SOVIET PHYSICS JETP VOLUME 34, NUMBER 6 JUNE, 1972

Fe^{57} NMR Due to Domain-Boundary Oscillations in Hydrothermal Crystals of the Weak Ferromagnetic Substance $YFeO_3$[1]

A. V. Zalesskiĭ, A. N. Lobachev, L. N. Dem'yanets, A. N. Ivashchenko, O. K. Mel'nikov, and T. G. Lebedeva

Crystallography Institute, USSR Academy of Sciences

Submitted June 29, 1971

Zh. Eksp. Teor. Fiz. **61**, 2337–2346 (December, 1972)

The NMR of Fe^{57} in a zero field is investigated at temperatures between 77 and 400°K in large $YFeO_3$ single crystals grown by the hydrothermal technique. The effect of crystallographic orientation of the crystals with respect to external stationary or radio-frequency fields on the NMR intensity and frequency is investigated. It is shown that the two NMR lines previously found with frequencies ν_d and ν_w correspond to Fe^{57} nuclei in the domain boundaries. Thus in fields which saturate the magnetization of the crystal, both signals disappear simultaneously. Appearance of domain boundaries in a coercive field induces a repeated appearance of the signals. It is shown that resonances at frequencies ν_d and ν_w correspond to the edges of the complex NMR absorption band produced as a result of variation of the hyperfine field of Fe^{57} nuclei from a value H_a (along the a axis at the edges of the domain boundary) to H_c (along the c axis in the middle of the boundary) and $H_a > H_c$. The frequency ν_w is independent of the magnitude and direction of the external stationary field H in the ab plane. On the other hand, for $H \| a$, a shift of the high-frequency line of frequency $\nu_d = \gamma_n H_a / 2\pi$ toward lower frequencies which is proportional to $H_a - H$ has been detected. The lines coincide for $H_a - H = H_c$ and both lines disappear for $H_a - H < H_c$. This effect has never been explained before. Similar cases of NMR frequency splitting within domain boundaries found in other ferromagnetic materials are discussed.

1. INTRODUCTION

In [1] one of us (A.V.Z.) reported observation in yttrium orthoferrite crystals of two resonant NMR lines of Fe^{57} having different temperature dependences. It was proposed that the higher-frequency line corresponds to the NMR frequency of the Fe^{57} nuclei in the domains, and the lower-frequency line to the NMR frequency in the domain boundaries, both signals being due to the gain resulting from the oscillations of the domain boundaries. The $YFeO_3$ crystals used for the NMR observations measured 1–3 mm and were synthesized under hydrothermal conditions. Subsequently, sufficiently large $YFeO_3$ single crystals were grown and it became possible to obtain more profound information on the nature of the NMR in the $YFeO_3$ by investigating individual crystals differently oriented relative to the radio-frequency (RF) and constant external fields. We present in this paper the results of such an investigation.

Concerning the crystal structure of $YFeO_3$ and its magnetic properties, the authors refer the reader to the rather extensive literature on orthoferrites (see, for example, the review [2]).

2. SAMPLES AND EXPERIMENTAL PROCEDURE

1. Production of $YFeO_3$ crystals. Large $YFeO_3$ crystals were grown under hydrothermal conditions. The primers were YFO_3 crystals measuring 1–3 mm, synthesized by spontaneous crystallization of a mixture of the oxides Y_2O_3 and Fe_2O_3 in high-temperature aqueous solutions of KOH. The solvents were aqueous solutions of sodium and potassium hydroxide at room temperature. The yttrium orthoferrite was characterized by a positive solubility coefficient, so that the direct temperature drop method was used. Special autoclaves lined with silver or platinum were used and made it possible to regulate the oxidation-reduction potential of the system. The crystal growth conditions were close to those described in [3]. The initial charge was a mixture of the oxides Y_2O_3 and Fe_2O_3 with natural content of the isotope Fe^{57}. The temperature of the dissolution band was 380–450°C, the temperature drop was 15–50°, and the pressure inside the reactor was 500–1000 atm. The obtained crystals had the following crystallographic shapes: pinacoids $\{100\}$, $\{010\}$, and $\{001\}$, rhombic prisms $\{101\}$ and $\{110\}$, and a rhombic bipyramid $\{111\}$. The ratio of the growth rates of the faces along the crystallographic axes was close to unity. The growth rate reached 0.15 mm per day. The crystals were frequently formed in the form of twins with a common (110) plane.

To investigate the NMR we chose two single crystals weighing 0.55 and 1.35 g and having the following dimensions along the rhombic axes a, b, and c: $4 \times 5 \times 6$ mm and $5 \times 7 \times 8$ mm. The crystal orientation was with the aid of an optical goniometer.

2. NMR observation procedure. The NMR in a zero field was observed with the aid of frequency-modulated spectrometers of the stationary type, such as are used for nuclear quadrupole resonance. Two types of spectrometer were used for this purpose, one designed by the Institute of Radio and Electronics of the U.S.S.R. Academy of Sciences, and the other by the British DECCA RADAR firm. In both spectrometers, the RF generators were superregenerators. The choice of the particular spectrometer depended principally on its design features and was governed by the concrete purposes of the experiment.

In plotting the NMR spectra at low temperatures (from 77° K to room temperature), the coil with the

---

[1] Work performed under contract no. 818/RB for the International Agency for Atomic Energy.

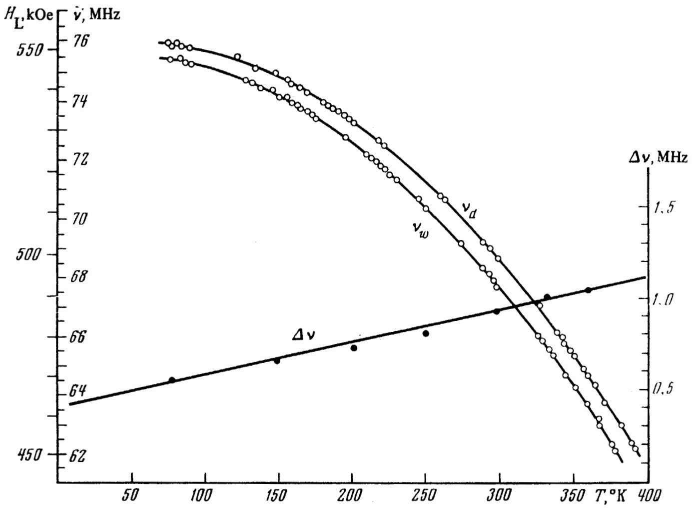

FIG. 1. Temperature dependence of the NMR frequencies ν_d and ν_w, of the corresponding local fields H_L, and of the splitting $\Delta\nu = \nu_d - \nu_w$ in $YFeO_3$.

crystal was placed in a Dewar, whereas above room temperature (up to 120–130° C), an ordinary drying oven was modified. In the latter case, the most effective way of obtaining the best signal-to-noise ratio was to pass through resonance not by varying the frequency but by varying the temperature. The resonance was observed at a constant generator frequency, chosen such that at sufficiently slow rise (or lowering) of the temperature it was possible to cover the resonance region.

To apply weak constant fields (up to 100 Oe) to the crystal, we used a small solenoid. Stronger fields were produced with an electromagnet.

The NMR fields in $YFeO_3$ could be registered by using magnetic modulation in accordance with the principle described in [4] for NMR in hematite. However, in this case there was no gain in signal intensity as compared with frequency modulation.

3. RESULTS OF INVESTIGATION OF NMR IN $YFeO_3$

1. Temperature dependence of the NMR frequencies. The results obtained with the two single crystals coincided fully and confirmed the presence of the two resonant signals of close frequency, which were observed earlier in [9] in a mixture of small crystals. We shall designate by ν_d and by ν_w the higher- and lower-frequency NMR signals, respectively. The temperature dependence of the frequencies ν_d and ν_w, and of the corresponding local fields H_L at the Fe^{57} nuclei in the 77–400°K range are shown in Fig. 1. The experimental frequency difference $\Delta\nu = \nu_d - \nu_w$, shown in the same figure by the black circles, is satisfactorily described by the linear relation $\Delta\nu = (0.44 \pm 0.04) + (1.70 \pm 0.15) \times 10^{-3}\, T$ (straight line in Fig. 1) in the entire interval of employed temperatures.

2. Dependence of NMR intensity on the crystal orientation relative to the RF field h. Both signals have a maximum intensity at $h \parallel c$ (i.e., when h is parallel to the ferromagnetic moment m_s in the domains and to the domain boundaries) and are absent when $h \parallel a$ and $h \parallel b$. Therefore in all the subsequent measurements the RF field was applied parallel to the rhombic axis c. When h is directed at an angle to the c axis, the intensity is determined by the projection of the field h on the c axis.

3. Influence of constant field H, directed along the c axis, on the NMR intensity. In this case H coincides with the direction of m_s in the domains and is parallel to the domain boundaries.

It is known from the literature[5] that $YFeO_3$ crystals become single-domain in fields $H \parallel c$ on the order of 50–100 Oe, and that the single-domain state is retained in them also after the field is turned off. The magnetization and reversal of magnetization of the crystal follow a rectangular hysteresis loop exclusively as a result of the annihilation and creation of 180° domain boundaries parallel to the c axis, in the absence of rotation processes.

The influence of an external field $H \parallel c$ was investigated by two methods. We first wished to trace the influence of the transition of the crystal from the multidomain state to the single-domain state on the intensity of the NMR signals. Therefore the NMR intensity was first measured after keeping the crystal in a field $H \parallel c$ for one minute and turning H off. The field H was then increased in succession. The results are shown in Fig. 2a, from which it is seen that after application of the fields in the intervals 0–80 Oe to a demagnetized crystal, the intensity of the signals is restored (thus evidencing restoration of the initial density of the domain boundaries), whereas after fields 80–85 Oe both signals vanish simultaneously (the crystal has gone over into the single-domain state). The signals again appeared suddenly after application of a certain field of opposite sign with intensity 5–15 Oe, at which an instantaneous "sprouting" of the domain boundaries occurs. With further change of the magnitude and sign of H, the process of change of intensity repeats, although certain ambiguity in the values of the saturating and coercive fields was observed. The intervals of the coercive and saturating fields are shown shaded in Fig. 2.

In the second case, the intensity of the NMR signals was measured in the presence of a constant field $H \parallel c$ that varied in magnitude and in sign (Fig. 2b). The in-

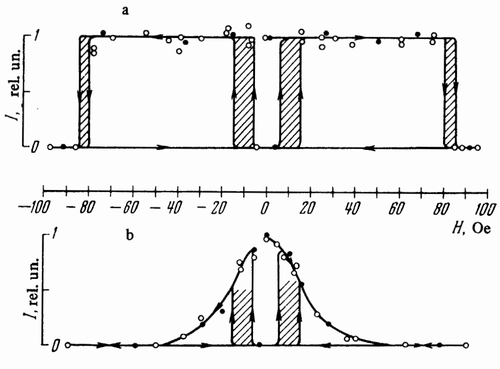

FIG. 2. Intensity I of the signal at the frequencies ν_w (light circles) and ν_d (black circles) at 77°K vs. the magnitude and sign of the constant field H parallel to the c axis. The initial intensities of both signals for a demagnetized crystal are made to coincide and equal unity. Cases a and b correspond to intensity measurements with the field H turned off and on, respectively. The shaded areas correspond to the intervals of saturating and coercive fields obtained after multiple passage along the hysteresis loop.

tensity decreased smoothly with increasing H owing to the decrease of the density of the domain boundaries. Both signals became comparable with the noise in fields on the order of 40 Oe, but, according to Fig. 2a, this field is still not saturating. Therefore, to plot the hysteresis loop of the NMR intensity, the magnitude of the field in each direction was brought up to 90 Oe. The signals were produced at the same values of the coercive fields as in the preceding case, but the previously observed variation in the values of the coercive fields remained in force.

4. Influence of constant fields H, lying in the ab plane, on the NMR intensity. In this case the external field is perpendicular to m_s in the domains, and therefore it should cause no displacement of the boundaries. The character of the decrease of the intensity is determined principally by the component H ∥ c, which is present because of the inaccuracy with which the crystal is oriented and because of the inhomogeneity of the field. It is clear from Fig. 2b that it suffices for this component to exceed 40 Oe in order for both signals to vanish. However, in the case of a very careful orientation of the crystal, when the external field is strictly perpendicular to the domain boundaries, we observed distinct NMR signals in fields up to 8000 Oe.

5. Influence of constant field H in ab plane on the NMR frequencies. In the investigation of NMR in fields H ∥ (ab) at room temperature, we observed a shift of the high-frequency line ν_d towards lower frequencies when H was directed along the rhombic axis a. The resonant frequency v_w remained unchanged in this case. The influence of the field H ∥ a on the frequencies ν_d and ν_w is shown in Fig. 3. Separate signals were observed until the frequency ν_d became equal to ν_w under the influence of the field H ∥ a. The NMR signal vanished when the frequency ν_d shifted beyond the limits of the width of the low-frequency line. The upper part of Fig. 3 shows the experimentally obtained NMR spectra, which show how the coincidence and the vanishing of the signals take place. The dependence of ν_d on H ∥ a satisfies quite well the equation $\nu_d = \gamma_n(H_a - H)/2\pi$, where $H_a = 493$ kOe is the value of the local field for the high-frequency signal at H = 0 and γ_n is the gyromagnetic ratio of the Fe^{57} nuclei ($2\pi/\gamma_n = 7.25$ kOe/MHz). This dependence is shown in Fig. 3 by an inclined straight line.

At H ∥ b, the resonant frequencies ν_d and ν_w do not change. When the field H rotates in the ab plane, the frequency ν_w remains unchanged, and the magnitude of the shift of ν_d is determined by the projection of the field H on the a axis.

6. Line shape. Useful information concerning the nature of the NMR signals in $YFeO_3$ might be obtained from a knowledge of the true shape of the resonance lines. As is well known, the NMR signal obtained with the aid of a superregenerator for lines whose width is comparable with the extinction frequency is a complicated superposition of a central line and sidebands. It is therefore not suitable for an analysis of the line shape. Our attempts to plot the spectra with the aid of a regenerator, which gives an undistorted line shape, turned out to be unsuccessful because of the insufficient sensitivity of the latter. However, we were able to observe distinct NMR signals by lowering the extinction frequency to 5 kHz. With decreasing extinction frequency below 10 kHz, the signal shape ceases to vary. It can be assumed that the line shape observed at such a low extinction frequency approaches the true first derivative, since the width of the resonance line in this case is at least 20 times larger than the extinction frequency. Figure 4a shows the NMR spectrum (first derivative) for $YFeO_3$, obtained at an extinction frequency 5 kHz and a temperature 77°K. The line shape at room temperature can be evaluated from the spectra in Fig. 3. It is seen from Figs. 3 and 4a that the low-frequency signal has a shape reminiscent of dispersion, whereas the high-frequency signal is close to the absorption signal in shape. Figures 4b and 4c will be discussed below.

4. DISCUSSION

The results reported in subsections 2 and 3 of Sec. 3 indicate unambiguously that both of the resonance lines at the frequencies ν_d and ν_w, as assumed in [1], are due to nuclei in domain boundaries that oscillate under

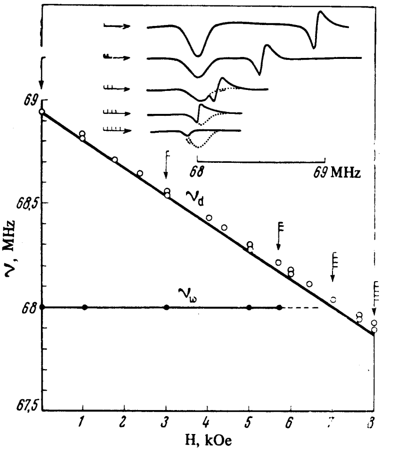

FIG. 3. Dependence of the frequencies ν_d and ν_w at 294°K on the constant field H directed along the a axis. The upper part of the figure shows the NMR spectra (first derivative) obtained at the field values marked in the figure by the vertical arrows.

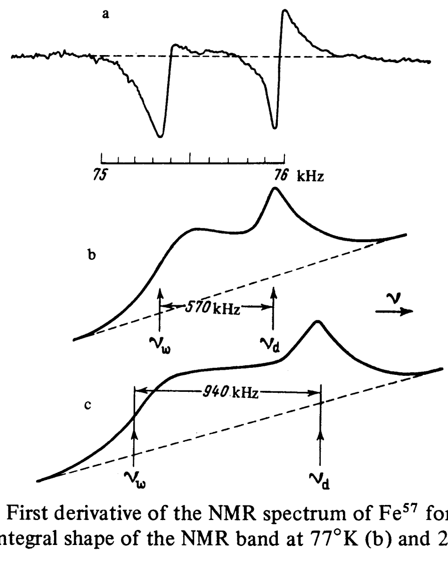

FIG. 4. First derivative of the NMR spectrum of Fe^{57} for $YFeO_3$ at 77°K (a), integral shape of the NMR band at 77°K (b) and 294°K (c).

the influence of the RF field. The observed hysteresis of the intensity and the synchronism in the behavior of the signals upon reversal of magnetization can be attributed only to the creation and annihilation of domain boundaries, namely, when the crystal is magnetized to saturation and there are no domain boundaries, neither signal is present; the appearance of domain boundaries in a coercive field immediately causes signals to appear. It is universally known that, on the one hand, the domain boundaries in orthoferrites have a high mobility and, on the other hand, that there are no rotation processes even in relatively strong fields. One can therefore hardly expect any NMR enhancement mechanism other than enhancement in the domain boundaries.

In order to understand the cause of the occurrence of two NMR lines, it is necessary to see how the local field H_L at the nuclei, which determines the NMR frequency, varies in the transition layer between neighboring domains. To this end, we assume domain boundaries of a type in which the antiferromagnetism axis (OA) rotates in the plane ac, since only such a boundary structure, as will be shown below, agrees with the results reported in subsection 5 of Sec. 3 (the possibility of another structure of a transition layer in orthoferrites has been theoretically demonstrated when OA rotates in the ab plane and m_s vanishes at the center of the boundary.[6]

In rhombic-symmetry crystals, to which $YFeO_3$ belongs, there are three possible principal values of the local (or hyperfine) field H_a, H_b, and H_c along the directions of the axes a, b, and c, corresponding to the three principal values of the components of the hyperfine fine interaction tensor A_{ij}. Since rotation of the spins is accompanied by a change of the hyperfine field from H_a at the edge of the domain boundary to H_c at its center, the NMR frequency will also change from $\nu_d = \gamma_n H_a/2\pi$ corresponding to the NMR frequency in the domain to $\nu_w = \gamma_n H_c/2\pi$ at the center of the domain boundary. The difference between the frequencies can also be influenced by the dipole field applied by the surrounding spin moments F^{3+} (rhombic surrounding) and having different projections on the hyperfine field at the edges and at the center of the domain boundary. Thus, nuclear resonance in domain boundaries corresponds to a certain resonance-frequency band, contained between ν_d and ν_w.

Turov, Tankeev, and Kurkin[7] have shown that for an analysis of the NMR absorption spectrum from the nuclei in the domain boundaries it is necessary to take into account the damping of the "intraboundary" magnons. Such an allowance causes the local width of the NMR line at the boundary, δ_n, to become a function of the angle θ that determines the change of the direction of the spins in the boundary: $\delta_n = \delta_{w1}\sin^2\theta + \delta_{w2}\sin^4\theta + \delta_d$, where δ_d is the line width for nuclei in the domains, and δ_{w1} and δ_{w2} are two additional contributions for the nuclei at the center of the boundary, due to the scattering of the "intraboundary" magnons. The latter play the principal role in the line broadening for nuclei in the domain boundary ($\delta_{w1} + \delta_{w2} \gg \delta_d$). Under definite conditions, which depend on the NMR frequency difference between the domain and the center of the boundary $\Delta\nu = \nu_d - \nu_w$ and on the parameters of the broadening of δ_d, δ_{w1}, and δ_{w2}, separate peaks at frequencies ν_d and ν_w can appear on absorption and dispersion curves and have widths of the order of $\Delta\nu$. It should be recognized that the resonant line for nuclei in the domain boundaries constitutes a mixture of dispersion and absorption, and that the degree of the displacement β, strictly speaking, is also a function of θ (if for no other reason than the change in the gain inside the boundary).

By integrating the experimental shape of the first derivative, we obtained the approximate shape shown in Figs. 4b and 4c for the nuclear resonance absorption band in $YFeO_3$ at temperatures 77 and 294°K. The obtained band shape is very similar to the absorption curves given in [7]. Unfortunately, the presence of a large set of unknown parameters (δ_{w1}, δ_{w2}, δ_d, and β) makes a more detailed comparison of the NMR line shape in $YFeO_3$ with the conclusions of [7] meaningless.

We thus arrive at the conclusion that the recorded two NMR signals in $YFeO_3$ correspond to the edges of a broad complicated absorption band, contained between the frequencies ν_d and ν_w, of the Fe^{57} nuclei in the domain boundaries.

With increasing temperature, the band edge corresponding to the signal at the frequency ν_w, as follows from Fig. 1, shifts more rapidly towards lower frequencies, causing by the same token an increase in the width $\Delta\nu$ of the band (compare Figs. 4b and 4c). According to spin-wave theory, this can be attributed to thermal excitation of the spins in the domain boundaries (the translation branch of the spin waves has a maximum excitation amplitude at the center of the boundary), which causes them to be additionally "reduced" in proportion to T, compared with the spins in the domains.

The shift of the NMR line under the influence of the field has apparently been observed for the first time for nuclei in the domain boundaries. Contributing to the observation of this effect was the rare possibility of retaining the domain boundaries in relatively strong fields. So far, the frequency shift in ferro- or ferrimagnets has been observed only for the single-domain state (enhancement as a result of rotation), when there are no domain boundaries and the magnetic moments of the sublattices are collinear with the direction of H. The shift of the NMR line towards lower frequencies in such a case is evidence of a negative sign of the local field.

Owing to the almost antiferromagnetic ordering of the spins in the domains along the positive and negative directions of the a axis (a noncollinearity of 0.5° can be neglected) and owing to the absence of rotation of the magnetic moments of the sublattices, we are justified in expecting in a field $H \parallel a$ a splitting of the frequency ν_d, which is determined by the local field H_a, into two branches: $\nu_d(+,-) = (\gamma_n/2\pi)(H_a \pm H)$. On the other hand, the field $H \parallel b$, as follows from experiment, should not influence the frequency ν_d, since it is perpendicular to H_a. This raises the question as to which of the split frequencies will now determine the high-frequency edge of the resonance-frequency band in the domain boundaries. Experiment shows that the edge of the band becomes the low-frequency branch $\nu_d(-)$, which falls in the region of the initial resonant frequencies $\nu_w < \nu_d(-) < \nu_d$. With increasing $H \parallel a$, the signal at the frequency $\nu_d(-)$ approaches ν_w (see Fig. 3) until both signals become superimposed on one another. When the field $H_a - H$ becomes equal to H_c at the center of the boundary, the resonance-frequency band vanishes ($\Delta\nu = 0$), and the resonance is no longer observed. This effect calls for a theoretical explanation.

Doubt may arise as to whether the vanishing of the resonance is not simply connected with the fact that the field $H \parallel a$ of intensity 8000 Oe accidentally coincided with the field necessary to suppress the domain boundaries. To verify this assumption, repeated experiments were performed at which the crystal was reoriented again each time. The vanishing of the signals occurred at a sufficient margin of intensity, and even after a field $H \parallel a$ of intensity 10 000 Oe was applied the crystal remained single-domain. This gives grounds for assuming that the vanishing of the resonance is not connected with the suppression of the domain boundaries. The absence of the influence of the field H (independently of its direction in the ab plane) on the frequency ν_w indicates that the OA at the center of the boundary and the corresponding local fields are directed along the c axis.

One can indicate at least three known published analogous cases of splitting of the NMR frequency in domain boundaries. The first publication dates back to 1963[8] and is devoted to an investigation of NMR of Co^{59} in metallic cobalt at 300–900°K. With increasing temperature, in the region 500°K, the authors observed the appearance of a splitting with symptoms analogous to those described in subsections 1 and 6 of Sec. 3. Superposition of a field decreased synchronously the intensity of both signals. The authors of [8] reached the conclusion that both signals are due to nuclei in domain boundaries, but the reason for the splitting remained unclear. One can attempt to explain the appearance of the splitting from the same point of view as in our case. Indeed, let us assume that at low temperatures the frequencies ν_d and ν_w are close to each other and that resonant absorption of the Co^{59} nuclei in the domain boundaries corresponds to an asymmetric peak whose first derivative is represented by a single line. When the temperature is increased, owing to the different temperature dependences of the boundary frequencies ν_d and ν_w, the peak broadens and becomes a band. The increase of $\Delta\nu$ with temperature leads ultimately to the appearance of separate peaks corresponding to the frequencies ν_d and ν_w.

The second paper[9], which was published almost simultaneously with [1], was devoted to NMR of Mn^{55} and P^{31} in the rhombic compound MnP. A splitting of the NMR of Mn^{55} and P^{31} was observed, with symptoms analogous to those described in subsections 1, 2, and 6 of Sec. 3. The authors concluded that the resonances of both frequencies are due to nuclei in the domain boundaries, and that the resonance at the frequency ν_d is excited at the nuclei in the near-boundary sections of the domains. Analyzing the experimental results, they obtained a theoretical resonance line shape quite close to that shown in Fig. 4. Similarly, the authors interpreted the results of their own preceding investigation[10] of NMR of Mn^{55} and B^{11} in MnB, where it was assumed that the splitting was due to the existence of two types of domain boundaries.

Thus, two resonant lines at the frequencies ν_d and ν_w, due to vibration of the domain boundaries, were observed in a metallic ferromagnet[8] in the metallic compounds MnP and MnB,[9, 10] and in the weak ferromagnet $YFeO_3$,[1] which belongs to the class of oxide compounds. It follows from this fact that the frequency splitting of the NMR from nuclei in domain boundaries is in itself not a property peculiar only to the weak ferromagnetism of $YFeO_3$.

Note added in proof (October 14, 1971). Investigations at 77°K have shown that after the frequencies ν_d and ν_w are made to coincide in a field $H = H_a - H_c$, there is observed one strongly smeared line, which on further increases of the field $H \parallel a$ decreases in intensity and continues to shift towards lower frequencies. At room temperature, this singularity could not be observed, owing to the considerable decrease of the total intensity of the NMR signal.

[1] A. V. Zalesskiĭ, Zh. Eksp. Teor. Fiz., Pis'ma Red. **12**, 468 (1970) [JETP Lett. **12**, 326 (1970)].

[2] R. L. White, J. Appl. Phys. **40**, 1061 (1969).

[3] E. D. Kolb, D. L. Wood, and R. A. Laudise, J. Appl. Phys. 39, p. II, 1362 (1968).

[4] A. V. Zalesskiĭ, I. S. Zheludev, and R. A. Voskanyan, Zh. Eksp. Teor. Fiz. **59**, 673 (1970) [Sov. Phys. JETP **32**, 367 (1971)].

[5] R. C. Sherwood, J. P. Remeika, and H. J. Williams, J. Appl. Phys. **30**, 217 (1959).

[6] L. N. Bulaevskiĭ and V. L. Ginzburg, Zh. Eksp. Teor. Fiz., Pis'ma Red. **11**, 404 (1970) [JETP Lett. **11**, 272 (1970)].

[7] E. A. Turov, A. P. Tankeev, and M. I. Kurkin, Fiz. Metal. Metalloved. **28**, 358 (1969); Fiz. Metal. Metalloved. **29**, 747 (1970).

[8] R. C. La Force, L. E. Toth, and S. F. Ravitz, J. Phys. Chem. Solids **24**, 729 (1963).

[9] H. Nagai, T. Hihara, and E. Hirahara, J. Phys. Soc. Jap. **29**, 622 (1970).

[10] T. Hihara and E. Hirahara, J. Phys. Soc. Jap. **20**, 873 (1965).

Translated by J. G. Adashko
245