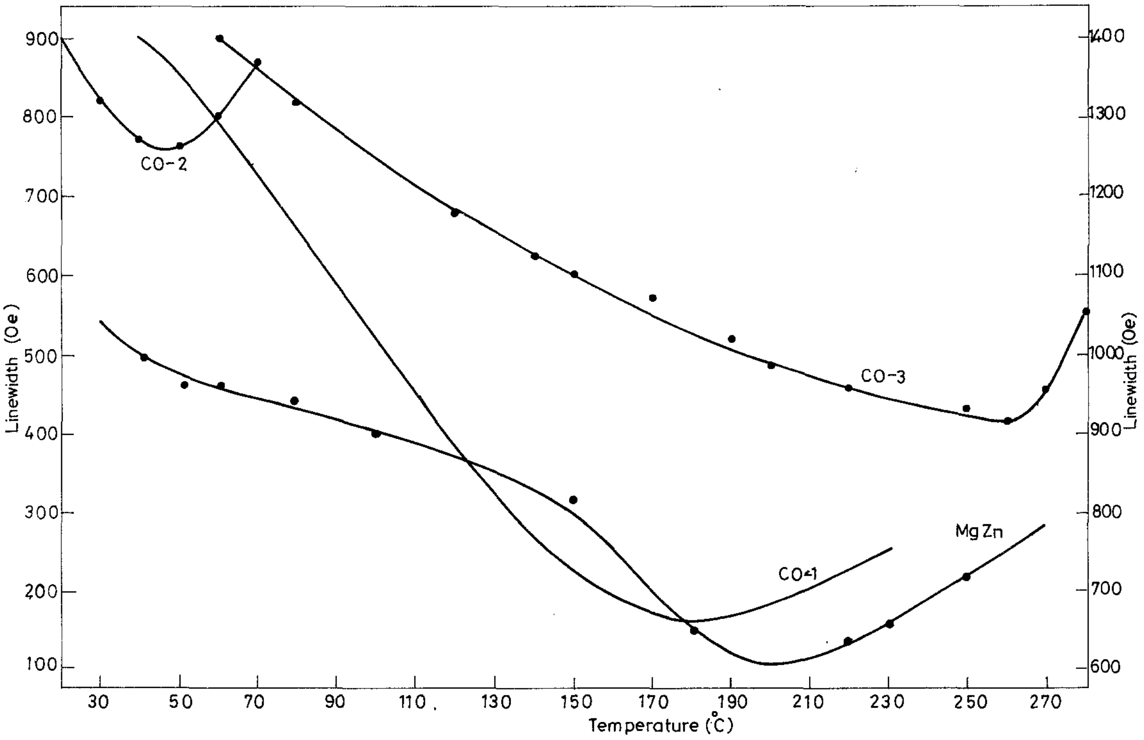

Figure 6 Effect of temperature on the line widths of the ferrites.

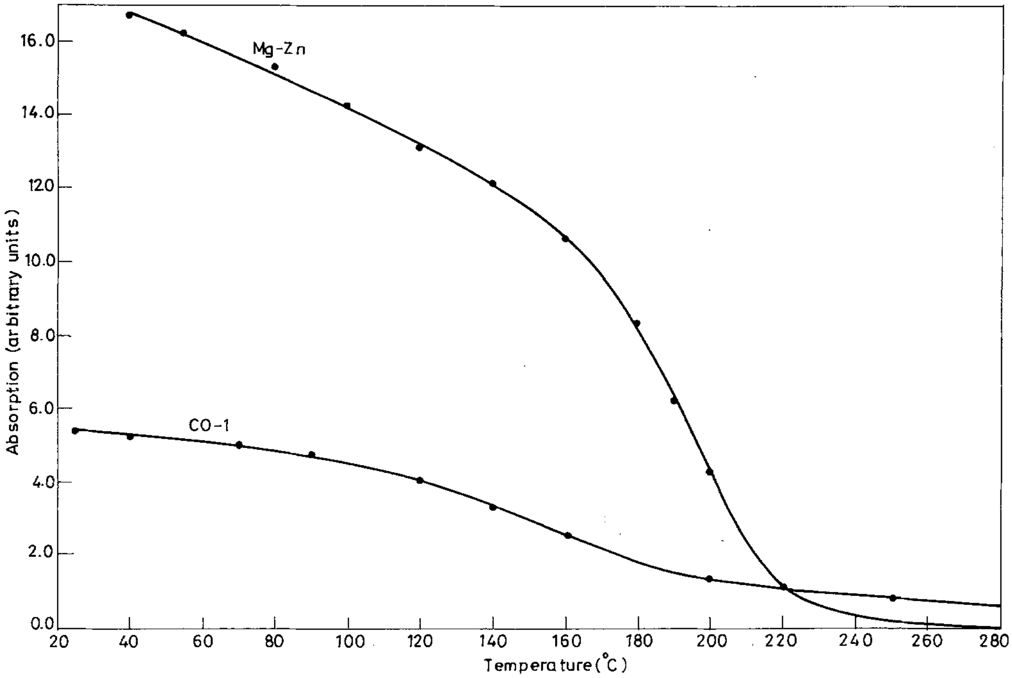

Figure 7 Variation of the absorption with temperature for the ferrites.

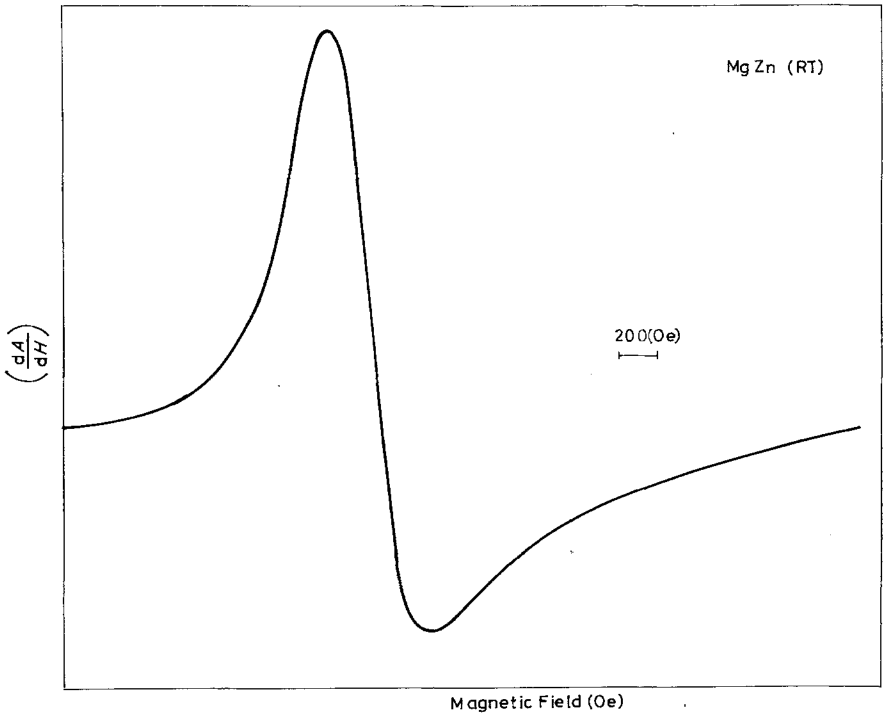

Figure 8 Recorded FMR spectrum of MgZn at room temperature.

TABLE I Resonance fields, linewidths, area under the curve and Curie temperature at room temperature

Code	Sample	H_0 (G)	H (G)	Area (arb. units)	T_c* (° C)	T_c† (° C)
Co-1	$Co_{0.14}Zn_{0.86}Fe_2O_4$	3160	1045	5.72	182	188
Co-2	$Co_{0.32}Zn_{0.68}Fe_2O_4$	2610	1320	12.72	50	53
Co-3	$Co_{0.49}Zn_{0.51}Fe_2O_4$	1340	1920	24.24	290	292
Co-4	$Co_{0.74}Zn_{0.26}Fe_2O_4$	1560	1640	22.12	–	398
MgZn	$Mg_{0.25}Zn_{0.75}Fe_2O_4$	2060	540	5.21	200	204
BaFe	$Ba Fe_{12}O_{19}$	2180	1400	7.06	–	450

*From FMR measurements.
†From oscillator technique.

vary linearly. At the middle concentration, the magnetization value is high and so the contribution from $K_1/2M$ becomes small, and hence an increase in linewidth is expected. A maximum in linewidth was also observed in NiO $Fe_{2-t}Al_tO_4$ for a certain concentration of aluminium [10].

Srivastava and Patni [5] have studied the linewidth of polycrystalline $Ni_{1-x}Zn_xFe_2O_4$ as a function of x and observed that ΔH decreases and remains constant above a particular concentration of zinc. They have attributed this to the possible narrowing of the line due to the presence of Yafet Kittel angles in the systems. In $Mn_{1-x}Mg_xFe_2O_4$ a minimum in ΔH at $x = 0.5$ was observed. Similar observations were made by Belov *et al.* [11] in single crystal Mg–Mn ferrites. The reduction in the linewidth was attributed to the presence of non-magnetic cations in the system which may cause a reduction in the density of degenerate magnon modes due to the loss in the translational invariance. In the present study, the small linewidth value for Mg–Zn ferrite compared to other ferrites is due to the presence of more non-magnetic ions in the system.

It is known that if the difference between the linewidth in the ordered and disordered state is taken as a measure of the intrinsic linewidth in single crystals, this happens to be equal to 10 G. This compares with a linewidth of 15 G for single crystal $NiFe_2O_4$ and Mg–Mn ferrites. The lowest linewidth of 8.4 G has been observed for $Mn_{0.47}Mg_{0.53}Fe_2O_4$ [12].

Fig. 2, indicates the importance and the effect of internal fields on the total linewidths and resonance fields. For the lowest concentration of cobalt in cobalt zinc ferrites, the internal magnetic field is less, known from the magnetic moment values. So the resonance field should be high to satisfy $\omega = \gamma H$ where $\gamma = ge/2mc$. For middle concentrations, the field is very high and resonance is expected at lower d.c. magnetic fields. This is experimentally observed and this field rises once again due to the smaller internal field for the next highest concentrations of cobalt. Thus the effect of magnetic moment on the d.c. resonance fields can be seen in Fig. 2.

The behaviour of linewidth as a function of temperature is shown in Fig. 6. It is observed that the behaviour of linewidth with temperature depends strongly on the composition. A peak in linewidth has been observed in nickel ferrite containing excess divalent iron. White [13] has observed that the addition of small amounts of Zn^{2+} ions to the iron-rich manganese ferrite greatly reduces the concentration of iron. White pointed out that any transition element whose lowest lying state is not an orbital singlet, will increase the linewidth of the sample. It can be seen that the linewidth reduces from a higher value at room temperature to a lowest value at the Curie temperature. At the Curie temperature the ferromagnetic nature disappeared and a paramagnetic powder spectra was observed with both $g_{\parallel}$ and $g_{\perp}$ components. The effective g values were calculated and are given in Table II. Watanabe *et al.* [14] observed the increasing tendency in the linewidths towards lower temperature and its size dependence, in addition to the asymmetrical line shapes. Bhagat and Libitz [15] have studied the temperature variation of ferromagnetic relaxation in 3d transition metals and applied the normal conductivity theory to calculate the linewidths theoretically for cobalt whiskers above 250 K. Buffler [16] has calculated the magnetic field and the magnetogyric ratio for both the single crystal and polycrystalline samples at 40 GHz and the obtained values were equal to $H_a = 17\,000$ G and $\gamma = 2.87\ \text{MHz}\ \text{G}^{-1}$ for $BaFe_{12}O_{19}$.

From Figs. 4 and 5, it can be seen that the resonance magnetic field shifts to higher fields with an increase in temperature. Similar behaviour was observed in $Mn_{1.03}Fe_{1.77}O_4$ with resistivity equal to 556 Ωcm at room temperature, by Watanabe *et al.* [14].

From Table I, it can be seen that with the increase of zinc in cobalt zinc ferrites, the Curie temperature begins to decrease from 520° C. Zn^{2+} ions prefer tetrahedral sites and will reduce the number of Fe^{3+} ions at A sites. This reduces the A–B exchange interaction. Thus the substitution of zinc reduces the A–B interaction which, in turn, reduces the Curie temperature in mixed cobalt zinc ferrites with a spinel structure. Similar observations were also made on $Mn_{1-x}Zn_xFe_2O_4$, $Ni_{1-x}Zn_xFe_2O_4$ and other spinel ferrites [17]. It can also be seen that the Curie temperatures obtained from FMR and oscillator technique agree well.

Thus the present study confirms the strong effect of magnetic moment on the total resonance fields and linewidths, which in turn depend on the concentration of cobalt in cobalt zinc ferrites. In addition, the Curie temperatures can be obtained from the variation of linewidth with temperature. The temperature where the linewidth becomes minimal can be taken as the Curie temperature of the material. Above this temperature, the generally known powder paramagnetic spectrum of the material will appear. The Curie temperatures obtained were compared with those values obtained using an oscillator technique and it is found that the agreement is good. Thus the present study paves an easy way for finding the Curie temperatures of the magnetic materials.

5. Conclusions

1. Resonance is observed at lower fields, in the case of Co-3, where the internal field is high.
2. The variation of linewidth shows a maximum with cobalt concentration.
3. A minimum in linewidth is observed at the Curie temperature.
4. An easy way for finding the Curie temperatures of magnetic materials is established.

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