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To cite this version:

HAL Id: jpa-00213920
https://hal.archives-ouvertes.fr/jpa-00213920
Submitted on 1 Jan 1971

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NEUTRON DIFFRACTION AND MÖSSBAUER STUDIES OF ZINC FERRITE

by U. KÖNIG (*), E. F. BERTAUT (**), Y. GROS (***) and G. CHOL (****)

Résumé. — On montre par diffraction neutronique et spectrométrie Mössbauer que la formation d'ordre magnétique à longue distance dans le ferrite de zinc dépend de façon sensible de la teneur en fer bivalent. Les données expérimentales sont en faveur d'un modèle de structure magnétique non colinéaire.

Abstract. — It is shown by neutron diffraction and Mössbauer spectrometry that the formation of a long range magnetic order in zinc ferrite depends sensitively on the content of divalent iron. The experimental data favour a non collinear model of the magnetic structure.

Zinc ferrite is a normal spinel with the tetrahedral A sites occupied by \( \text{Zn}^{2+} \) ions and the octahedral B sites occupied by \( \text{Fe}^{3+} \) ions. Any magnetic order therefore is due to the nearest or more distant B-B interactions of the \( \text{Fe}^{3+} \) ions.

Measurements of the susceptibility [1], of the specific heat [2], studies by neutron diffraction [3] and Mössbauer spectrometry [4] have shown that below 10 \(^0\text{K}\) an antiferromagnetic order appears. The neutron diffraction patterns of J. M. Hastings and L. M. Corliss [3] and recently also one of M. K. Fayek et al. [5] have only shown broad magnetic lines, typical for short range order. From these experiments there was some doubt that a long range order can exist in ZnFe\(_2\)O\(_4\) [6].

We show first that the formation of the magnetic order depends very sensitively on the stoichiometry of the sample, especially from the \( \text{Fe}^{2+} \) content.

Figure 1 (left) shows Mössbauer spectra of a sample with a content of 0.002 \( \text{Fe}^{2+} \) per molecule. We observe well shaped Zeeman spectra, indicating a long range magnetic order up to temperatures just below the Neel point.

Figure 1 (right) also shows Mössbauer spectra of ZnFe\(_2\)O\(_4\) with a content of 0.01 \( \text{Fe}^{2+} \) per molecule. In this sample line broadenings occur and at 10 \(^0\text{K}\) we observe a superparamagnetic behaviour.

This is in agreement with neutron diffraction results (Fig. 2). The sample with small \( \text{Fe}^{2+} \) content shows well resolved and strong magnetic peaks, whereas the sample with a content of 0.01 \( \text{Fe}^{2+} \) shows only broad lines, thus indicating short range order.

These observations may explain the published results mentioned above.

Recently, B. Boucher et al. [7] independently confirmed our experimental results. Their neutron diffraction pattern of a sample with small \( \text{Fe}^{2+} \) content agrees very well with our measurements.

It may be mentioned that the neutron diffraction patterns of the two samples of figure 2 show no difference at room temperature.

The results of our investigation of the sample with low \( \text{Fe}^{2+} \) content have been reported in [8]. The Mössbauer measurements have shown a deviation of the \( H(T) \) vs. \( T \)-plot from the Brillouin B (\( S \)) behaviour and the occurrence of a quadrupolar shift below the
Neel point, indicating a non-collinear magnetic structure.

The magnetic peaks of the liquid helium temperature neutron diffraction diagram (Fig. 2) can be indexed in a tetragonal cell \( a = b = 8.43 \) Å and \( c = 16.86 \) Å, as suggested by M. K. Fayek et al. [5]. The selection rule of the magnetic lines \( h_1 + h_2 = 2n + 1 \) and \( h_3 = 2n + 1 \) indicates a propagation vector of the magnetic mode \( \mathbf{k} = [10 \frac{1}{2}] \). In order to determine the magnetic structure, we have used the theory of magnetic modes as given by representation analysis [9]. If we look for the symmetry operation of highest order which leaves \( \mathbf{k} \) invariant modulo a vector of the reciprocal \( F \)-centered spinel lattice, we find the rotation inversion \( 4 \).

By inspection of the irreducible representations of the space groupe \( F \bar{4} \), we find a non-collinear arrangement as shown in figure 3. Collinear spin arrangements non parallel to \( O_z \) would require a spin Hamiltonian of an order higher than two.

An essential feature of the model are parallel \( z \)-components of groups of four neighbouring iron spins. Our model agrees with the first of the three models given by B. Boucher et al., but they predict zero \( z \)-components from the experimental evidence.

We obtained the best agreement between observed and calculated magnetic intensities for \( s_z = s_{zy} \). An arrangement along the \( c \)-axis can be ruled out, but for \( s_z = 0 \) the \( R \)-factor increases only slightly, so that a clear decision between the model \( s_z = s_{zy} \) and \( s_z = 0 \) cannot be made on the basis of the present experimental data.

We observed a low magnetic moment of 4.2 \( \mu_B \), extrapolated to 0 K, which may be explained by covalency effects and partially by competitions of short range order scattering (Fig. 2). Evidence that the electron configuration of \( \text{Fe}^{3+} \) changes when crossing the Neel temperature is also given by the observation of a discontinuity of the isomeric shift of \( -0.03 \text{ mm/s} \).

X-ray investigations have shown that any detectable tetragonal distortion should be smaller than 0.01 Å.

References