

at 15 Å, and a gently sloping maximum at 40 Å. No definite statements can be made concerning the behavior of the curve at large thicknesses, owing to the small number of points in this region. It is possible that the curve remains oscillatory at these thicknesses. In our experiments we observed a definite correlation between the critical temperatures of the samples and their resistivities in the normal state.

The influence of the coating on T_c of thin films was investigated by many authors [2 - 5]. As a rule, a small ($\sim 0.1^\circ\text{K}$) rise or fall in the critical temperature, practically independent of the coating thickness, was observed. The change of T_c was attributed in these papers to a decrease in the electron concentration, owing to the escape of electrons into the barrier layer and formation of the contact potential difference between the film and the coating.

Naugle [5], in a study of the influence of germanium coating on the critical temperature of thallium films, obtained a dependence on the coating thickness with a maximum at a Ge layer thickness of 10 Å. The rise in the critical temperature at the maximum was only 0.1°K .

Neither the oscillating $T_c = f(d_c)$ curve which we obtained, with a very narrow first maximum having an appreciable amplitude ($\Delta T_c = 1.4^\circ\text{K}$) nor the non-monotonic $T_c = f(d_{\text{Ge}})$ curve observed in [5] can be attributed to a contact potential difference at the boundary between the metallic film and the coating. It can be assumed that in all probability an important role is played here by changes occurring in the electron or phonon spectrum of the system comprising the metallic film and the coating when the coating thickness amounts to several monatomic layers.

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NUCLEAR ECHO IN THE TRANSPARENT ANTIFERROMAGNET FeF_3

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Iron trifluoride FeF_3 is an antiferromagnet that has a weak ferromagnetic moment [1, 2]. The crystal belongs to the space group $R\bar{3}C$, the elementary chemical cell contains two molecular units, and the chemical and magnetic cells coincide [3]. The iron ions are in several distorted octahedra made up of the fluorine ions. The Neel temperature lies near $362 - 363^\circ\text{K}$ [4, 5]. FeF_3 single crystals are transparent in the visible part of the spectrum [6].

We present here the first report of an investigation of nuclear magnetic resonance in FeF_3 . The sample was an assembly of small (~ 0.1 mm) single

crystals with a total volume of $\sim 0.5 \text{ cm}^3$. The samples were prepared by T.G. Petrov and co-workers at the Leningrad State University.

The magnetic properties of FeF_3 are very similar to those of FeBO_3 [6]. Both compounds are weak ferromagnets with "easy plane" isotropy. The magnetic moments of the sublattices lie in the basal plane perpendicular to the threefold axis.

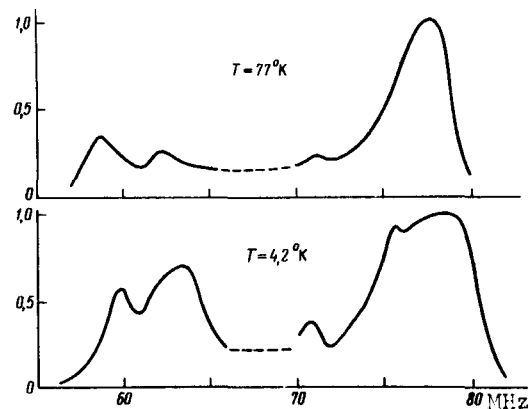
Taking into account the similarity of the magnetic properties, we expected to observe a nuclear-echo signal from the Fe^{57} nuclei, analogous to the signal which we observed in FeBO_3 [7], i.e., a very narrow and intense NMR line in the band from 45 to 80 MHz from room temperature to 12.2°K. We actually observed at $T = 291^\circ\text{K}$ a rather intense and narrow (<100 kHz) echo signal at 55.7 MHz.

It is natural to attribute this signal to the Fe^{57} nuclei. Such an assumption agrees with Mossbauer effect data [5]. The local magnetic field corresponding to the Fe^{57} NMR frequency 55.7 MHz is 404.2 kOe. This value is close to the 415 kOe determined from the data of [5]. When the temperature was lowered, however, we observed a new rather unexpected echo spectrum, the form of which is shown for two temperatures in the figure.

As seen from the figure, the spectrum extends from 55 to 80 MHz. (The data in the 70 - 75 MHz interval are shown dashed, since the measurements were made in the presence of radio interference.) We measured the intensity and the shape of the spectrum as functions of the external magnetic field at $T = 77^\circ\text{K}$. When an external field was superimposed, the signal intensity decreased appreciably and the echo could no longer be observed on the oscilloscope at a field 2.5 - 3 kOe. A change in shape and a broadening of the spectrum were observed with increasing field. The edges of the spectrum broadened at a rate 1.5 kHz/Oe.

In addition to investigations in the magnetic field, measurements were made of the nuclear relaxation, and their results are given in the table.

$T, ^\circ\text{K}$	f, MHz	T_1, sec	T_2, msec	Nucleus
4.2	75.0	10.000	1.00	F^{19}
	64.0	1.000	0.25	
77.0	75.0	0.004	0.10	
	64.0	0.003	0.15	
291.0	55.7	-	0.08	Fe^{57}



Frequency dependence of the intensity of the nuclear echo of F^{19} in FeF_3 in a zero magnetic field at liquid-nitrogen and liquid-helium temperature.

We assume that the echo spectra observed at low temperatures are due to F^{19} and not to Fe^{57} . The grounds for this assumption are as follows. First, if we assume that the spectrum belongs to the iron nuclei, then the width of the spectrum cannot be explained. The iron ions occupy crystallographically equivalent positions, so that there is no reason for the appearance of several NMR lines, and it is not realistic to assume that one NMR line of Fe^{57} has a width of 30 MHz, since this interval greatly exceeds the widths of the single

NMR lines of iron in the experiments known to date. We note at the same time that at high (room) temperatures the echo signal agrees fully with the typical NMR parameters of Fe^{57} .

Second, the integrated intensity of the signal is too large to be caused by the Fe^{57} nuclei, which have a natural isotope concentration of only 2.2°.

A third reason lies in the behavior of the spectrum width in an external magnetic field. The shift of the iron NMR lines by the external field cannot occur at a rate faster than 137.8 Hz/Oe, since this is precisely the value of the gyromagnetic ratio for Fe^{57} , but the experimentally observed shifts of the line edges have a rate of 1500 Hz/Oe.

At the same time, all these factors can be easily explained if it is assumed that the signal is due to the fluorine nuclei. The high signal intensity is characteristic of fluorine nuclei with 100% of the F^{19} isotope and having a large gyromagnetic ratio (4 kHz/Oe). The observed line width is easily explained by the fact that all six fluorine ions in the cell occupy magnetically non-equivalent positions, and consequently the spectrum of the magnetic field is, in the general case, a superposition of six NMR lines. In addition, fluorine is characterized by the presence of dipole and anisotropic hyperfine interaction [8], which results in considerable broadening in a polycrystal, as well as in the presence of a domain structure.

The last reason is that the shift of the spectral line edges for fluorine can occur at a rate reaching 4 kHz/Oe, which does not disagree with experiment. A lower shift rate is perfectly feasible if the local hyperfine field is directed at an angle to the external field H_0 .

The local fields at the fluorine nuclei range from 13 to 20 kOe at 4.2°K.

The presence of large local fields at the fluorine nuclei points unambiguously to decompensation of the electron shells of the F^- ion, i.e., to a transfer of the spin density from the Fe^{3+} ions to the F^- ions. The gain of the radio-frequency field [8] is $\eta \approx 10^3$ at 77°K for F^{19} and $\eta \approx 10^4$ at 291°K for Fe^{57} .

Attention is called to the strong dependence of the transverse-relaxation time (T_2) on the temperature for the fluorine echo. This dependence explains why the signal from fluorine is not observed at room temperature. At high temperatures the transverse relaxation is apparently so rapid that it is impossible to observe the echo at the delays, of the order of $(30 - 40) \times 10^{-6}$ sec, which are permissible in our apparatus. At the same time, these conditions are acceptable for the observation of a single signal from Fe^{57} . At low temperatures, observation of the signal from iron is hindered by the powerful signal from fluorine, which is in the same frequency range.

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