

IONO-COVALENT AND YAFET KITTLE (YK) ANGLE STUDIES OF SLOW COOLED AND QUENCHED CuZn-SYSTEM

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ABSTRACT

Compositional variation of bond lengths R_A and R_B suggests that iono-covalent character in CuZn ferrite decreases from CuFe_2O_4 to ZnFe_2O_4 . On quenching, the iono-covalent character increases and this is related to the migration of Cu^{+2} ions. For the low Zn^{+2} content, all Zn^{+2} ions stay on A-site increasing the magnetization while with higher Zn^{+2} content some Zn^{+2} may migrate to the B-site reducing magnetization. This possibility is greater with quenched samples when the migration of Cu^{+2} ions to the A-site enhances magnetization. YK angles do not appear on addition of Zn up to 20% in MgZn and NiZn ferrites while YK angles are favoured when the Zn^{+2} is added up to 20% in CuZn system.

INTRODUCTION

CuFe_2O_4 and MgFe_2O_4 are sensitive to heat treatment and CuFe_2O_4 shows electrical switching¹, tetragonality variation² and changing semiconducting properties³. Mössbauer studies of CuZn ferrite have also been carried out⁴.

The properties of CuZn system are explained by the cation migration⁵ of Cu^{+2} . However Zn^{+2} ions also can migrate to the B-site. It is with this aim that the present studies on magnetization are carried out and magnetization in NiZn, MgZn and CuZn ferrites is compared. The iono-covalent character of CuZn system is also explained.

EXPERIMENTAL

X-ray diffraction studies were carried out on a diffractometer (Phillips PM 9920) using iron target at 1.937 \AA FeK_α radiation. The curie temperatures were measured by the technique suggested Laoria and Sinha⁶. Magnetization was studied using a high field loop tracer.

RESULTS AND DISCUSSION

In figures 1 and 2 compositional variation of bondlengths R_A and R_B is shown. It is seen that both R_A and R_B increase linearly from CuFe_2O_4 to ZnFe_2O_4 with increase in Zn content. R_A and R_B values were evaluated using the relations

$$R_A = a \sqrt{3} \left(\delta + \frac{1}{8} \right),$$

$$R_B = a \left(3\sigma^2 - \frac{1}{2}\delta + \frac{1}{16} \right)^{\frac{1}{2}},$$

$$\delta = u - 0.375.$$

The u values were taken from the data reported earlier⁷. In table 1 data on bond length and YK angle are presented. In table 2 data on cation temperature and curie temperature are presented. The cation distribution is evaluated using the method of Gilleo⁸.

Levine's work on bond susceptibility in spinels showed⁹ an inverse relationship between the covalent character of the spinel and the bond length. Thus the iono-covalent character in our system decreases from CuFe_2O_4 to ZnFe_2O_4 . In figure 3 the variation of R_A and R_B with quenching temperature is shown. Higher the quenching temperature, lower are the values of R_A and R_B indicating that on quenching the iono-covalent character increases.

For copper ferrite Cu^{+2} can form tetrahedral SP^3

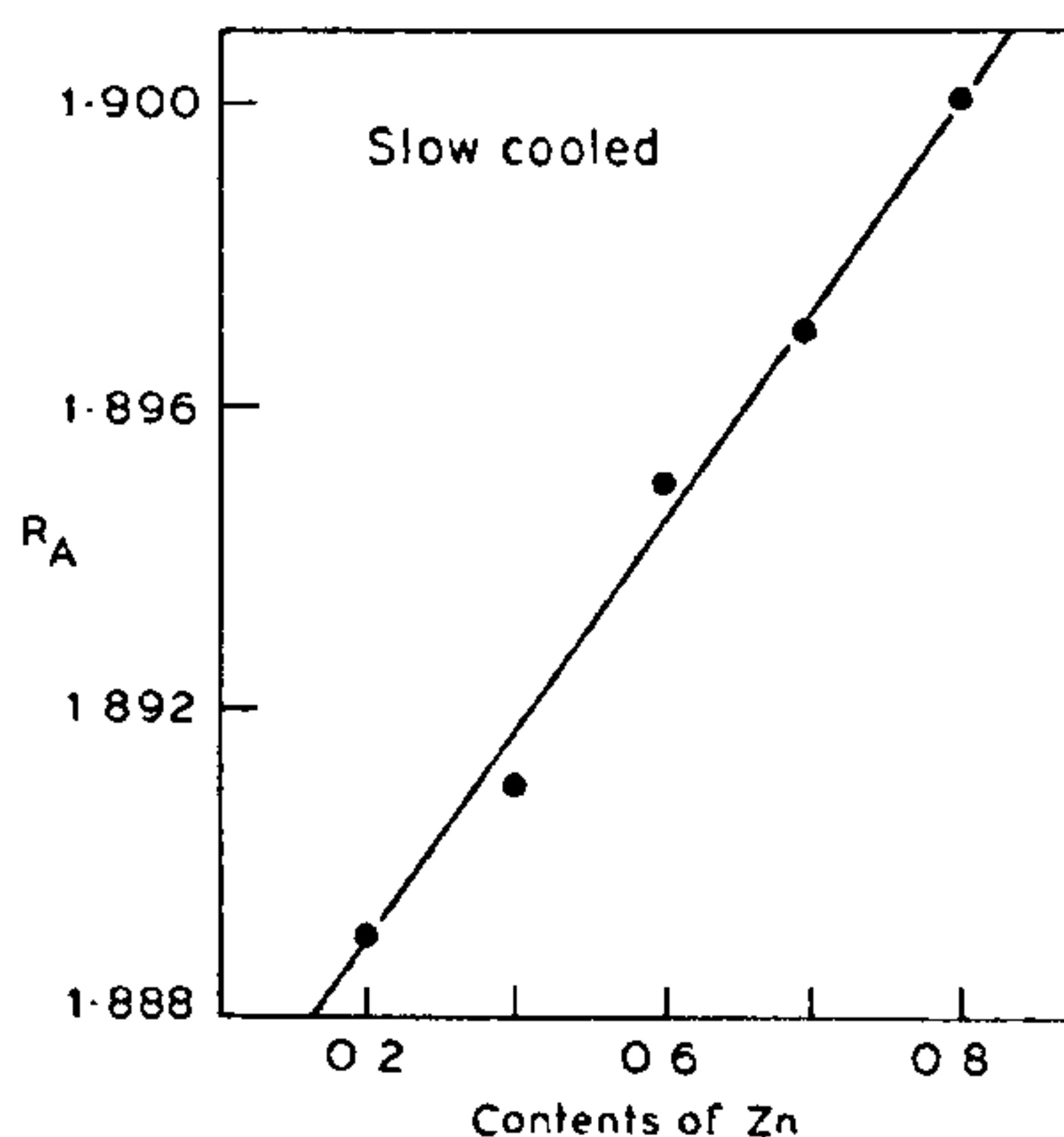


Figure 1. Compositional variation of bond length R_A .

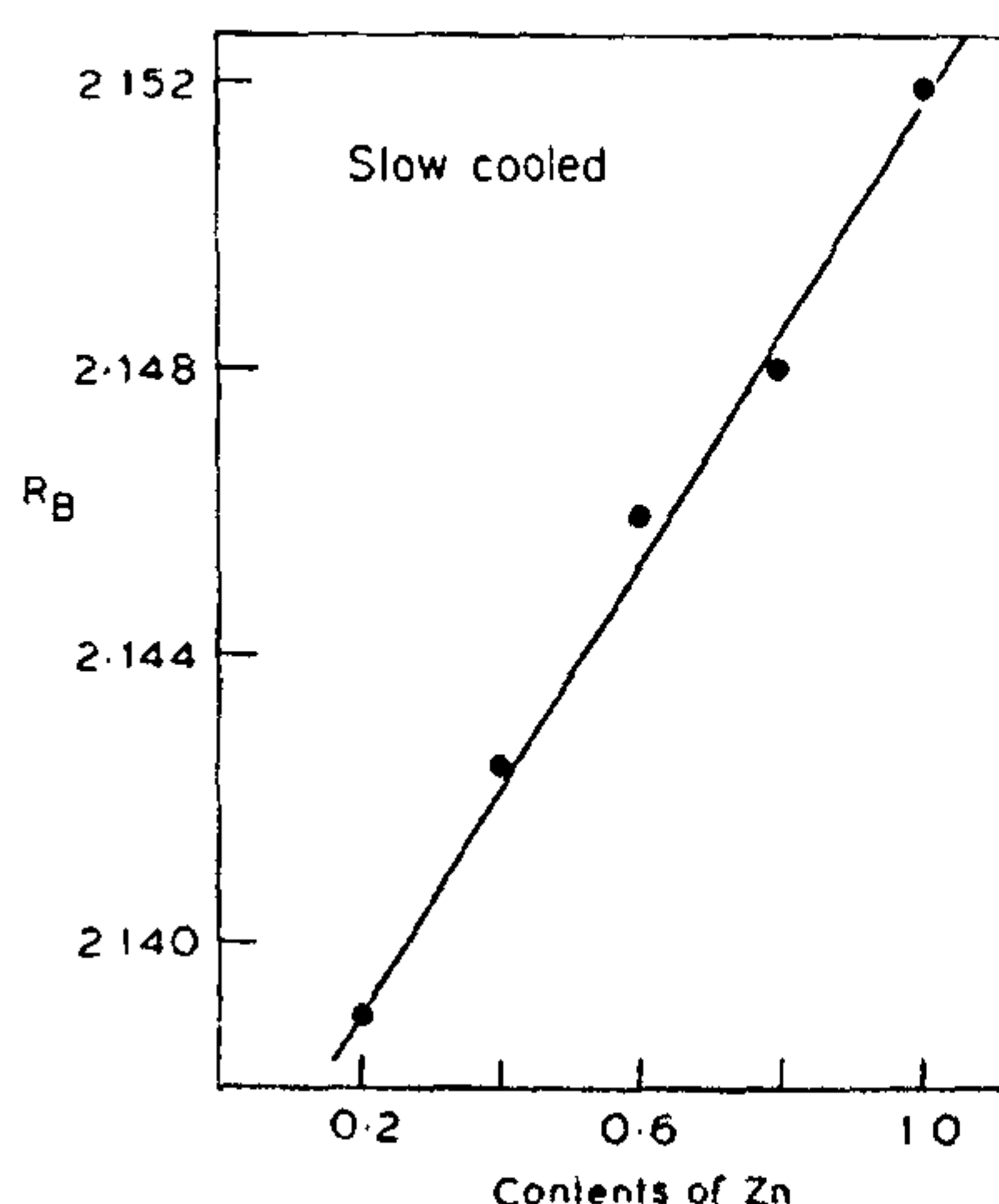
Table 1 Bond lengths R_A , R_B and YK angle for slow cooled and quenched samples of $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$

| Sample-history | $\text{Cu}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ | | | $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ | | | $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ | | | $\text{Cu}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ | | | ZnFe_2O_4 | | |
|------------------------|---|--------|---------------|---|--------|---------------|---|-------|---------------|---|-------|---------------|---------------------------|-------|---------------|
| | R_A | R_B | α_{YK} | R_A | R_B | α_{YK} | R_A | R_B | α_{YK} | R_A | R_B | α_{YK} | R_A | R_B | α_{YK} |
| Quenched from 800°C | 1.884 | 2.134 | 3.25 | 1.889 | 2.1395 | 33.12 | 1.894 | 2.146 | 54.00 | 1.896 | 2.148 | 90 | 1.900 | 2.152 | 90 |
| Quenched from 700°C | 1.885 | 2.1359 | 6.51 | 1.889 | 2.1407 | 34.40 | 1.895 | 2.146 | 54.53 | 1.896 | 2.147 | 90 | 1.900 | 2.152 | 90 |
| Quenched from 600°C | 1.887 | 2.1377 | 9.2 | 1.890 | 2.1420 | 36.87 | 1.894 | 2.146 | 55.10 | 1.897 | 2.148 | 90 | 1.900 | 2.152 | 90 |
| Slow cooled from 950°C | 1.889 | 2.1390 | 16.00 | 1.891 | 2.1423 | 37.00 | 1.895 | 2.146 | 57.50 | 1.897 | 2.148 | 90 | 1.900 | 2.152 | 90 |

Table 2 Cation distribution and curie temperature for $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ system evaluated using Gallios model

| Sample | Slow cooled from 950°C | Cation distribution $T_c^\circ\text{C}$ | Quenched from 800°C | $T_c^\circ\text{C}$ |
|---|--|--|---|---------------------|
| CuFe_2O_4 | $(\text{Cu}_{0.15}\text{Fe}_{0.85})^A(\text{Cu}_{0.85}\text{Fe}_{1.15})^B\text{O}_4$ | 430 | $(\text{Cu}_{0.25}^{+2}\text{Fe}_{0.75}^{+3})(\text{Cu}_{0.75}^{+2}\text{Fe}_{1.25}^{+3})^B\text{O}_4$ | 360 |
| $\text{Cu}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ | $(\text{Cu}_{0.15}\text{Zn}_{0.12}\text{Fe}_{0.65})^A(\text{Cu}_{0.65}\text{Fe}_{1.35})^B\text{O}_4$ | 350 | $(\text{Cu}_{0.28}^{+2}\text{Zn}_{0.2}^{+2}\text{Fe}_{0.52}^{+3})^A(\text{Cu}_{0.52}\text{Fe}_{1.48}^{+3})^B\text{O}_4$ | 260 |
| $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ | $(\text{Cu}_{0.06}^{+2}\text{Zn}_{0.4}^{+2}\text{Fe}_{0.54}^{+3})^A(\text{Cu}_{0.54}\text{Fe}_{1.46})^B\text{O}_4$ | 270 | $(\text{Cu}_{0.2}^{+2}\text{Zn}_{0.4}^{+2}\text{Fe}_{0.4}^{+3})^A(\text{Cu}_{0.4}\text{Fe}_{1.6}^{+3})^B\text{O}_4$ | 150 |
| $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ | $(\text{Cu}_{0.06}^{+2}\text{Zn}_{0.6}^{+2}\text{Fe}_{0.34}^{+3})^A(\text{Cu}_{0.34}\text{Fe}_{1.66})^B\text{O}_4$ | 100 | $(\text{Cu}_{0.05}^{+2}\text{Zn}_{0.6}^{+2}\text{Fe}_{0.35}^{+3})^A(\text{Cu}_{0.35}\text{Fe}_{1.65})^B\text{O}_4$ | 80 |

orbitals or square dSP^2 orbitals¹⁰. In spinel structure, the formation of square dSP^2 orbital is more

**Figure 2.** Compositional variation of bond length R_B .

favourable leading to the covalent character of copper ferrite¹¹. For zinc ferrite the tetrahedral orbit formation is more favourable and favour hybridization of SP^3 orbitals. In the case of CuFe_2O_4 , the degree of inversion is high¹¹, and it is the transfer of copper on the B-site which may be responsible for the covalent behaviour as suggested earlier¹¹.

Table 1 reveals more migration of the copper on B-site, as the samples are quenched from the elevated temperatures. Hence the ionic-covalent behaviour increases.

In table 2 the data on YK angle and magnetic moment for slow-cooled and quenched system are presented. Srivastava *et al*¹² calculated YK angles for $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$. Kulkarni *et al*¹³ carried out studies on zinc containing ferrite and calculated the theoretical values of YK angle using the relation

$$\cos \alpha_{YK} = \frac{5(1-x)^2\alpha + 25(1-x^2)\beta}{(1-x^2)r + 25(1+x^2)\delta + 10(1-x^2)\epsilon}$$

They have used the values of the exchange constants

Table 3 Data on α_{YK} angles of various ferrites

| Ferrite | α_{YK} | Ferrite | α_{YK} | Ferrite | α_{YK} |
|---|---------------|---|---------------|---|---------------|
| CuFe_2O_4 | 0 | MgFe_2O_4 | 0 | NiFe_2O_4 | 0 |
| $\text{Cu}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ | 16° | $\text{Mg}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ | 0 | $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ | 0 |
| $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ | 37° | $\text{Mg}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ | 31° | $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ | 14° |
| $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ | 58° | $\text{Mg}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ | 66° | $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ | 47° |
| $\text{Cu}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ | 90° | $\text{Mg}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ | 90° | $\text{Ni}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ | 80° |
| ZnFe_2O_4 | 90° | ZnFe_2O_4 | 90° | ZnFe_2O_4 | 90° |

as follows:

$$J_a = -5.25; J_b = -14.8; J_d = -10; \\ J_\gamma = 389; J = -4.53$$

and these are calculated by Srivastava *et al*¹².

We have used the following formula to calculate the YK angles

$$n_B = (6 + X) \cos \alpha_{YK} - 5(1 - X),$$

where n_B is expressed in the units of Bohr-magneton and X represents the zinc content. The experimental values of magnetic moment were obtained using the formula¹⁴

$$n_B = (\text{mol wt} \times M_s) / (5585 \times ds),$$

where ds is the density of the sample and σ_s , the saturation magnetization in e.m.u. per g. M_s was calculated as $(1 - P) \sigma_s ds$, where, P is the porosity.

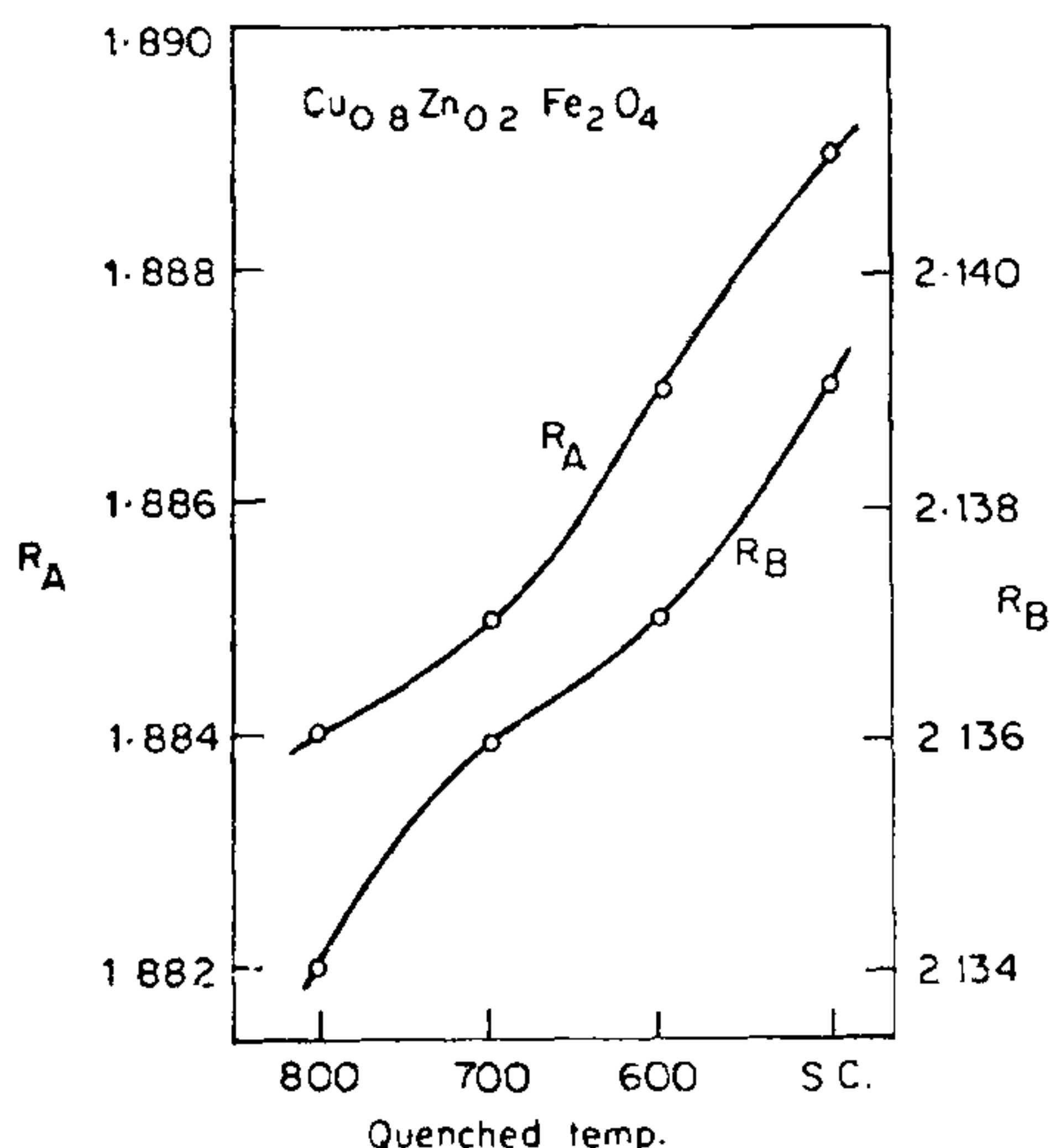


Figure 3. Variation R_A and R_B with quenching temperature.

Table 2 indicates that the triangular type of spin arrangements is not favoured in copper ferrite, hence its magnetization can be explained by Néels two-sublattice model. When zinc is added in excess of 20%, the triangular spin arrangements are favoured and the YK angle keeps increasing with the addition of zinc. While the YK angle decreases on quenching, the greater is the YK angle as a larger triangular arrangement is favoured leading to decrease in magnetization. Magnetization in the system collapses when zinc is added in excess of 60%.

YK angles are not favoured to a large degree when Zn^{+2} is added up to 40%. However with further addition of Zn^{+2} , these angles tend to increase. The distribution of Zn^{+2} beyond 40% content of Zn^{+2} is temperature-dependent. Hence when the Zn^{+2} content is low all Zn^{+2} ions stay on A-site and replace an equal quantity of Fe^{+3} ions to the B-site, leading to enhanced magnetization. On quenching it is the migration of Cu^{+2} from B-site to A-site which forces Fe^{+3} ions to B-site increasing the magnetization. For higher Zn^{+2} content, it is possible and more so on quenching that some Zn^{+2} ions go to the octahedral site reducing the magnetization.

A comparative data on the magnetization of slow cooled samples of Cu-Zn Ferrite, Mg-Zn Ferrite and Ni-Zn Ferrite are given in table 3. It is seen that in Mg-Zn and Ni-Zn Ferrite, the YK angles are not immediately favoured on addition on Zn^{+2} , while in Cu-Zn ferrite the YK angles are immediately favoured on addition to Zn^{+2} . Also the YK angles are considerably less in Ni-Zn ferrite when compared with Mg-Zn and Cu-Zn ferrite; the YK angles however in Mg-Zn ferrite are comparable with those in Cu-Zn ferrite.

13 July 1987

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NEWS

EATING AWAY AT OIL SPILLS

...“When oil [from spills] washes up on beaches, it kills off plant and animal matter, providing a natural feast for bacteria. These microbes will feed on oil, but it's not their favourite food. ‘For [the microbes] almost anything is better than eating oil,’ says Eric Levy, a researcher with the Bedford Inst. of Oceanography [Dartmouth, Nova Scotia]. The oil stays relatively untouched until the microbes finish gobbling up tastier foods. Since fertilizer contains nitrogen, an essential foodstuff for bacteria, applying it triggers a population explosion — and the more microbes there are, the less time it takes for them to get around to eating the oil.... The

technique is relatively inexpensive, too: it costs the same as fertilizing a farm field. Earlier attempts to clean up polluted beaches with fertilizer failed, but according to the Nova Scotia researchers, the reason is that the material wasn't given enough time to work; microbes take a few days to colonize the oil.” [Stephen Strauss (*Globe and Mail*, Toronto, Canada) in *Technology Review* 91(3):12-4, April 88. Reproduced with permission from Press Digest, *Current Contents*®, No. 21, May 23, 1988, p. 13. (Published by the Institute for Scientific Information®, Philadelphia, USA.)]

ERRATUM

In the article on “Synthesis of novel polynucleotide: Potential R-L Model” by R. K. Mishra and S. K. Brahmachari, published in *Curr. Sci.*, June 5, 1988, Vol. 57, No. 11, p. 574: The underlines for the

sequence have been inadvertantly omitted on the second column first line. The corrected sequence may please be read as follows:

GAATTCTCATGTTGACAGCTTATCATCGATAAGCTTTAA
R
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R
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