MÖSSBAUER STUDY OF FERRIMAGNETIC ORDERING IN NICKEL FERRITE
AND CHROMIUM-SUBSTITUTED NICKEL FERRITE

J. Chappert* and R. B. Frankel
National Magnet Laboratory,† Massachusetts Institute of Technology, Cambridge, Massachusetts
(Received 24 July 1967)

Mössbauer-effect measurements in external magnetic fields show that the magnetic
structure of ferrimagnetic NiFe₂O₄ is the collinear Néel type. NiFe₀.₃Cr₁.₇O₄ is shown
to have a triangular structure with θₐ = 20±10° and θᵦ = 50±4°.

In a recent Letter, Kedem and Rothem have presented Mössbauer data which they propose
is evidence for a Yafet-Kittel triangular spin arrangement in the ferrimagnetic spinel NiFe₂O₄.
Their conclusions are in sharp disagreement with the results of susceptibility measurements
by Jacobs, who proposed a Néel collinear model for this material. We report here Mössbauer measurements in external magnetic fields which provide conclusive evidence for the Néel model and thus support the conclusions drawn by Jacobs. In addition, we show that the chromium substituted ferrite NiFe₀.₃Cr₁.₇O₄ is consistent with a Yafet-Kittel model.

Many of the magnetic properties of the ferrimagnetic spinel compounds M₂₊N₂⁺O₄ are
well understood on the basis of the Néel collinear model. However, for spinels with large
amounts of chromium, the spontaneous magnetization is lower than the expected from this
model and is usually interpreted in terms of

the Yafet-Kittel triangular arrangement in which each tetrahedral A and octahedral B sublattice
is divided into two sub-sublattices; the resultant moments of the two triangular sublattices
are antiparallel. Experimental evidence for the Yafet-Kittel model has been established
by high-field susceptibility measurements and neutron-diffraction experiments. Previous nmr and Mössbauer studies of NiFe₂O₄ indicate two different hyperfine fields, corresponding to the iron ions on the A sites and the B sites. However, Kedem and Rothem have concluded, mainly from the width of the Mössbauer lines, that there are four hyperfine fields and that this observation constituted experimental evidence for the Yafet-Kittel model.

Our samples were made by firing mixed oxides including Fe₂O₃ enriched in Fe⁵⁷ in a platinum crucible at 1200°C in air for ten hours; the resulting product was then ground to a pow-
der, heated in a nitrogen atmosphere at 1200°C for 12 hours, and then allowed to cool slowly. X-ray diffraction analysis confirmed the spinel structure and the absence of other phases.

The Mössbauer experiments were performed using a conventional constant acceleration electromechanical drive system together with a multichannel analyzer for collecting and storing the data. The magnetic field was produced by a Nb$_3$Sn superconducting solenoid operating in the persistent mode up to 75 kOe.

Most of the experiments were carried out with the magnetic field applied along the $\gamma$-ray propagation direction. If the moments are collinear with the field, the polarization conditions require the disappearance of the $\Delta m = 0$ lines in the hyperfine pattern. Figure 1 (a) shows the results for NiFe$_2$O$_4$ at 4.2°K.

The zero field spectrum indicates two hyperfine fields $H_{hf}(A)$ and $H_{hf}(B)$, the widths of the lines are greater than those obtained with an $\alpha$-Fe$_2$O$_3$ absorber, but this is expected in a powder sample. The effect of applying a longitudinal field to the NiFe$_2$O$_4$ sample is also shown in Fig. 1(a); one observes the disappearance of the $\Delta m = 0$ lines at about $H_0 = 12$ kOe, and a further increase of the external field splits the outer $\Delta m = \pm 1$ lines into doublets of equal intensity, corresponding to the spin-up and spin-down sublattices. The measured fields at the nuclei $H_n$ for the sublattices $T = 4.2°K$ and $H_0 = 70$ kOe are $-574 \pm 5$ kOe ($A$ site) and $-477 \pm 5$ kOe ($B$ site), and using the relation

$$H_n(Z) = H_{hf}(Z) \pm H_0, \quad Z = (A, B),$$

where $H_{hf}(Z)$ are the hyperfine fields, we find $H_{hf}(A) = -504 \pm 5$ kOe and $H_{hf}(B) = -547 \pm 5$ kOe in agreement with the hyperfine fields measured at $H_0 = 0$: $-506 \pm 5$ kOe ($A$) and $-548 \pm 5$ kOe ($B$). These observations constitute definitive evidence for the Neél model in NiFe$_2$O$_4$. A 0.005-in.-thick NiFe$_2$O$_4$ single crystal, the plane of which is perpendicular to the [100], was also studied. Application of a small transverse field (1.25 kOe) in the plane of the absorber fully aligned the moments as evidenced by the relative intensities of the $\Delta m = 0$ and $\Delta m = \pm 1$ hyperfine lines, indicating very low anisotropy. A portion of the crystal was crushed to make a polycrystalline absorber and was studied in high external magnetic fields; the results were identical with the powder spectra.

The hyperfine spectra of NiFe$_{0.3}$Cr$_{1.7}$O$_4$ are shown in Fig. 1(b). It has been generally supposed$^{11,12}$ that Fe$^{3+}$ ions are situated on the $A$ sites. However, the 70-kOe spectrum [Fig. 1(b)] indicates that approximately $\frac{1}{3}$ of the Fe$^{3+}$ ions are on the $B$ sites. The hyperfine fields for the two sites overlap at 4.2°K in zero external field and have the value $-498 \pm 5$ kOe. Unlike the NiFe$_2$O$_4$, at $H_0 = 70$ kOe the $\Delta m = 0$ lines [lines $\alpha$ in Fig. 1(b)] are still relatively intense and the $\Delta m = \pm 1$ lines ($\beta$) do not correspond to Eq. (1). Assuming no large magnetocrystalline anisotropy,$^9$ this may be explained by a Yafet-Kittel arrangement in which the spins on each sublattice $Z = (A, B)$ make an angle $\theta_Z$ with the external field direction. For this model, the field at the nucleus $H_n(Z)$ in an external field $H_0$ is given by

$$H_n(Z) = H_{hf}(Z) - 2H_0 \cos \theta_Z - H_0^{1/2}.$$

From the observed spectrum we find $\theta_A = 20 \pm 10°$ and $\theta_B = 50 \pm 4°$. Using these values of
we are able to calculate the expected values of the relative intensities of the \( \Delta m = 0 \) lines. These values (\( x = 0.3 \) for the \( A \) site, 1.8 for the \( B \) site) are in good agreement with the fit indicated for the 70-kOe spectrum of Fig. 1(b). Taking into account the presence of iron in the \( B \) site, one finds that the spontaneous moment calculated for such a model is equal to 1.3 ± 0.5 \( \mu_B \), which is significantly lower than the moment expected from a Néel model (3.2 \( \mu_B \)). Furthermore, the \( B \) site moment is dominant in agreement with susceptibility data. We note that the observation of only two hyperfine fields is consistent with both the Yafet-Kittel as well as the Néel model and is therefore not sufficient to distinguish between these models.

We conclude that the magnetic structure of ferrimagnetic NiFe\(_2\)O\(_4\) is of the collinear Néel type. An example of a Yafet-Kittel structure is shown for the chromium substituted NiFe\(_{0.3}\)Cr\(_{1.7}\)O\(_4\).

We thank Professor A. J. Freeman for his interest and stimulation and Professor E. F. Bertaut, Dr. N. A. Blum, Dr. S. Foner, and Dr. I. S. Jacobs for useful discussions. We gratefully acknowledge Mr. J. E. C. Williams of the National Magnet Laboratory for design and construction of the superconducting magnet.

---

*On leave from the Centre d'Etudes Nucléaires, Grenoble, France. Supported by Commissariat à l'Energie Atomique, France.

†Supported by the U. S. Air Force Office of Scientific Research.