

Nuclear magnetic resonance of O^{17} in ferrites

N. M. Kovtun, A. M. Kotel'va, and A. A. Shemyakov

Donetsk Physicotechnical Institute

(Submitted 2 February 1987)

Pis'ma Zh. Eksp. Teor. Fiz. **45**, No. 5, 255–257 (10 March 1987)

The NMR spectra of O^{17} in magnetically ordered compounds have been measured for the first time. The isotropic and anisotropic parts of the local field at the O^{17} nuclei in $MnFe_2O_4$ have been determined at 1.8 K: 113.7 and 6.6 kOe, respectively.

A study of the local fields at the nuclei of anions in magnetically ordered compounds is important both for reaching an understanding of the nature of the appearance of these fields and for determining the role played by ligand ions in the exchange interaction. However, there has been no previous observation of NMR at oxygen nuclei in magnetically ordered compounds, apparently because of the extremely small natural abundance of the isotope O^{17} , which has a nuclear magnetic moment.

In this letter we report the first results of measurements of the local magnetic fields at oxygen nuclei in the magnetically ordered spinels $MnFe_2O_4$ and $Li_{0.5}Fe_{2.5}O_4$. The measurements were taken by an NMR method on a spin-echo spectrometer at liquid-helium temperatures. The single-crystal and polycrystalline samples of these spinels, with the natural abundance of the isotope O^{17} , were certified as being of single phase.

In the NMR spectra of $MnFe_2O_4$, along with the known lines of the ions Fe^{3+} (68–72 MHz), Mn^{3+} (250–420 MHz), and Mn^{2+} (580–600 MHz), we find a previously unobserved line at 58.0 MHz. The intensity of this line is two orders of magnitude lower than that of the NMR lines of Fe^{3+} .

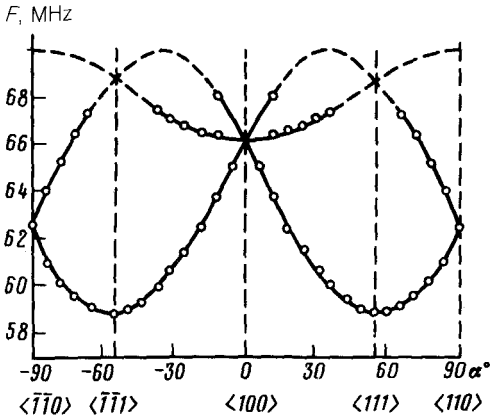


FIG. 1. Angular dependence of the NMR frequencies of Mn^{2+} . Here α is the angle between \mathbf{M} and $\langle 100 \rangle$.

To determine the particular nuclei to whose ions this NMR line belongs, we determined the local symmetry of these ions and their nuclear gyromagnetic ratio. For this purpose, we measured the resonant NMR frequencies to find their behavior as we varied the strength of the external magnetic field and its direction with respect to the crystallographic axes. The angular dependence was measured at 1.8 K with a cylindrical single-crystal sample of $MnFe_2O_4$, in which one of the $\langle 110 \rangle$ axes coincided with the axis of the cylinder. The sample was rotated around the axis of the cylinder in a 5-kOe magnetic field, which was directed perpendicular to this axis. Since the magnitude of this field exceeds the saturation field along the hard magnetization axis, a rotation of the cylinder resulted in a rotation of the magnetization vector in the (100) plane.

Figure 1 shows the angular dependence of the resonant NMR frequencies of the ions studied. It was not possible to take measurements above 68 MHz because of the frequency overlap with the NMR lines of Fe^{3+} , for which the angular dependence is shown in Fig. 2. Comparison of Figs. 1 and 2 shows that the local symmetry of the

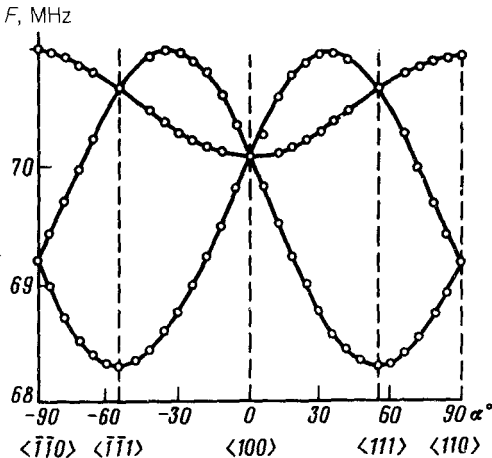


FIG. 2. Angular dependence of the NMR frequencies of Fe^{3+} in octahedral positions. Here α is the angle between \mathbf{M} and $\langle 100 \rangle$.

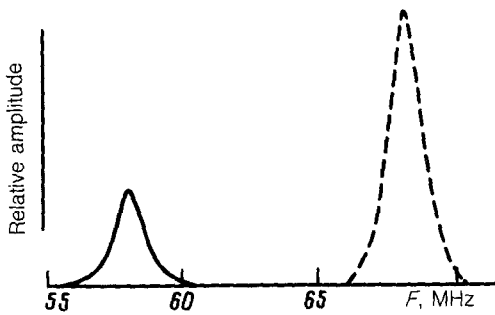


FIG. 3. The NMR spectrum of ^{17}O in MnFe_2O_4 .

ions under study is the same as that of the Fe^{3+} ions. We can therefore extrapolate the angular dependence of the resonant frequencies of the ions under study above 68 MHz (the results of this extrapolation are shown by the dashed line in Fig. 1), and we can also reconstruct the complete NMR spectrum of these ions in a zero external field (Fig. 3).

The angular dependence of the NMR frequencies of Fe^{3+} ions, shown in Fig. 2, corresponds to ions which have an axial local symmetry with threshold axes directed along the $\langle 111 \rangle$ axes of the crystal.¹ Since the angular dependence of the NMR frequencies of Fe^{3+} is completely identical to that of the ions under study, we can assume that the latter ions have the same local symmetry. In MnFe_2O_4 , the $\langle 111 \rangle$ axes are trigonal symmetry axes only for ions in octahedral positions and for oxygen ions.

To determine whether the observed line belongs to oxygen ions or to divalent iron ions in octahedral positions, we measured the nuclear gyromagnetic ratio. To avoid an error in the determination of this gyromagnetic ratio for these nuclei which would stem from the dependence of the NMR frequency on the angle between the direction of the external field and the crystallographic axes (Fig. 1), we oriented the sample precisely along a $\langle 111 \rangle$ axis, since the $\langle 111 \rangle$ axes are easy-magnetization axes at liquid-helium temperatures. The resonant NMR frequency of the ions under study increases with increasing external magnetic field, providing evidence that the direction of the local field at the nuclei of these ions is the same as the magnetization direction of the crystal. The measured value of the nuclear gyromagnetic ratio turns out to be 0.58 ± 0.03 MHz/kOe which corresponds to the tabulated value of this ratio for ^{17}O nuclei (0.5772 MHz/kOe).

The magnitude of the nuclear gyromagnetic ratio and the direction of the local symmetry axes of the ions under study thus provide evidence that the line which we observe at the frequency 58.0 MHz belongs to oxygen ions.

NMR signals corresponding to ^{17}O nuclei were also observed in the lithium ferrite $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ at the frequencies 47.6 and 48.6 MHz.

The angular dependence of the resonant NMR frequencies of ^{17}O , shown in Fig. 1, can be described by the well-known expression²

$$f = f_{\text{is}} + f_{\text{anis}} (1 - 3 \cos^2 \theta),$$

where f_{is} and f_{anis} are proportional to the isotropic and anisotropic components, respectively, of the local field at the O^{17} nuclei, and θ is the angle between the local trigonal symmetry axis of the particular ion and the magnetization of the crystal. Working from the experimental angular dependence of the NMR frequencies of O^{17} and this expression, we find the components of the local field to be $H_{\text{is}} = 113.7$ kOe, and $H_{\text{anis}} = 6.6$ kOe.

We wish to thank V. D. Doroshev for a discussion of the experimental results and for useful comments.

¹V. D. Doroshev and V. A. Klochan, *Phys. Status Solidi A* **9**, 679 (1972).

²C. Robert and F. Hartman-Botron, *J. Phys. Rad.* **23**, 574 (1962).

Translated by Dave Parsons