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Magnetic structure of zinc ferrite

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Abstract. A detailed analysis of the available experimental data has been made for the ordered phase of $ZnFe_2O_4$. The abnormally low T_N and the observed spin arrangement have been explained on the basis of the hybridization of orbitals on the oxygen ions which gives rise to an anisotropic exchange interaction. The variation of hyperfine field and susceptibility with temperature along with the zero point reduction of the magnetic moment indicate that the $ZnFe_2O_4$ is a two-dimensional antiferromagnet.

Keywords. Critical exponents; hyperfine fields; magnetic structure; overlap integrals; zinc ferrite.

1. Introduction

Zinc ferrite is a normal spinel with a cell constant of 8·44 Å. It is an antiferromagnetic material below 10 K. All the Zn ions occupy only tetrahedral (A) site and all the Fe ions occupy octahedral (B) site and the only exchange interaction present in $ZnFe_2O_4$ is the B–B interaction. However, its properties like sub-lattice magnetization and susceptibility do not show a general three-dimensional (3D) antiferromagnetic behaviour. Its Néel temperature T_N is abnormally low.

Neutron diffraction studies of $ZnFe_2O_4$ at 4·2 K by König *et al* (1970) and Boucher *et al* (1970) have indicated that the magnetic unit cell gets doubled and becomes tetragonal with $a = b = 8{\cdot}43$ Å and $c = 16{\cdot}86$ Å. The conclusions reached through these two studies are not similar. In one case (König *et al* 1970) there are two models which fit the intensities of lines, one collinear and the other non-collinear. In the collinear model the spins make an angle of 45° with the c-axis. In the model of Boucher *et al* (1970) the collinear structure has spins pointing along [100] and [010] directions. The magnetic moments on the Fe^{3+} ions in both cases which are close to 4·2 μ_B are much smaller than the expected value of 5 μ_B for Fe^{3+} ions.

Magnetic susceptibility of $ZnFe_2O_4$ has been measured by Lotgering (1966) and also by Arrot and Goldman (1955). At high temperatures ($T > 300$ K) the reciprocal susceptibility is linear (Lotgering 1966). But below 30 K the inverse susceptibility is almost constant with a broad minima at 15 K.

König *et al* (1970) analysed the Mössbauer spectra of $ZnFe_2O_4$ from 4·5 to 12 K. These studies have given the value of T_N as 10 K. The value of the hyperfine field (H_{hf}) extrapolated to 0 K is 515 kOe. They have shown that the H_{hf} variation is markedly different from the Brillouin function $B_{5/2}$.

Heat capacity of $ZnFe_2O_4$ has been measured by Edger *et al* (1957, 1958). There is a peak in the molar heat capacity versus temperature curve around 10 K indicating that T_N is 10 K.

In figure 1, we have plotted the observed values of T_N for several ferrites listed in table 1 as a function of the inverse of the overlap integral (S^{-1}) which for qualitative

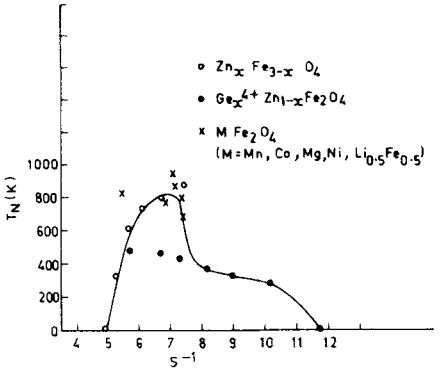

Figure 1. Variation of T_N with the inverse of the overlap integral S^{-1}.

Table 1. The Néel temperature (T_N) lattice constant (a) and the inverse of the overlap integral (S^{-1}) for several compositions of spinel ferrites

Composition	T_N (K)	a (Å)	S^{-1}	Composition	T_N (K)	a (Å)	S^{-1}
$MnFe_2O_4$	823	8·52	5·44	$Zn_{0.6}Fe_{2.4}O_4$	624	8·421	5·67
$CoFe_2O_4$	790	8·38	7·35	$Zn_{0.8}Fe_{2.2}O_4$	335	8·429	5·27
$NiFe_2O_4$	858	8·34	7·14	$ZnFe_2O_4$	10	8·440	4·95
$CuFe_2O_4$	759	8·28	6·83	$Ge_{0.25}Zn_{0.75}Fe_2O_4$	475	8·425	5·66
$Li_{0.5}Fe_{2.5}O_4$	943	8·33	7·08	$Ge_{0.5}Zn_{0.5}Fe_2O_4$	472	8·419	6·75
$MgFe_2O_4$	680	8·38	7·35	$Ge_{0.6}Zn_{0.4}Fe_2O_4$	430	8·415	7·32
Fe_3O_4	875	8·390	7·41	$Ge_{0.8}Zn_{0.2}Fe_2O_4$	325	8·410	8·94
$Zn_{0.2}Fe_{2.8}O_4$	788	8·399	6·69	$Ge_{0.9}Zn_{0.1}Fe_2O_4$	278	8·413	10·18
$Zn_{0.4}Fe_{2.6}O_4$	732	8·410	6·13	$GeFe_2O_4$	10	8·414	11·76

estimate can be defined as

$$S = [(r_a + r_0^{2-}) - \text{interatomic distance}]/[r_a + r_0^{2-}] \quad (1)$$

where r_a and r_0^{2-} are the radii of the cation on the A-site and O^{2-} respectively and the interatomic distance is obtained from the observed cell constant a and is equal to $a\sqrt{3}/8$. Like the Slater-Bethe curve (Slater 1930; Bethe 1933) for direct overlap in metals we find that in superexchange also the large overlap leads to smaller values of exchange and as the overlap decreases the strength of exchange interaction first increases goes to a maximum and then decreases. The significant reduction in T_N in $ZnFe_2O_4$ compared with T_N of other spinel ferrites appears to be a consequence of enhanced overlap.

We have attempted to explain these experimental observations assuming that the hybridized orbitals located on the oxygen ions introduce left-right asymmetry in the

exchange interaction. This has been explained using Anderson's model for superexchange.

2. Discussion

In the collinear model (König *et al* 1970) the alignment of spins along a few directions as shown in figure 2 is as follows:

[110] and [1$\bar{1}$0] - - - ↑ ↑ ↓ ↓ ↑ ↑ - - - - -

[101], [$\bar{1}$01], [011] and [01$\bar{1}$] - - ↑ ↓ ↓ ↓ ↓ ↑ ↑ ↑ ↑ ↓ ↓ - - -

This is a complicated structure and requires an asymmetric nearest neighbour exchange interaction. We assume that the dominant interaction between Fe^{3+} ions is along [110] and [1$\bar{1}$0] directions. In this case a pair of spins ferromagnetically coupled are antiferromagnetically arranged pairwise on the linear chain. A possible explanation for the asymmetric exchange interaction on the left and right of the central spin on a linear chain has to be provided in terms of hybridized sp type of orbitals associated with O^{2-} ions.

The 90° d^5–d^5, B–B super exchange has two types of major interactions, one ferromagnetic ($b_{\sigma\sigma'}$) and the other anti-ferromagnetic ($b_{\pi\sigma}$). These are shown in figure 3.

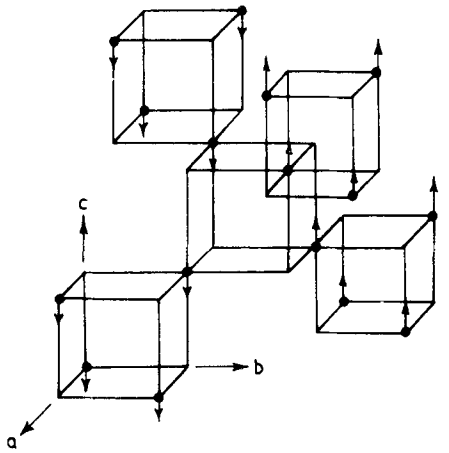

Figure 2. Spin arrangements in the collinear model (König *et al* 1970).

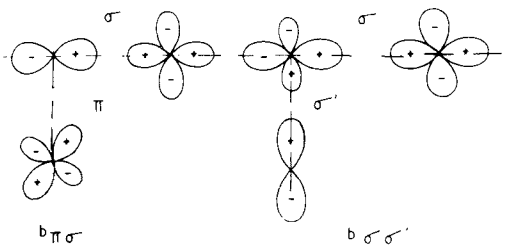

Figure 3. The $b_{\pi\sigma}$ and $b_{\sigma\sigma'}$ transfer integrals before hybridization.

Srivastava *et al* (1979) have shown that

$$J = -(1/25)[(4b_{\pi\sigma}^2/U) - (4b_{\sigma\sigma'}^2/U)], \tag{2}$$

where $U = 10$ eV. If the sp hybridization occurs on the O^{2-} sites the strength of the σ interaction increases while that of the π interaction is likely to decrease as shown in figure 4. Consequently, the strength of antiferromagnetic interaction $b_{\pi\sigma}^2/U$ goes down while that of the ferromagnetic interaction $b_{\sigma\sigma'}^2/U$ increases. In the case of pure orbitals without hybridization the magnitudes of $b_{\pi\sigma}$ and $b_{\sigma\sigma'}$ are 0·25 and 0·122 eV respectively (Srivastava *et al* 1979). The steep fall in T_N for $ZnFe_2O_4$ from the case of the ferrites $M_{1-x}^{2+}Zn_xFe_2O_4$ ($x \neq 1$, M = Fe, Ni, Mn, Co) shows that when Zn is completely occupying the A-site the effect of hybridization is most pronounced. A similar effect is observed in $Ge_xZn_{1-x}Fe_2O_4$ (Miyahara and Sai 1976; Hartmann-Boutron and Imbert 1968). In this system for $x = 1$, Ge^{4+} ions on the A-site have a very small radius but they have higher ionic charge. The nearest neighbour oxygen ions are therefore attracted towards this ion. Hence, this leads to more reduction in $b_{\pi\sigma}$ compared to $b_{\sigma\sigma'}$ and the 90° Fe^{3+}–Fe^{3+} interaction falls.

From the value of T_N for $ZnFe_2O_4$ which is 10 K assuming the two sublattice model we obtain in the mean field approximation

$$KT_N = (2/3)(-Z_F J_F + Z_A J_A) S(S+1), \tag{3}$$

where Z_F and Z_A are the number of nearest neighbour spins with parallel and antiparallel arrangements and J_F and J_A are the strength of ferromagnetic and antiferromagnetic couplings. Taking $Z_F = 4$, $Z_A = 2$, we have

$$J_A - 2J_F = 0{\cdot}86\,^{\circ}\mathrm{K}. \tag{4}$$

This effect of the asymmetric exchange is to reduce significantly the effective interaction and hence T_N. The spin arrangements discussed above would require that $ZnFe_2O_4$ should behave differently from a 3D antiferromagnetic system. From the observed variation of H_{hf} versus T data we have obtained the value of the critical exponent β as 0·125. This value supports the idea that $ZnFe_2O_4$ is close to a 2D antiferromagnet (Baker 1961). The data on magnetic susceptibility (Lotgering 1966) indicating a broad maximum near the transition region and the observed magnetic moment reduction of 15% at 0 K (König *et al* 1970; Boucher *et al* 1970) are also in agreement (Katsumota 1977; Johnson 1981) with a lower dimensionality of the magnetic ordering of $ZnFe_2O_4$.

3. Conclusion

The present available data on $ZnFe_2O_4$ show that the Sp-hybridization of oxygen ion orbitals leads to significant changes in the strength and isotropy of the 90° Fe^{3+}–Fe^{3+}

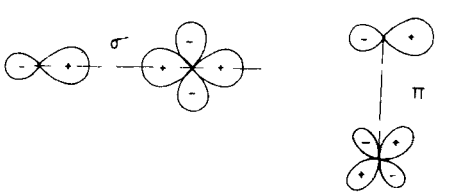

Figure 4. The $b_{\pi\sigma}$ and $b_{\sigma\sigma'}$ transfer integrals after hybridization.

superexchange interaction. The observed magnetic ordering has been attributed to these changes.

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References

Arrot A and Goldman J E 1955 *Phys. Rev.* **98** 1201
Baker G A Jr 1961 *Phys. Rev.* **124** 768
Bethe H 1933 *Handbuch der Physik* **24** Pt2 Ferromagnetism 443
Boucher B, Buhl R and Perrin M 1970 *Phys. Status. Solidi.* **40** 171
Edger F, Westrum J R and Grimes D M 1957 *J. Phys. Chem. Solids.* **3** 44
Edger F, Westrum J R and Grimes D M 1958 *J. Phys. Chem. Sol.* **6** 280
Hartmann-Boutron F and Imbert P 1968 *J. Appl. Phys.* **39** 775
Johnson J E 1981 *Proc. Int. Conf. Mössbauer effect*, Jaipur, India
Katsumota K 1957 *Solid State Commun.* **23** 481
König U, Bertaut E F, Gros Y, Mitrikov M and Chol G 1970 *Solid State Commun.* **8** 759
Lotgering F K 1966 *J. Phys. Chem. Solids* **27** 139
Miyahara Y and Sai F 1976 *J. Phys. Soc. Jpn* **41** 1522
Slater J C 1930 *Phys. Rev.* **36** 57
Srivastava C M, Srinivasan G and Nanadikar N G 1979 *Phys. Rev.* **B19** 499