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# Nuclear magnetic resonance investigation of photomagnetic phenomena in $FeBO_3$

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**Abstract**

For the first time the NMR technique has been applied to the investigation of photomagnetic phenomena in a magnetic material. In the transparent easy-plane weak ferromagnet $FeBO_3$ the $^{57}Fe$ NMR spectra were measured with and without light illumination. It was shown that the exposure to light leads to (i) a total NMR frequency shift, as a result of electronic magnetization change, and (ii) a NMR signal increase, which is spectrally inhomogeneous at small external magnetic fields, where NMR spectrum splitting exists. The suggested mechanism for signal enhancement was connected to the light induced decrease of the basic-plane magnetic anisotropy.

## 1. Introduction

The light effect on certain parameters of a magnetic substance called the photomagnetic phenomenon is under investigation (see, for instance, [2, 3]) for the first time since its first observation at the end of the 60s (see [1] and references therein). Photomagnetism has attracted growing attention over the last decade, not only because of its interest from the physical point of view but also because of its possible application in recording media.

Ferric borate, $FeBO_3$, being transparent in visible magnetically ordered material, is an appropriate crystal for photomagnetic phenomena investigations, and it has been carefully studied in this respect by different experimental techniques [4–11]. It has been shown that there is a number of photo-induced effects in the substance, which most probably could be explained by redistribution of energy level population of $Fe^{2+}$ ions, while the dopants, if they exist, only assist the process [10]. At the same time no NMR studies on the topic (except for a brief communication [12]) have been carried out on either ferric borate or magnetically ordered materials in general, in spite of the possibility of obtaining additional information by this method.

It is well known that NMR is an efficient tool for the investigation of substances with magnetic ordering [13]. An important peculiarity of such resonance is the possibility of

  

observing it in zero external field due to the existence of the internal local field $B_{\rm loc}$ at the nuclei of a magnetic element. It consists of hyperfine, dipolar and demagnetizing contributions with the predominance of a hyperfine field, $B_{\rm hf}$. The dipolar contribution is typically small compared with $B_{\rm hf}$, nevertheless, it may play a significant role in the formation of the spectrum fine structure. The NMR frequencies $f_{\rm ni}$ may be written in the antiferromagnet as $f_{\rm ni} = \gamma B_{\rm loc}$ and $B_{\rm loc} \cong \gamma A_0 \mu_i$, where $\mu_i$ is the electronic magnetization of the $i$ th magnetic sublattice, $\gamma$ is the nuclear magnetogyric ratio, and $A_0$ is the constant of hyperfine interaction.

Another unusual characteristic of NMR in magnetics is the so-called enhancement factor, $\eta$. The coupling between the radiofrequency (RF) field $B_{\rm rf}$, which excites the resonance, and the nuclear spin system in magnetic materials is indirect and realized through electronic magnetization. As a result, the enhanced RF field, $\eta B_{\rm rf}$, acts on nuclear spins, and the NMR signal amplitude is also proportional to $\eta$. When the NMR signal originates from the nuclei in magnetic domains

$$\eta = B_{\rm hf}/(B + B_{\rm a}) = A_0 \mu/(B + B_{\rm a}) = A_0 \chi_{\rm rot}, \tag{1}$$

where $B$ is a permanent external field, $B_{\rm a}$ is the effective field of magnetic anisotropy, and $\chi_{\rm rot}$ is rotational magnetic susceptibility. In the case when NMR is observed in domain walls, the $\chi_{\rm rot}$ in (1) should be replaced by the wall displacement susceptibility, $\chi_{\rm d}$. Normally $\chi_{\rm d}$ is much higher than $\chi_{\rm rot}$, and differs for different magnetic structures. For an easy-plane weak ferromagnet the 'enhanced' anisotropy field $\tilde{B}_{\rm a}$, equal to $B_{\rm a}(2B_{\rm E}/B_{\rm B})$, should be used in (1) instead of $B_{\rm a}$, where $B_{\rm E}$ and $B_{\rm D}$ are the exchange and Dzyaloshinsky fields respectively.

Thus, NMR allows the probing of a number of local magnetic properties of a magnetically ordered material, some of which cannot be studied by other methods [13]. If the magnetic parameters change under light illumination one can expect a change in the NMR characteristics, and the latter may, in turn, reflect important details of the photomagnetic effect. A goal of this work is to demonstrate the NMR potential for investigation of the phenomenon. Ferric borate is the most suitable model object for our purposes because of its unique combination of optical and magnetic properties and well investigated NMR [14, 15]. The material is an easy-plane weak ferromagnet with two slightly tilted sublattices and Nèel temperature $T_{\rm N} = 348$ K. The small in-plane anisotropy field $\tilde{B}_{\rm a}$ results, in accordance with the expression (1), in very high intensity of the NMR signal. The equivalence of sublattice magnetizations leads to a single $^{57}$Fe NMR line with an extremely narrow bandwidth.

## 2. Experimental procedure

The experiment was performed on a nominally pure ferric borate single crystal, up to 80% enriched in $^{57}$Fe isotope. It had the shape of a thin rectangular plate with the dimensions of $2 \times 2 \times 0.2$ mm, and the plane coincided with the easy plane of magnetic anisotropy. The freestanding (in order to avoid a stress) sample was placed in the RF excitation coil in such a way that the RF field was referred to the easy plane. The orientation of external fields in respect to the two-fold symmetry axis was not specified, i.e. the weak in-plane anisotropy was neglected. The experiment was carried out at 77 K.

NMR was observed by means of the free induction decay (FID) signal, driven by a RF pulse at a carrier frequency at about of 75.4 MHz. The pulse duration (300 $\mu$s) corresponded to a narrow bandwidth that permitted the detection of the NMR spectrum by point to point recording of the FID amplitude when the transmitter frequency was tuned. The RF transmitter power did not exceed 1 W, but in most experiments it was additionally attenuated in the range 20–40 dB. The intensity of the FID was measured at 20 $\mu$s after the end of the pulse.

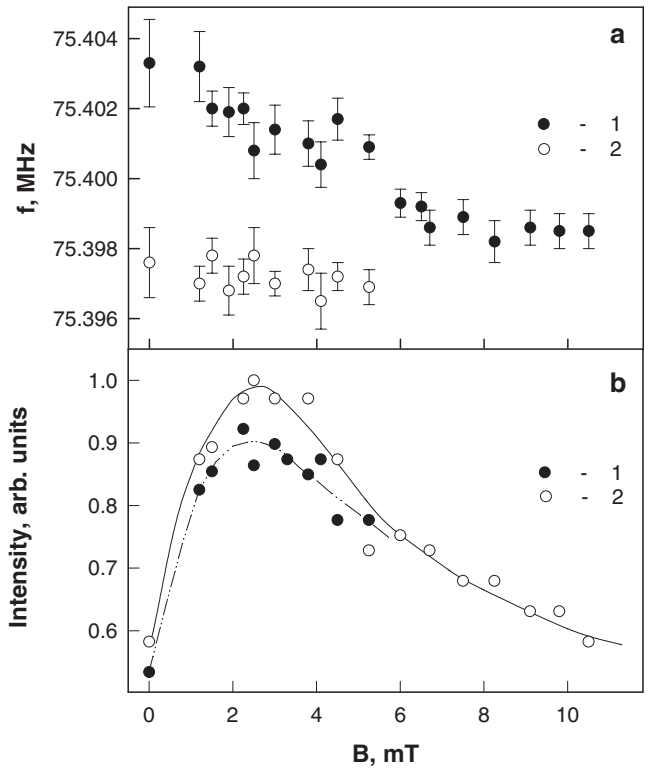


**Figure 1.** The $^{57}$Fe NMR frequencies (a) and FID amplitudes (b) versus magnetic field for high (1) and low (2) frequency peaks at $B = 2.5$ mT. $T = 77$ K.

A permanent magnetic field $B$ was used for the domain structure control. It was also applied in the easy plane, perpendicular to the RF field polarization, and could be varied from 0 to 10 mT (the Earth's magnetic field was not taken into account).

A lamp with a wide optic waveband was used as a light source. The radiation was transmitted to the sample by a fibre bundle and directed onto its surface through a diffuser in order to achieve homogeneity of illumination. The system provided a radiation power density of $\sim$0.1 W cm$^{-2}$. In all the experiments with light the sample was first cooled down to liquid nitrogen temperature in the dark and then exposed to light irradiation.

## 3. Results

At low external fields the NMR spectrum was split into two lines. As is shown in figure 1(a) the splitting starts from a value of 6 kHz at zero magnetic field and then slowly decreases down to its rather abrupt disappearance at between 5 and 6 mT. The line shape for different fields is demonstrated in figure 2. A function composed of two Lorenzians reveals a best fit for the observed double peak line (figure 2(a)), whereas the ordinary Lorenz function was the most suitable for a single peak at $B > 6$ mT (figure 2(b)).

The field dependence of the FID amplitude was measured at constant RF pulse intensity, which was optimal for NMR excitation at $B = 0$. As is seen from figure 1(b) it reaches a maximum at $B = 2.5$ mT and then decreases with increasing field.

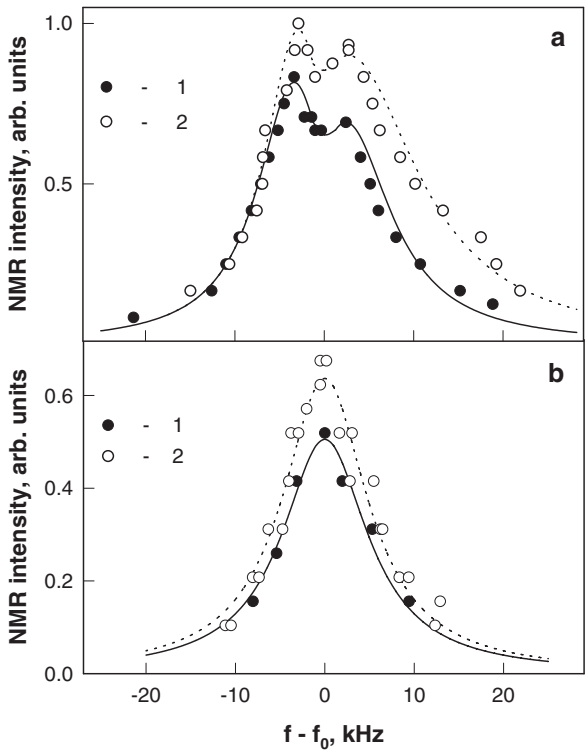


**Figure 2.** The $^{57}$Fe NMR FID amplitudes of non-illuminated samples (1) and (2) versus differential frequency at 2.5 mT (a) and 7.5 mT (b) magnetic field. $T = 77$ K.

Illuminating the sample leads to a sharp decrease of the NMR frequency for both the single and double peak line. The transient process, as in [5, 8], was not observed because the spectrum recording took a few minutes in our experiment. The frequency shift was practically equal for all the magnetic fields used, and accounted for 130 kHz, which corresponds to the sublattice magnetization change of 0.17%. As it was estimated using the data of [8, 11] the thermal contribution to this value does not exceed 10–15%.

Further we shall denote the central frequency of the NMR spectrum as $f_0$ for both the dark and illuminated samples. For the single-line spectrum $f_0$ is a frequency of the peak maximum, and for the case of the double-peak line it is the mean value between frequencies of the individual peaks. It is clear from figure 2(a) that the splitting does not change under the action of light, in contrast to other details of the spectrum. First, the FID amplitude increases under the action of light. This fact gives additional confirmation of the predominantly non-thermal nature of the electronic magnetization change (the FID magnitude, being proportional to the electronic and nuclear magnetization, could only decrease in the case of a pure thermal process). Second, the signal enhancement is spectrally inhomogeneous at the fields where the splitting exists. It is illustrated by figure 3, where the ratio of the Lorenz fittings for illuminated and non-illuminated samples is presented. It is seen that in the high-frequency part of the spectrum the FID amplitude for the illuminated sample is rather higher and more than two times higher as compared to the non-illuminated one. On the other hand, an increase of the FID signal for low frequencies is significantly lower. At the external fields corresponding to the single spectrum line, a small, somewhat spectrally homogeneous, enhancement was also detected (figure 2(b)).

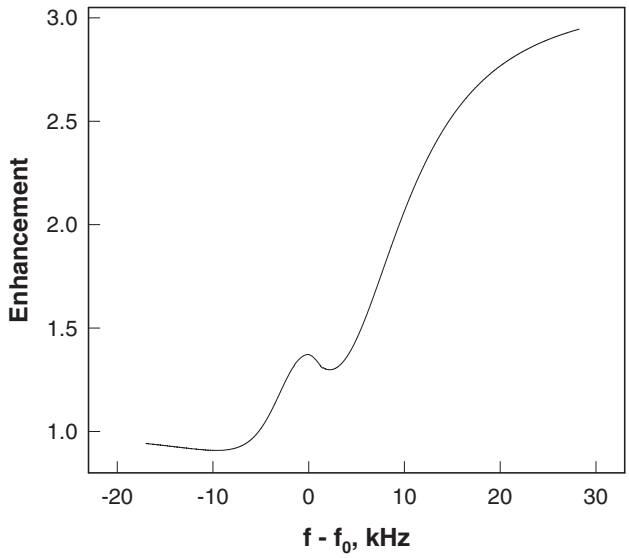


**Figure 3.** A spectral distribution of the FID amplitude enhancement under light illumination for the double-peak spectrum, $B = 7.5$ mT. The enhancement has been calculated for every differential frequency as the ratio of fitting functions of the irradiated and non-irradiated samples.

## 4. Discussion

### *4.1. NMR spectrum splitting*

The multiple-line $^{57}$Fe NMR spectrum in ferric borate was detected earlier [16, 17], but in the present work we deal with the other situation. The authors of [16] observed more than 1 MHz splitting at temperatures higher than 300 K by a steady state technique, and corresponded it to a simultaneous excitation of the domain and domain wall signals. Splitting of another kind (see [17] and references therein) was proportional to the external field and had a threshold behaviour, appearing only at relatively strong RF pulses. It was attributed to the domains with different magnetization orientations. By contrast, in our case a significantly lower pulse power was used, and the optimal pulse amplitude was nearly the same for both excited peaks. Therefore, the different peaks should be ascribed to the domain walls with different properties. As the Nèel walls disappear at $B > 0.05$ mT [18, 19] both of the peaks belong to Bloch walls. The fact that the lines merge at $B \approx 5$ mT (figure 1(a)), i.e. near the sample saturation field [20], confirms this conclusion.

At the moment we have no complete model for the NMR line splitting in walls of the same type. The most probable explanation is connected to the Bloch wall configuration detail. According to magnetocrystalline symmetry one can expect that the wall is a 120° one, which corresponds to the orientation of the neighbouring layer-domain magnetizations along the different two-fold easy axis. It is so, however, only for the ideal case when the sample is specially treated [18]. For a more realistic experimental situation the domain structure becomes rather irregular when the simultaneous presence of 120° and 90° walls is very possible [5, 19, 21]. The dipolar contribution to the local field could vary for the different walls [13], which results in different NMR frequencies for the two kinds of Bloch walls mentioned.

*4.2. Photomagnetic effect*

In the single-domain state, i.e. at $B = 7.5$ mT, the effect of the NMR signal increase is consistent with the light induced decrease of the basic plane anisotropy field. It was observed that in ferric borate $\tilde{B}_a$ was decreased by the light, while the other parameters like, for example, magnetoelastic constants, remain unchangeable [6]. The 25% enhancement (figure 2(b)) corresponds, in accordance with (1), to $\tilde{B}_a \approx 2$ mT instead of the initial 3 mT. This change in the anisotropy field seems reasonable for the much higher light intensity as compared to the result of [6].

In the case of the multidomain state the experimental data may also be attributed, in principle, to the light effect on the in-plane anisotropy. For the enhancement factor in the domain wall of an easy-plane antiferromagnet the following expression is valid, [19, 22]:

$$\eta = A_0\chi_d = \frac{2B_{hf}\mu \sin\phi}{m_w\delta[(\Omega^2 - \omega_n^2) + (\beta/m_w)^2\omega_n^2]^{1/2}}, \tag{2}$$

where $\phi$ is the angle between the electronic magnetization and the in-plane easy axis, $m_w$ is the mass of the wall, $\delta$ is the wall thickness, $\Omega$ is the angular frequency of the wall resonance, $\omega_n$ is the angular frequency of NMR, and $\beta$ is the damping coefficient in the equation of the wall motion. Some parameters for ferric borate at $T = 77$ K are available from the literature: $M_s \approx 1.5$ mT (saturation magnetization), $\delta = 5\ \mu$m [18], $\Delta B = 1$ mT at $\gamma_0 B_r = 9.8$ GHz [9] ($\Delta B$ is linewidth of magnetic resonance, $\gamma_0$ is the electronic magnetogyric ratio, $B_r$ is the resonance field of magnetic resonance), and others can be calculated. Using the standard relation, $\beta = 2\Delta B M_s/(\gamma_0 B_r)\delta$ [22], one can obtain $\beta \sim 10^{-4}$ g cm$^{-2}$ s$^{-1}$. The known formula for wall mass [22] gives $m_w = 1/8\pi\gamma_0^2\delta \sim 10^{-13}$ g cm$^{-2}$. $(\Omega^2 - \omega_n^2) \ll (\beta/m_w)^2\omega_n^2$, because $\Omega \sim 10^2$ MHz [18]. Implying that the light does not distort the wall structure, one can obtain from (2): $\eta'/\eta \cong \beta/\beta' = (\Delta B/\Delta B')(B_r'/B_r)$; the touch marks a light modified parameter. Finally, taking into account that the linewidth of magnetic resonance at $T = 77$ K almost does not change under the action of light [9], we obtain that the NMR magnitude should increase by the factor $\sim B_r'/B_r$. A rough estimation may also be taken from [9], where $B_r'/B_r \cong 1.15$. The spectrally inhomogeneous signal enhancement, shown in figure 3, for the low frequency peak is of tens of per cent, and does not exceeds three times for the higher frequencies. Thus, an order of magnitude increase of the NMR signal in the multidomain state is in agreement with the light induced anisotropy decrease, followed by the change in the domain wall susceptibility. This is directly confirmed by the light-stimulated growth of the initial magnetic susceptibility observed in [4, 5].

The spectral distribution of the enhancement is not yet clear. It is obvious that it cannot be explained by the spatial inhomogeneity of light intensity along the sample thickness, because in that case the resonance peaks should be eroded, but they, on the contrary, are rather well pronounced both for dark and illuminated crystals (figure 2(a)). The effect is probably connected to the different change of dynamic characteristics of 120° and 90° walls. Also it is possible that the localized photosensitive centres [6, 10] act as pinning ones, and their influence on wall motion is different for different kinds of wall.

## 5. Conclusions

In summary, we have demonstrated a potential of the NMR technique for the investigation of the photomagnetic phenomenon in magnetically ordered materials using $FeBO_3$ as an example. The amplitude of the NMR signal in illuminated samples exhibits sensitivity to some details of the domain structure and properties. It has been shown that the observed effect of NMR

enhancement under light exposure can be explained by a light induced decrease of the easy-plane magnetic anisotropy, that agrees with other data on the photomagnetic phenomenon in this crystal.

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