DOMAIN-STRUCTURE GOVERNED FEATURES OF NMR OF Fe^{57} IN HEMATITE CRYSTALS[1)]

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A frequency-modulated radiospectrometer was used to study the influence of a constant field H on the NMR of Fe^{57} and the resonance of the domain boundaries in synthetic hematite crystals enriched with Fe^{57}. The nature of the NMR signal in hematite is discussed by comparing the intensities of the NMR and domain-boundary resonance signals following magnetization of the crystals. Such a comparison shows that at H = 0 the NMR signal is due principally to oscillations of the domain boundaries. On the other hand, certain properties of the NMR, which become manifest when $H \neq 0$, offer evidence of a contribution to the intensity by the oscillations of the magnetic moment inside the domains, particularly if H and the radio-frequency field are transversely located in the basal plane. It is shown that the intensity of the NMR signal in pure hematite has hysteresis in weak fields. A change in the line shape with increasing H was observed. Possible causes of this change are discussed. The possibility of using magnetic modulation to register NMR in hematite is demonstrated in the Appendix.

1. INTRODUCTION

UNLIKE nonferromagnetic substances, when NMR is excited in ferromagnets, the nuclei are acted upon not by the external radio-frequency (RF) field itself, but by the much larger ac component of the local field at the nucleus. As a result, in real ferromagnetic materials, the observed intensity of the NMR signal is determined by magnetization processes that occur at radio frequencies, namely the reversible displacement of the domain boundaries and rotation of the magnetization in the domains. Therefore NMR in ferromagnets can be regarded as one of the methods of investigating the domain structure.

The influence of the domain structure on NMR becomes manifest when a static field is applied to the sample and causes realignment of the domain structure. From this point of view, the most interesting objects are crystals of uniaxial ferromagnets, characterized by a strong anisotropy of the magnetic properties. The latter include hematite, a typical representative of weak ferromagnets.

In a study of NMR in a natural hematite crystal with rather high content of Ti (0.4%), Anderson[1] observed certain peculiarities in the behavior of the NMR signal intensity in weak fields. He has shown, apparently for the first time, that the intensity of the NMR signal in a ferromagnet has hysteresis, as well as many other properties determined by the domain structure. In explaining the nature of amplification of the NMR signal in hematite, Anderson gave preference to the mechanism of rotation of the magnetization in the domains. Sedlak[2], who had at his disposal impurity-free hematite crystals, did not observe the peculiarities found by Anderson in weak fields. Sedlak reached the conclusion that the NMR signal in hematite comes from the walls.

Thus, the nature of the amplification of the NMR signal in hematite crystals is not yet sufficiently clear. Nor is it known whether the peculiarities observed by Anderson are due to the Ti impurity or whether they are possessed by pure hematite.

To understand the process of hematite magnetization in RF fields, and consequently to understand the mechanism of amplification of the NMR, it was very useful, as shown in our earlier paper[3], to compare the signal intensities of NMR and of the domain-boundary resonance (DBR) following application of a static field, since the DBR intensity gives an idea of the density of the domain boundaries and the role of their displacement in the RF field. In[3], the measurements were made in relatively strong static fields. In the present paper we present results of an investigation of NMR and DBR in hematite crystals in weaker fields, in which the properties of the crystal are determined by the state of the domain structure.

We show in the Appendix that the change of the NMR parameters following application of the field makes it possible to employ magnetic modulation to register the NMR signal in hematite.

2. SAMPLES AND EXPERIMENTAL PROCEDURE

The hematite crystals were grown by the method published in[4]. To investigate the NMR we used crystals grown from iron oxide enriched with the Fe^{57} isotope. A sample with total weight of approximately 0.2 g was made up of several plate-like crystals glued to one another at the basal plane (111).

The NMR and DBR were observed by means of a frequency-modulated spectrometer of the static type, developed by the Design Office of the Radio and Electronics Institute of the USSR Academy of Sciences. To analyze the line shape of the NMR signal, we used as the detector a regenerator operating at a low level of RF oscillations. The minimum RF voltage on the tank circuit was about 1 mV. In those cases when it was necessary to trace small changes of the signal intensity, for example in plotting the hysteresis loop, we used a more sensitive superregenerative regime, which increased the signal-to-noise ratio by almost one order of magnitude. To obtain a DBR spectrum of sufficient

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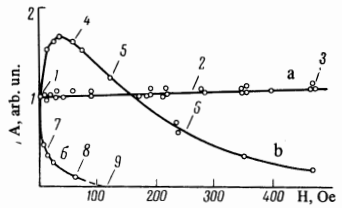

FIG. 1. NMR signal amplitude A against the intensity of the constant field H and its direction relative to the RF field h in the (111) plane: a–$\mathbf{H} \perp (111)$, $\mathbf{h} \parallel (111)$; b–$(\mathbf{H} \parallel (111)$; c–$(\mathbf{H} \perp \mathbf{h}) \parallel (111)$. The amplitude A for the demagnetized state is arbitrarily taken to be unity. The numbers denote the states for which the DBR spectra are shown in Fig. 2.

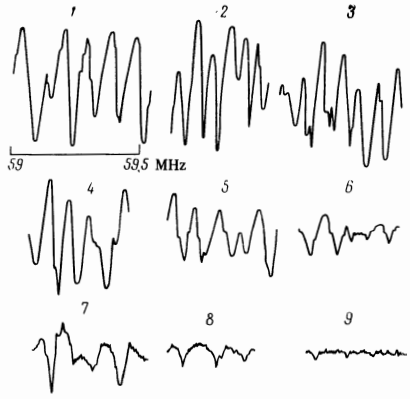

FIG. 2. DBR spectra for hematite in the 59-MHz region for the states correspondingly numbered in Fig. 1.

intensity, we used samples made up of a larger number of crystals (in which case, of course, there was no need to use enriched crystals), and the RF oscillation level in the superregenerator was raised to 0.1–0.2 V. The frequency range for the observation of the RDB was chosen such as not to overlap the NMR frequency, but still be close enough to the latter. The constant magnetic field was produced with a solenoid.

3. EXPERIMENTAL RESULTS

Figure 1 shows a plot of the NMR signal amplitude of hematite crystals against the direction and magnitude of the constant field H, while Fig. 2 shows examples of the DBR spectra obtained at different points of this plot. The RF field was directed in all cases in the (111) plane. The anisotropy in the (111) plane could not be determined, since the crystals were glued together with the basal planes randomly oriented. The amplitude of the NMR signal in Fig. 1 at H = 0, set arbitrarily equal to unity, corresponds to the demagnetized state of the sample. The demagnetization was effected by rotating the sample in the (111) plane in an alternating field parallel to this plane and decreasing the field slowly from 500 Oe.

It is seen from Fig. 1 that a field $\mathbf{H} \parallel (111)$ (curve a) has practically no influence on the NMR signal amplitude, at least up to 500 Oe. The same can be stated also with respect to the DBR intensity (spectra 1, 2, and 3 in Fig. 2). The field H directed along the RF field h in the basal plane suppresses the NMR signal (curve b in Fig. 1) and the DBR signal (spectra 7, 8, and 9 in Fig. 2) in fields on the order of 100 Oe.

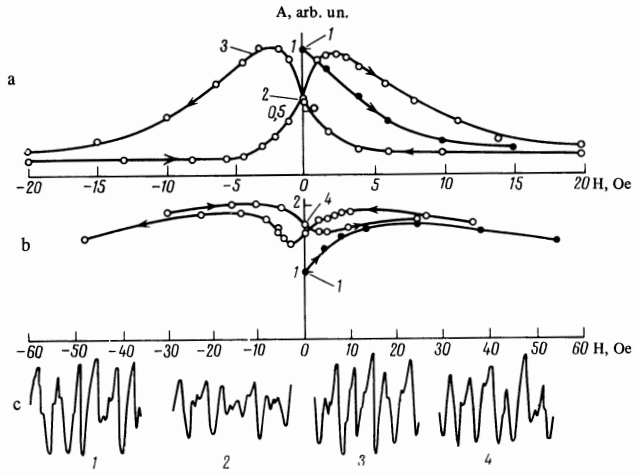

FIG. 3. Hysteresis of the NMR signal amplitude A for hematite in weak fields: a–$(\mathbf{H} \parallel \mathbf{h}) \parallel (111)$; b–$(\mathbf{H} \perp \mathbf{h}) \parallel (111)$; c–DBR spectra near 59 MHz for the states correspondingly numbered on the hysteresis curves. The amplitude A for the demagnetized state is taken to be equal to unity.

If H and h are perpendicular to each other, an increase of the NMR amplitude (curve c in Fig. 1) is observed, and the signal intensity begins to drop only in fields exceeding ~50 Oe.

The intensity of the DBR spectrum in the case $\mathbf{H} \perp \mathbf{h}$ (curves 4, 5, and 6 in Fig. 2) decreases smoothly and reveals no growth in fields corresponding to the maximum of the NMR signal on curve c of Fig. 1.

Figures 3a and b show that in weak fields the intensity of the NMR signal in hematite reveals a hysteresis of the "butterfly" type, characteristic of many ferromagnetic-material properties determined by the domain structure. During the plotting of the hysteresis curve, the field H was varied in the range ±300 Oe. Just as in Fig. 1, the initial point corresponds to the demagnetized state of the sample. The hysteresis is most clearly pronounced at $\mathbf{H} \parallel \mathbf{h}$ (Fig. 3a). The NMR signal amplitude corresponding to the residual magnetization is lower in this case than for the demagnetized state, and the coercive field corresponds to a signal maximum approximately equal to the amplitude for the demagnetized state. Although the intensity of the DBR spectrum can be characterized only approximately by a certain amplitude averaged over the frequency band, it is nevertheless seen from the curves 1, 2, and 3 of Fig. 3c that the DBR intensity behaves in analogy with the NMR signal intensity in the case when $\mathbf{H} \parallel \mathbf{h}$.

If H is perpendicular to h (Fig. 3b), the NMR signal amplitude corresponding to the residual magnetization is higher than for the demagnetized sample, and in the case of a coercive field it has a tendency to decrease. In the state with residual magnetization, the intensity of the DBR spectrum at $\mathbf{H} \perp \mathbf{h}$ remains approximately the same, or even somewhat lower, than for the demagnetized state, as can be seen from a comparison of the spectra 1 and 4 in Fig. 3c.

In the investigation of the NMR signal line shape with the aid of the regenerator, it was observed that definite intervals of the fields H correspond to different line shapes. Figure 4 shows the dependnce of the shape of the first derivative of the NMR signal on the direction and magnitude of H for the cases $(\mathbf{H} \parallel \mathbf{h})$

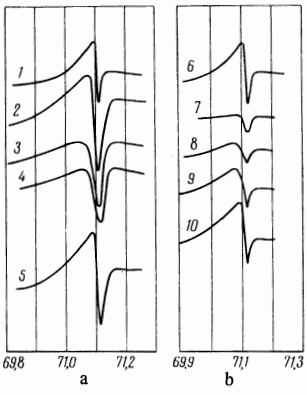

FIG. 4. Change in the form of the first derivative of the NMR signal in hematite at 295 °K as a function of the field intensity H and its direction relative to the RF field h: a–(**H** ⊥ **h**) ∥ (111): 1–demagnetized state, 2–H - 35 Oe; 3–H = 116 Oe; 4–H = 170 Oe; 5–residual magnetization; b–(**H** ∥ **h**) ∥ (111): 6–demagnetized state; 7–H = 12 Oe; 8–H = 3 Oe with decreasing H; 9–residual magnetization; 10–H - 3 Oe upon reversal of the direction of H.

∥ (111) and (H ⊥ h) ∥ (111). The line shape corresponding to the demagnetized state of the sample is close to the absorption curve, with the asymmetry inherent in ferromagnets. The curve is characterized by a gentle rise on the low-frequency side and by a steeper drop on the high-frequency side. With increasing field H, the curve is deformed and acquires a more symmetrical dispersion shape. In the case (H ∥ h) ∥ (111), the curve assumes the dispersion shape in fields on the order of 12–15 Oe, while in the case (H ⊥ h) ∥ (111) this occurs at H ~ 200–250 Oe. Curves 1–10 of Fig. 4 illustrate also the hysteresis behavior of the NMR signal intensity.

4. DISCUSSION OF RESULTS

Investigation of NMR in artificial hematite crystals has shown that in weak fields they possess singularities qualitatively similar to those observed in natural crystal containing Ti[1]. The main difference is that the coercive force drops from 20–30 Oe and the maximum of the NMR signal intensity drops in the case H ⊥ h from 60–80 Oe for the crystal with Ti impurity to 2 Oe and 20–30 Oe respectively for crystals that contain no Ti. The difference in the indicated characteristics can be attributed to the fact that the increased Ti content in the hematite increases the energy of the magnetic anisotropy in the basal plane.

Anderson[1] attempted to explain the behavior of the NMR signal intensity following application of an external constant field H as being due almost exclusively to the rotation mechanism. Satisfactory agreement was obtained in this case only for strong fields.

As follows from the results given in the present paper, the change of the DBR intensity under the influence of H, with the exception of certain singularities that become manifest in the case H ⊥ h, is analogous to the change of the NMR signal intensity. This gives grounds for concluding that the main amplification process (at any rate when H = 0) is the displacement (oscillation) of the domain boundaries.

On the other hand, the increase of the NMR signal intensity in the case H ⊥ h, which is not accompanied by an increase of the DBR, can apparently not be explained without taking the mechanism of rotation (oscillation) of the magnetization inside the domains into account. The possibility of simultaneous existence of two magnetization processes in RF fields–rotation and displacement–is due to the exceedingly low magnetic-anisotropy constant K of the hematite in (111) plane. According to the published data, the values of K for different crystals ranged from 1 to 10 erg/cm^3. The amplification coefficient η_{dis} within the domain boundaries, according to the data of[5], is 2.5×10^4 for hematite. The amplification coefficient corresponding to rotation in the absence of H, according to Anderson's calculations[1], can be estimated from the formula $\eta_{rot} \approx |4 \times 10^4/K|$. Thus, η_{rot} and η_{dis} can be comparable in magnitude. Since η_{rot} and η_{dis} are proportional to the corresponding reciprocal susceptibilities χ_{rot} and χ_{dis}[6], this means that $\chi_{rot} \approx \chi_{dis}$, in contrast to most ferromagnets, where usually $\chi_{dis} \gg \chi_{rot}$.

For a rigorous estimate of the contributions made to the NMR intensity by nuclei in domains and domain boundaries, and also for an analysis of the NMR signal line shape, it is necessary to know the exact values of the susceptibilities χ_{dis} and χ_{rot}, to take into account the dynamics (the oscillation spectrum) of the domain boundaries and of the domains, and to make allowance for the inhomogeneity of the amplification as a result of the redistribution of the angles between **h** and **M** in the real domain structure. In the presence of an increasing constant field H, the problem is aggravated by the realignment of the domain structure and by the change of the ratio of the contributions from the nuclei in the domains and in the boundaries, as a result of the vanishing of the boundaries and of the rotation of **M** in the domains. It was not our purpose in this investigation to solve such a problem, and we therefore confine ourselves only to a qualitative explanation of the results. In considering the domain structure, we shall start from the assumption that 180° boundaries exist in the hematite, since boundaries of just this type were observed so far experimentally[7].

The absence of an influence of a field H ⊥ (111) on the intensity of the NMR and the DBR is most understandable, since application of a field along the trigonal axis of the hematite, owing to the anisotropic properties of the latter, can cause neither a displacement of the domain boundaries nor a rotation of the ferromagnetic moment **M** lying in the (111) plane. A certain influence can be attributed to the inevitability of the appearance of an H component parallel to (111), owing to the inaccurate orientation of the crystals.

The strong suppression of the NMR and DBR by a field H ∥ h can be explained as being due to the fact that in this case the field H destroys primarily the boundaries that are parallel to the RF field **h**. It is precisely these boundaries, which have the maximum oscillation amplitude, which determine the main contribution to the intensity from the nuclei in the domain boundaries. The contribution made to the NMR intensity by the nuclei inside the domains also decreases relatively rapidly because of the rotation **M** in the direction of H, which coincides with the RF field **h**. As a result of the exchange, the intensity of NMR signal decreases rapidly with the field H in the case H ∥ h, as shown by curve b of Fig. 1, mainly as a result of the vanishing of the oscillating domain boundaries, since the NMR signal disappears at approximately the same fields as the DBR.

Proceeding to the case H ⊥ h, it must be empha-

sized that the absence of a growth in the DBR intensity in fields at which an increase takes place in the NMR intensity indicates that a field $\mathbf{H} \perp \mathbf{h}$ causes neither an increase of the domain-boundary oscillation amplitude nor an increase in the density of the domain boundaries parallel to **h**. This indicates that the cause of the increased NMR intensity is not connected with the domain boundaries and must be sought in the increasing role of the nuclei in the domains.

When $\mathbf{H} \perp \mathbf{h}$ the boundaries that vanish predominantly are those perpendicular to the RF field **h**, on which the latter does not act, and the vanishing of the boundaries parallel to **h**, as shown by measurements of the DBR (spectra 4, 5, and 6 on Fig. 2), occurs gradually as **M** turns in the direction perpendicular to **h**. This turning, which apparently begins in relatively weak fields (since $\chi_{rot} \approx \chi_{dis}$), should cause an increase in the NMR intensity, owing to the appearance of the possibility of oscillations of **M** inside those domains, whose ferromagnetic moment **M** is oriented parallel or antiparallel to the RF field **h** when $H = 0$.

Thus, the maximum on curve c of Fig. 1 can be attributed to the competition between two processes, the gradual decrease of the signal as a result of the decreased number of boundaries close to parallelism with **h** as **M** rotates, and the increase of the intensity, caused by the same rotation, and due to the increase of the number of nuclei that resonate as a result of the oscillations of **M**.

The fact that when $\mathbf{H} \perp \mathbf{h}$ the NMR signal does not vanish in fields exceeding 500 Oe, in which the existence of the main boundaries is already excluded, is due to the remaining possibility of resonance of the nuclei as a result of the oscillations of **M**, since **M** is perpendicular to **h**.

The singularities of the hysteresis in the NMR signal intensity can be understood if an attempt is made to explain why for a crystal in the state of residual magnetization the NMR signal intensity is lower than in the demagnetized state when $\mathbf{H} \parallel \mathbf{h}$ and higher when $\mathbf{H} \perp \mathbf{h}$. In the former case the hysteresis is most strongly pronounced and is determined mainly by the change in the number of the boundaries parallel to **h**, owing to the irreversibility of the displacement of the domain boundaries upon remagnetization by means of the field **H**. This is evidenced by the fact that the hysteresis appears also in DBR measurements. The decrease of the NMR and DBR intensities in the state of residual magnetization in the case when $\mathbf{H} \parallel \mathbf{h}$ can be attributed to a decrease in the density of the domain boundaries parallel to **H** and **h**, owing to the increase in the volume of the domains having **M** directed predominantly along the preceding direction of **H**.

In the case $\mathbf{H} \perp \mathbf{h}$, the increase of the NMR intensity in the state of residual magnetization is due to the increase of the contribution due to the oscillation of **M** inside the domains, owing to the irreversibility of the rotation processes during the remagnetization by means of the field **H**. The irreversibility of the rotation processes produces, in the state of residual magnetization in the basal plane, a definite texture of the domains with **M** directed along the preceding field direction. The direction of the texture axis along **h** ($\mathbf{H} \parallel \mathbf{h}$) contributes to a decrease of the NMR signal intensity compared with the demagnetized state, and the mutually perpendicular direction ($\mathbf{H} \perp \mathbf{h}$) contributes to an increase of the intensity owing to the increase in the number of domains in which **M** makes a nonzero angle with **h**. The irreversible change of the number of boundaries parallel to **h** in the state with the residual magnetization, compared with the demagnetized state in the case $\mathbf{H} \perp \mathbf{h}$, apparently influences the intensity to a lesser degree than the irreversibility of the rotation. This is confirmed by the fact that in the case $\mathbf{H} \perp \mathbf{h}$ the intensity of the dBR corresponding to the residual magnetization remains practically unchanged, or is even somewhat lower than for the demagnetized state.

Perhaps the most interesting and fundamental fact is the observed change in the NMR signal line shape with increasing field H. A change in the NMR signal line shape in a ferromagnet under the influence of a field H is mentioned in[8], where NMR is nickel was investigated. It is noted in that reference that the change of the line shape in a certain interval of H is analogous to that occurring when the RF field is decreased, i.e., it is connected with the change of the amplification coefficient. In our case the change of the line shape recalls the change occurring upon saturation with increasing h. It is known that the saturation condition corresponds to the inequality $(\gamma_n \eta h)^2 T_1 T_2 \gtrsim 1$, where γ_n is the nuclear gyromagnetic ratio and T_1 and T_2 are the longitudinal and transverse relaxation times. Thus, saturation at constant h can occur either as a result of an increase of η or as a result of an increase of T_1T_2. The former assumption contradicts both theory and experiment, and the latter needs theoretical verification.

The line-shape deformation may also be unconnected with the saturation phenomenon. As shown in[8], in ferromagnets the NMR signal is proportional to $\chi'' + \beta_0 \chi'$ at constant h, i.e., it is a combination of the imaginary and real parts of the complex nuclear susceptibility. The coefficient β_0, which determines the degree of mode displacement, is proportional to the coefficient of electronic damping λ in the Landau-Lifshitz equation. In addition, λ enters in the expression for the parameter that determines the damping in the equation of motion of the domain boundary. It must therefore be assumed that the observed change in the line shape is due to an increase of the damping upon application of the field H. There are no published data on the influence of H on λ in hematite.

Attention is called to the fact that the line finally assumes a symmetrical dispersion shape approximately in fields that correspond, according to DBR measurements, to the vanishing of the domain boundaries. This suggests that the cause of the change in the line shape must be sought in the increasing role of the oscillations of **M**. The slow rise of the curve on the low-frequency side, which is always observed in the region of H in which an important role is still played by the domain boundaries, can be attributed to the inhomogeneity of the amplification in the domain boundaries. Inasmuch as the amplification due to the oscillations of **M** is more homogeneous (especially in the presence of the orienting action of the constant field) compared with the domain boundaries, the vanishing of the domain boundaries can lead to a more homogeneous

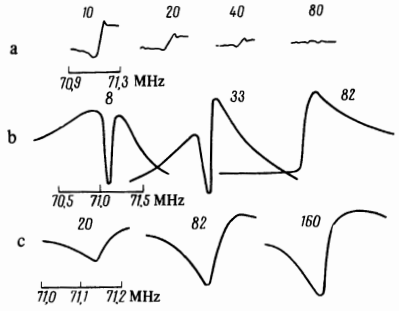

FIG. 5. Examples of NMR signals recorded with the aid of magnetic modulation at different amplitudes and directions of the alternating field $\mathcal{H}$: a–($\mathcal{H} \parallel \mathbf{h}$) $\parallel$ (111); b–($\mathcal{H} \perp \mathbf{h}$) $\parallel$ (111); c–$\mathcal{H} \perp$ (111), $\mathbf{h} \parallel$ (111). The numbers over the curves denote the maximum value of the alternating field $\mathcal{H}$ in Oe.

amplification and consequently to the appearance of a more symmetrical line than observed in experiment.

APPENDIX

USE OF MAGNETIC MODULATION TO REGISTER THE NMR SIGNAL IN HEMATITE

The change of the NMR signal amplitude following the action of a relatively weak field, accompanied by a change in the line shape, and the existence of hysteresis in both quantities, makes it possible to use in the case of hematite a high frequency alternating field $\mathcal{H}$ to modulate the NMR signal.

For magnetic modulation we used the same solenoid that produced the constant field. It was connected to the output of a 100-watt low-frequency amplifier. The input to the amplifier was a sinusoidal modulation voltage, which in the case of frequency modulation was connected to a varicap diode. The frequency of the modulation current was 85 Hz, and the frequency of the reference voltage of the synchronous detector was 170 Hz.

Magnetic modulation was used to register a NMR signal of complicated form at different intensities $\mathcal{H}$ for all the possible orientations: ($\mathbf{H} \parallel \mathbf{h}$) $\parallel$ (111), ($\mathbf{H} \perp \mathbf{h}$) $\parallel$ (111) and $\mathbf{H} \perp$ (111), $\mathbf{h} \parallel$ (111) (see Fig. 5). In the case ($\mathbf{H} \parallel \mathbf{h}$) $\parallel$ (111) the signal is suppressed already in weak fields. When $\mathcal{H} \perp \mathbf{h}$, the signal is observed in a wide interval of $\mathcal{H}$, and in the case $\mathcal{H} \perp$ (111) the signal intensity increases apparently as a result of the increase of the component $\mathcal{H} \parallel$ (111). In other words, the alternating-field intervals in which the signal is observed with the aid of magnetic modulation reflect the regularities that hold when a constant field H is applied.

We note that the signal amplitude at $\mathcal{H} \perp \mathbf{h}$ is larger by at least three times than in the case of ordinary frequency modulation, a fact worth bearing in mind when searching for NMR signals in weak ferromagnets similar to hematite.

Magnetic modulation is applicable also for the registration of NMR signals in certain strong ferromagnets[9]. In this case, however, the application of an alternating field produces frequency modulation, but this modulation is due not to the change of the capacitance of the tank circuit, as is usually the case, but to changes in its inductance. The change of inductance in magnetic modulation does not play an important role in the case of hematite, owing to the weak ferromagnetism of the latter.

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