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EFFECT OF HYPERFINE INTERACTION ON ELECTRON AND NUCLEAR RESONANCE IN ANTIFERROMAGNETIC $MnCO_3$

V. A. TULIN

Institute for Physical Problems, USSR Academy of Sciences

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The effect of hyperfine interaction on the antiferromagnetic and nuclear resonance spectra in antiferromagnetic $MnCO_3$ is investigated at helium temperatures. The dependence of the AFMR line shift in a magnetic field on the NMR saturation frequency is derived. The dependence of the power required for saturating NMR on the angle between the rf magnetic field and the direction of the external magnetic field is determined. The angular dependence is found to be different for the power required for saturation of NMR and for disappearance of NMR saturation. When AFMR is employed as a detector of the temperature of the nuclear system, the spin-lattice relaxation time for the Mn^{55} nuclei is found to be 0.53 ± 0.1 ms. The dependence of the modified NMR spectrum on the external magnetic field is investigated for a constant nuclear temperature. The rf absorption curves are measured at high power in a magnetic field. The dependence of the power required for saturation in the nuclear system on the frequency difference of the exciting generator and the modified NMR frequency is investigated. The experimental results are discussed and compared with theory.

In the majority of antiferromagnets, anisotropy has the deciding influence on the high-frequency magnetic properties. For many antiferromagnets, with the usual magnitudes of crystalline anisotropy, all other influences on the position of magnetic resonances are much weaker, and it is very difficult to isolate them for independent investigation.

At the present time, a large number of antiferromagnets with small crystalline magnetic anisotropy is known; these are substances with cubic or almost cubic symmetry, as well as those antiferromagnets in which the spins in the ordered state are directed perpendicular to an axis of high order. In such substances, other characteristics can show up in the magnetic resonances, and their effect on the positions of the resonances is comparable to or even greater than the effect of anisotropy. Such characteristics are the magnetostrictive phenomena in hematite, α-Fe_2O_3,[1] and the hyperfine interaction in a number of substances containing manganese ions.[2-9]

In this paper we investigate the effect of hyperfine interaction on the high-frequency magnetic properties of antiferromagnetic manganese carbonate, $MnCO_3$. We have observed a change in the antiferromagnetic resonance (AFMR) spectrum during nuclear magnetic resonance (NMR) saturation,[1)] as well as a number of peculiarities in the NMR arising in this substance as a result of the coupling between the nuclei and the collective system of electrons in the ordered state.

To take the effect of hyperfine interaction on AFMR into account, it is necessary to add to the Hamiltonian of the antiferromagnetic system a term of the form $A(\mathbf{M}_1\cdot\mathbf{m}_1+\mathbf{M}_2\cdot\mathbf{m}_2)$, where A is the hyperfine interaction constant, $\mathbf{M}_1$ and $\mathbf{M}_2$ are the magnetizations of the electronic sublattices, and $\mathbf{m}_1$ and $\mathbf{m}_2$ are the magnetizations of the nuclear sublattices. If one considers the Hamiltonian of the magnetic system as a function of the generalized coordinates $\mathbf{M}_i$ and $\mathbf{m}_i$, then it is obvious that the presence of such terms must lead to a coupling of the vibrations of the electronic and nuclear systems of magnetic moments and thus to a change in their eigenfrequencies. The degree of this change depends on the closeness of these frequencies for the non-interacting systems, as well as on the magnitude of the average nuclear magnetization

$$\frac{N}{2}\frac{\langle I_z\rangle}{\gamma_n}=\langle m\rangle=\frac{N}{2}\frac{I(I+1)AM_i}{\gamma_n{}^2kT},\qquad(1)$$

where $\langle I_z\rangle$ is the average value of the spin projection on the direction of magnetization of the electrons, N is the number of magnetic atoms in 1 cm³, I is the nuclear spin, γ_n is the nuclear gyromagnetic ratio, k is Boltzmann's constant, and T is the absolute temperature. The quantities A and M_i are considered to be independent of temperature ($T \ll T_N$).

For a two-sublattice antiferromagnet, the analysis of the equations of motion of the electronic and nuclear systems coupled by hyperfine interaction leads to the following expressions for the four eigenfrequencies of the total system[6,10]:

$$\omega_{e12}^2=\omega_{e12}^{(0)2}+\omega_{en}^2,\qquad(2)$$

$$\omega_{n12}^2=\omega_{n0}^2\left(1-\frac{\omega_{en}{}^2}{\omega_{e12}^{(0)2}+\omega_{en}^2}\right),\qquad(3)$$

where ω_{e12} are the two branches corresponding to electronic AFMR, $\omega_{e12}^{(0)}$ are the resonance frequencies of the antiferromagnetic system without hyperfine interaction, $\omega_{en}^2=\gamma_e^2 2H_E H_T$, $H_T=A\langle m\rangle$ is the average effective field acting on an electronic sublattice from the nuclear sublattice due to hyperfine interaction, H_E is the exchange field, γ_e is the electronic gyromagnetic ratio, ω_{n12} are the two frequencies corresponding to NMR, $\omega_{n0}=\gamma_n H_{hf}$, $H_{hf}=AM_i$ is the average effective field of the electronic sublattices acting on

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[1)] The results of this part of the work was reported at the XI All-Union Conference on Low-Temperature Physics in Minsk, 1964.

the nuclear sublattices.

For the considered case of $MnCO_3$

$$\omega_{e1}^{(0)2} = \gamma_e^2 H(H + H_D), \tag{4}$$

where H is the applied magnetic field and H_D is the Dzyaloshinskiĭ field. It is seen from Eqs. (2) to (4) that in the electronic AFMR spectrum there arises an additional gap, the magnitude of which depends on the nuclear magnetization $\langle m \rangle$ in the hyperfine field of the electron, i.e., on the temperature of the nuclear system, and in the NMR spectrum there arises a dependence of frequency on the magnitude of the dc magnetic field, because of the field dependence of $\omega_{e12}^{(0)}$, and also a dependence on the intrinsic magnetization $\langle m \rangle$.

An effect of hyperfine interaction on the eigenfrequencies of the antiferromagnetic system was found in the AFMR study of $KMnF_3$.[2] In that study a strong dependence of the position of the AFMR resonance line on temperature was observed below 4.2°K. It was hypothesized that this dependence was caused by the change of magnetization of Mn^{55} nuclei, which are already noticeably polarized at helium temperatures. To check this, a double resonance experiment was carried out,[2] in which the temperature of the nuclear system was varied and the phenomenon of NMR saturation was employed; a change in the position of the AFMR line at constant sample temperature was observed. The results of this experiment confirmed the hypothesis.

EXPERIMENTAL ARRANGEMENT

In our work we used a 3-cm transmission spectrometer with low-frequency field modulation to observe the AFMR (Fig. 1). An H_{011} cylindrical resonator was used as the absorption cell. The signal from the crystal detector was fed to a narrow-band amplifier tuned to the field modulation frequency, a phase detector, and the Y axis of an X-Y recorder. The signal from a Hall probe was connected to the X axis. The AFMR line was traced out during a slow magnetic field scan. The sample was placed on the axis of the resonator in a coil, the axis of the coil being perpendicular to the axis of the resonator. The coil had several turns of 0.3-mm copper wire and was 3 to 4 mm in diameter and 3 to 4 mm in length. The coil was driven by a GSS-12 oscillator (150 to 1000 MHz, output power not less than 1 W). A pickup loop connected to a crystal detector and meter, placed near the coil, served to monitor the rf power level within it. The dc field of the electromagnet was perpendicular to the resonator axis and could be rotated relative to the polarization of the rf field in the coil, which always remained perpendicular to the resonator axis so as not to affect the operation of the 3-cm spectrometer.

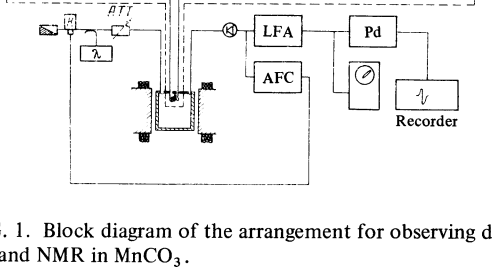


FIG. 1. Block diagram of the arrangement for observing double AFMR and NMR in $MnCO_3$.

CRYSTALS

The crystals we investigated were monocrystals of $MnCO_3$ prepared by the hydrothermal process of Ikornikova[11] in the Crystallographic Institute, USSR Academy of Sciences. The samples of $MnCO_3$ crystal (which are rhombohedral) were in the form of platelets about 0.1 mm thick and 1 to 2 mm wide; the [111] axis (the principal axis of the crystal) was perpendicular to the plane of the platelet. Below the Néel temperature T_N = 32.5°K, manganese carbonate goes over into an antiferromagnetic state which possesses weak ferromagnetism. If it is one of the well-studied antiferromagnets, and thorough investigations of its static[12] and resonance[13] magnetic properties have been made. The experimental data agree well with each other and with thermodynamic theory.[12,14] In the ordered state the antiferromagnetic vector lies in the (111) plane,[15,22] and the weak ferromagnetic vector also is in this plane and is directed perpendicular to the antiferromagnetic vector. Anisotropy in the (111) plane is very small, which leads to the presence of a low-frequency branch in the AFMR spectrum.

OBSERVATION OF DOUBLE RESONANCE

As was shown earlier, the position of the AFMR line depends on the temperature of the nuclear system. By using the phenomenon of NMR saturation, it is possible to change the nuclear spin temperature and observe a shift of the AFMR line. Thus it is possible to obtain data on the temperature of the nuclear spin system and on the processes which establish equilibrium in the nuclear system. The idea of double resonance is based on this.[2] The crystal was placed in the resonator of the 3-cm spectrometer, inside the coil driven by a generator of decimeter waves; by varying the rf field intensity, we observed a change in the AFMR resonance field. The dc magnetic field, the rf magnetic field, and the microwave field were mutually perpendicular, and the dc field and the rf field were arranged parallel to the (111) plane crystal, whereas the microwave field was perpendicular to this plane. With such an orientation of the fields, it is possible to observe the low-frequency branch of the AFMR and saturate the low-frequency branch of the NMR.

The experimental data are shown in Fig. 2, which gives the dependence of the AFMR resonance magnetic field on the frequency at which the NMR was saturated. It turned out that the NMR can be saturated over a wide range of frequencies (from 540 to 640 MHz in the given experiment), and each frequency has its own value of AFMR line shift, i.e., its own definite nuclear temperature. The position of the unshifted line is indicated in Fig. 2 by the dashed line. The width of the AFMR line under the given conditions was about 100 Oe and for the most part was less than the magnitude of the shift.

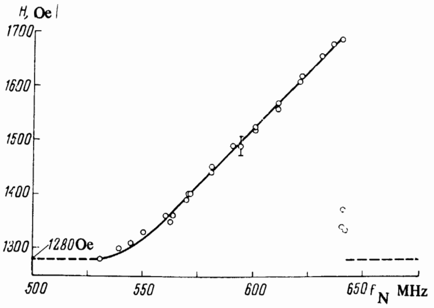


FIG. 2. Position of the AFMR line as a function of the frequency of NMR saturation.

The character of the shift of the AFMR line in its general features is the same at all investigated frequencies and takes place as follows. At first, increasing the power does not lead to any shift in position of the AFMR line. Upon attainment of a certain critical power level p_{cr}, which at a given frequency depends on the magnetic field, the AFMR line suddenly shifts its position. Upon further increase of power this new position does not change. The shifted line is somewhat less intense and has a smoother structure. When the power is decreased from some sufficiently high value, the AFMR line remains in the shifted position for values of power less than p_{cr}, and then there is a region of power change in which the shifted and unshifted lines exist simultaneously. The intensity of the unshifted line grows from zero to its maximum value, and the intensity of the shifted line falls off from the value observed at higher powers of the rf field to zero. If one does not leave this double-line region toward lower powers, the process is reversible upon decreasing or increasing the power. But if we descend below this region, then in order to saturate the NMR it is necessary again to ascend to the value p_{cr}. The hysteresis of this phenomenon may be characterized by two power levels: p_{cr} and $p_{1/2}$, where $p_{1/2}$ is the power at which the shifted and unshifted AFMR lines have the same intensity.

The dependence of the hysteresis on the angle between the direction of the dc magnetic field $\mathbf{H}_0$ (i.e., the vector of the weak ferromagnetic moment) and the polarization of the rf field was investigated. The obtained dependence of p_{cr} and $p_{1/2}$ on the angle $(\mathbf{H}_0, \mathbf{h}_{rf})$ is given in Fig. 3. The quantity $p_{1/2}$ varies as $1/\cos^2(\mathbf{H}_0, \mathbf{h}_{rf})$; any departure from this can be attributed to inaccuracy in orienting the crystal relative to the direction of the rf magnetic field. The quantity p_{cr} varies more slowly, and at angles differing from zero by an amount of the order of 10^0 (depending on frequency) p_{cr} becomes less than $p_{1/2}$ and the hysteresis disappears.

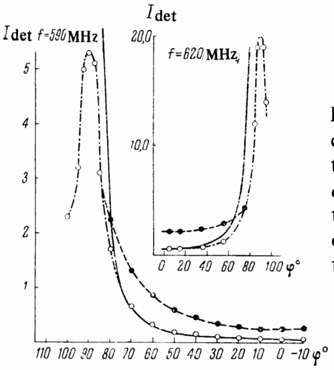


FIG. 3. Angular dependence of P_{cr} (solid circles) and $p_{1/2}$ (open circles) on the angle of rotation of the magnet (position of the maxima corresponds to the case H parallel to the axis of the coil). I_{det} is the detector current, proportional to the rf power.

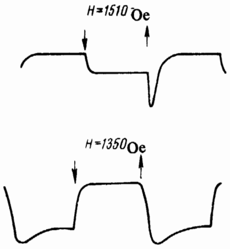


FIG. 4. Oscillograms showing observation of AFMR with NMR saturation by pulse-modulation of the rf power. The minima of the curves correspond to maxima of absorption in the antiferromagnetic system (the down arrows correspond to the start of the pulse, the up arrows to its end).

RELAXATION TIME OF THE NUCLEAR SYSTEM

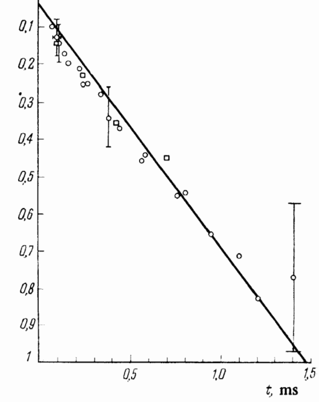
The spin-lattice relaxation time of Mn^{55} nuclei in $MnCO_3$ was determined by the double resonance method. The nuclear system was saturated at a certain frequency by rf power modulated by rectangular pulses. The process of reestablishment of equilibrium with the lattice was investigated. The position of the AFMR line served to measure the temperature of the nuclear system. The dc magnetic field was set at values between the shifted and unshifted positions of the AFMR line, and the time after the end of the pulse that it took to go through a maximum of AFMR absorption at this field was observed.[2] The signal from the crystal detector of the 3-cm spectrometer was observed directly on an oscilloscope, where the time was also measured from markers. Oscillograms for two values of the magnetic field are shown in Fig. 4.

To determine the relaxation time from these data, we used Eq. (2), which may be written in the following form:

$$(\omega_{e1}/\gamma_e)^2 = H(H+H_D) + 2H_EA[\langle m\rangle - (\langle m\rangle - m_\omega)e^{-t/\tau}]. \quad (5)$$

This takes into account the change of the nuclear magnetization from the value m_ω, the magnitude of the nuclear magnetization established on saturation of the NMR at frequency ω, to the value $\langle m\rangle$, which corresponds to the lattice temperature. For the time, the following equation is obtained:

FIG. 5. Graph for determining the relaxation time of Mn^{55} nuclei (circles correspond to NMR saturation frequency of 635 MHz, the squares to 594 MHz). The quantity represented by Eq. (6) is plotted as the ordinate.



$$0.434\tau = \log\{[H(H+H_D) + 2H_E A\langle m\rangle] - (\omega/\gamma_e)^2\} - \ln[2H_E A(\langle m\rangle - m_\omega)]. \tag{6}$$

The magnitude of the AFMR line shift, or more precisely, the ratio of the line shift to its width, has an important effect on the accuracy of the measurements; hence it is better to investigate the establishment of equilibrium in the nuclear system at frequencies of NMR saturation close to ω_{n0}, where the AFMR line shift is great.

The results of this experiment are given in Fig. 5. The NMR was saturated at the frequencies 635 and 594 MHz, the AFMR line shift being 360 and 210 Oe, respectively, with a line width of about 100 Oe. With an increase in the measured value of the time, i.e., at values of the dc field close to the unshifted position of the AFMR line, the line observed on the oscilloscope was very much spread out (Fig. 4, lower oscillogram), and the position of the maximum could not be determined very precisely. The relaxation time determined from the results shown in Fig. 5 is 0.53 ± 0.1 ms and was the same for both frequencies, within experimental error. The relaxation time obtained in this experiment is very much less than those of Mn^{55} in $KMnF_3$ and $CsMnF_3$, which are 18.5 and 14.5 ms, respectively.[6] It should be noted that during observation of the process of establishment of saturation in the sample, i.e., at the leading edge of the pulse, the resonance signal was not observed on the oscilloscope (Fig. 4). This indicates that establishment of saturation in the sample does not take place simultaneously over the whole sample.

DIRECT OBSERVATION OF ABSORPTION IN THE NUCLEAR SYSTEM

The investigation of NMR by double resonance has a number of drawbacks. The first of these is the fact that in working with a single spectrometer we are limited to a narrow region of magnetic field, since observation is possible only from the position of the unshifted AFMR line to the position of the maximum shift. The second is that each point in the spectrum of the nuclear system is taken at a different nuclear spin temperature. Hence it was of interest to make a direct observation of absorption in the nuclear system.[16,17]

For direct observation of absorption at radiofrequencies, the $MnCO_3$ crystal was placed in a coil connected to a generator of decimeter waves and in a dc magnetic field. A pickup loop was placed close to the coil, and the voltage induced in it was detected and then amplified by a narrow-band amplifier turned to the magnetic field modulation frequency (see Fig. 1). After phase detection, the derivative of the absorption signal was recorded on an X-Y recorder relative to the signal from a Hall probe placed in the magnetic field. The signal was traced out in a slow magnetic field scan.

For sufficiently small rf powers, the average nuclear magnetization $\langle m\rangle$ is almost constant, and, by observing resonance at different frequencies, we can investigate the NMR spectrum modified by hyperfine interaction as a function of magnetic field at a constant nuclear temperature.[2)]

We found the dependence of the resonance magnetic field on generator frequency for two temperatures: 4.2 and 1.8°K. The results are shown in Fig. 6. For comparison with theory, Fig. 6 includes continuous curves which correspond to the formula

$$\omega_{n1} = \omega_{n0}\left(1 - \frac{\omega_{en}^2}{\omega_{c1}^2}\right)^{1/2} = \omega_{n0}\left(1 - \frac{2H_E A\langle m\rangle}{H(H+H_D) + 2H_E A\langle m\rangle}\right)^{1/2} \tag{7}$$

with the following constants: H_D = 4.4 Oe; $2H_E A\langle m\rangle$ equal to 3.5 and 1.6 Oe^2 for the temperatures 1.8 and 4.2 K, respectively, taken from[13]; $\omega_{n0}/2\pi$ = 640 MHz, the frequency for which the maximum shift of the AFMR line occurs in double resonance.

It is seen from Fig. 6 that the theoretical curves agree well with the experimental results. A strong frequency dependence of the resonance field is observed due to the appearance of resonant properties of the electronic antiferromagnetic system in the oscillations of the nuclear magnetic moments.

We now pass to a description of effects associated with absorption at high powers, i.e., to the case when $\langle m\rangle$ changes significantly. For observation of absorption in this case the signal from the crystal detector was connected directly to the recorder, and the change in intensity of this signal was traced out as a function of magnetic field. Upon increasing the power from small values, the absorption curve broadened and the absorption maximum shifted toward smaller values of the dc field. The change in shape of the absorption curve is shown in Fig. 7 where successive traces of the detector signal for different values of power are given. At a certain value of the power, the appearance and disappearance of absorption sets in stepwise from the side of small values of the magnetic field at the crystal. In this case phenomena occur that are analogous to that described in the section on double resonance, except that in this case $\omega_n = f(H)$ varies, and not the rf power. With further increase in power, the step in the absorption with decreasing magnetic field disappears, the absorption gradually falls to zero, and at even greater values of power the absorption, having arisen stepwise upon increasing the magnetic field from H = 0, now does not disappear when the field is reduced even at H = 0. The absorption curve has a rather complex character and a large spread over magnetic field: from the value of the field H_{res} corresponding to the resonance field of the modified branch of the NMR (Eq. (7)) for a given frequency, to $-H_{res}$.

At frequencies to 500 MHz and with sufficient power, the absorption curves behave in similar fashion, but at frequencies somewhat lower than this, we were not able to obtain absorption near H = 0 at the maximum power we applied; in a certain region near 450 MHz the absorption appears and disappears in stepwise fashion in both directions of magnetic field change. At frequencies below 450 MHz, it is impossible to obtain steps, and a smooth curve without hysteresis is observed (Fig. 8). With further decrease of frequency the intensity of absorption rapidly falls off (Fig. 8).

At frequencies higher than 500 MHz, we investigated the dependence of the magnitude of the magnetic field at

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[2)] A preliminary report of these measurements was made earlier.[16]

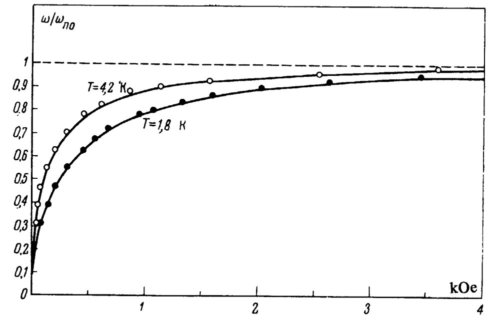


FIG. 6. Dependence of the frequency of the modified NMR spectrum on the magnitude of the applied magnetic field.

which absorption arises in stepwise fashion on the rf power applied to the coil containing the sample. The data of this experiment are given in Fig. 9, where we plot the crystal detector current $I_{\rm det}$, which is proportional to power, versus $[\omega_n(H)/\omega_{n0}]^2$, the relative value of the frequency calculated from the value of the magnetic field at which the step occurs. The constancy of the coefficient of proportionality between the detector current and the power in the coil for the different frequencies was not controlled in any way; hence we can speak only of the character of the curves for each frequency. From the experimental data it is seen that the character of the dependence of power necessary for saturation of the nuclear spin system on the relative detuning $[\omega_{\rm gen}^2 - \omega_n^2(H)]/_{n0}^2$ is different for different frequencies. For frequencies close to ω_{n0} it is linear, but it is non-linear at lower frequencies.

DISCUSSION

The basic peculiarity of all the phenomena investigated in this work is the strong dependence of the frequencies of AFMR and NMR on the degree of ordering of the nuclei $\langle m \rangle$. The double resonance data show that the NMR may be saturated over a wide range of frequencies and that to each frequency corresponds a unique nuclear magnetization, i.e., nuclear temperature. This can be easily understood on the basis of simple considerations.

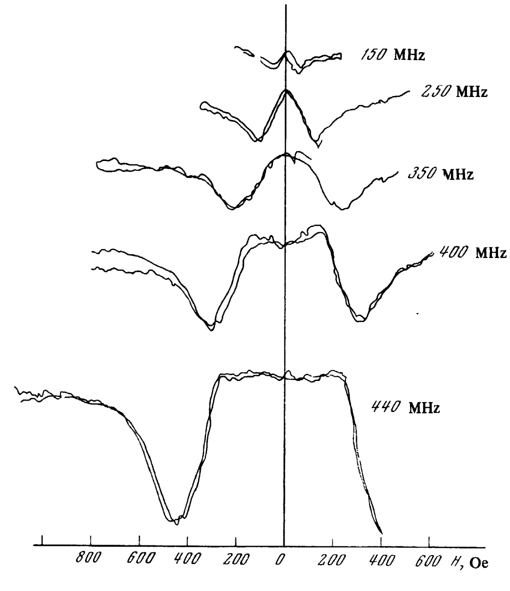


FIG. 8. Curves of absorption in the sample at different frequencies as a function of magnetic field. The minima of the curves correspond to maxima of absorption.

Let us assume that we saturate the NMR at a frequency ω_g less than $\omega_{n0} = \gamma_n AM_i$, but greater than the resonance value $\omega_n(H, T)$ for a given value of the dc magnetic field and sample temperature (see Fig. 6). In a certain range of rf power there will be practically no significant absorption in the sample and change of the degree of magnetization of the nuclear sublattices $\langle m \rangle$, if the generator frequency is sufficiently different from $\omega_n(H, T)$ ($[\omega - \omega_n(H, T)] \gg \delta\omega_n$, where $\delta\omega_n$ is the NMR line width). Upon attainment of some power level there arises some small change of $\langle m \rangle$ corresponding to heating of the nuclear system to the temperature T'; this leads to an increase in the nuclear resonance frequency to the value $\omega_n(H, T')$ in accordance with Eq. (3), and a decrease in the difference between the frequencies of the generator and the NMR leads to an increase in absorption of energy and to a further decrease of the nuclear magnetization $\langle m \rangle$, and so forth. As a result, the nuclear system attains

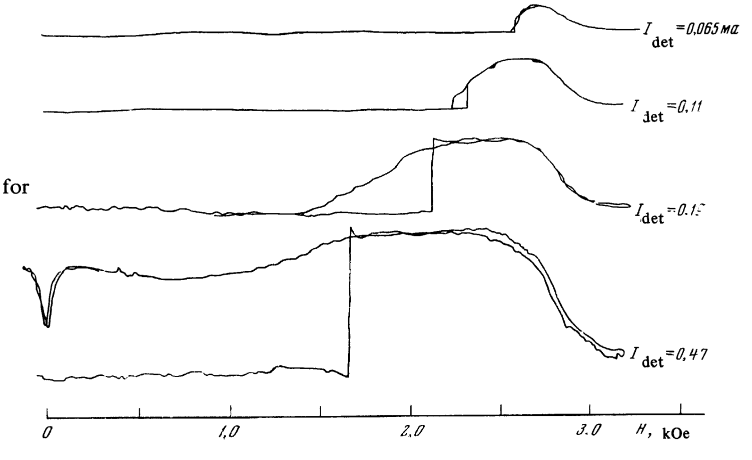


FIG. 7. Curves of absorption in the $MnCO_3$ sample at 600 MHz for different values of crystal detector current $I_{\rm det}$.

that temperature T'' for which $\omega_g = \omega(H, T'')$, Upon further decrease of $\langle m \rangle$ the resonance frequency $\omega_n(H, T)$ becomes greater than ω, and the detuning should increase. At the end of this process there is established such a value of the magnetization of the nuclear sublattices $\langle m \rangle^*$ for which $\omega = \omega_n(H, T^*) - \Delta\omega(p)$. Here $\omega_n(H, T^*)$ is the NMR frequency in magnetic field H and at temperature T^* corresponding to the value of magnetization $\langle m \rangle^*$. The quantity $\Delta\omega(p)$ is the deviation of the generator frequency ω from the NMR resonance frequency, which indeed determines the amount of energy absorbed by the crystal necessary to maintain the average magnetization of the nuclear sublattices equal to $\langle m \rangle^*$.

Since when we changed the rf power in the double resonance experiments to the state when the nuclear system was saturated to the equilibrium value we did not observe an additional dependence of the position of the AFMR line on power, we may assert that the width of the intrinsic NMR line $\delta\omega$ is small and $\langle m \rangle^*$ is approximately equal to $\langle m \rangle''$, the value of the magnetization of the nuclear system for which $\omega = \omega_n(H, T'')$. Considering this and knowing that under the conditions of double resonance ω_{e1} is constant, we can find from Eq. (3) the dependence of the relative magnitude of the gap in the AFMR spectrum observed after NMR saturation on the frequency at which saturation is effected.

$$\frac{\omega_{en}^2}{\omega_{e1}^2} = \frac{\gamma_e^2 2H_E A \langle m \rangle}{\omega_{e1}^2} = 1 - \left(\frac{\omega}{\omega_{n0}}\right)^2. \tag{8}$$

Figure 10 shows the dependence of this gap on $(\omega/\omega_{n0})^2$, where $\omega_{n0}/2\pi = 640$ MHz is set to the frequency at which the maximum shift in the position of the AFMR line is observed. The solid circles in Fig. 10 are the results obtained by Fink and Shaltiel,[9] who observed double resonance at an AFMR frequency of 6.15 GHz and at 4.2°K. The experimental points of both our work and theirs lie well on straight lines with a slope of 45°. Both experiments show the presence of a residual gap in the AFMR spectrum: ours, $H_{\Delta 0}^2 = 0.39 \pm 0.1$ kOe^2, theirs, $H_{\Delta 0}^2 \approx 1$ kOe^2, which apparently means that our crystal was of higher quality.

With direct observation of NMR at small powers, the experimental results on the dependence of the NMR frequency on the magnitude of the dc magnetic field (Fig. 6) agree with the theoretical formula (3). This agreement allows us to use this same theory for the description of the other experimental data. Below we shall give a possible qualitative explanation of the complex character of the absorption curves at high power levels (see Fig. 7).

From the double resonance experiments it is clear that in the case of sufficiently high powers, each frequency ω has its own value $\langle m \rangle_\omega$, the magnetization of the nuclear sublattices. It is possible to obtain the theoretical dependence of $\langle m \rangle_\omega$ on the magnitude of the magnetic field. For this, we rewrite Eq. (3) in the form

$$\omega_n^2 = \omega_{n0}^2 \frac{\omega_{e1}^{(0)2}}{\omega_{e1}^{(0)2} + \omega_{en}^2}, \tag{9}$$

from which we find, considering that $\omega_{en}^2 = \gamma_e^2 2H_E A \langle m \rangle_\omega$,

$$\langle m \rangle_\omega = \frac{\omega_{e1}^{(0)2}}{\gamma_e^2 2H_E A}\left(\frac{\omega_{n0}^2}{\omega^2} - 1\right). \tag{10}$$

Substituting the expression for $\omega_{e1}^{(0)}$ for the case of MnCO$_3$, we obtain

$$\langle m \rangle_\omega = \left(\frac{\omega_{n0}^2}{\omega^2} - 1\right)\frac{H(H + H_D)}{2H_E A}. \tag{11}$$

Thus, at sufficiently high rf power for $H < H_{res}(\omega, T)$ (H_{res} is the magnetic field of NMR at frequency ω and at lattice temperature T) we obtain $\langle m \rangle_\omega \sim H(H + H_D)$. This formula is valid when $H_{\Delta 0}^2$, the residual gap in the AFMR spectrum is small compared to $H(H + H_D)$.

If we assume that the phenomena in the nuclear system associated with the action of the rf field are described by the Bloch equations, then the relation between the absorption and the magnetization of the nuclear sublattices should have the form[18]

$$v = \frac{\langle m \rangle_0 - \langle m \rangle_\omega}{\gamma_n h_1 T_1}, \tag{12}$$

where γ_n is the nuclear gyromagnetic ratio, h_1 is the amplitude of the rf magnetic field at the nuclear, T_1 is the spin-lattice relaxation time of the nuclear system, $\langle m \rangle_0$ is the magnetization of the nuclear sublattices at a temperature of the nuclear system equal to the lattice temperature, and $\langle m \rangle_\omega$ is the magnetization of the nuclear system established under the action of the high-frequency magnetic field. The amplitude of the high-frequency field at the nuclei for the case of strongly coupled electronic and nuclear spin systems will be amplified on account of the susceptibility of the electrons at the NMR frequency. The high-frequency field oscillates the electron spin and along with it also the effective field of the hyper-

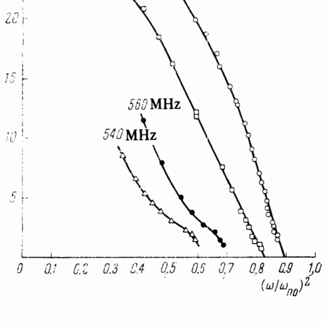
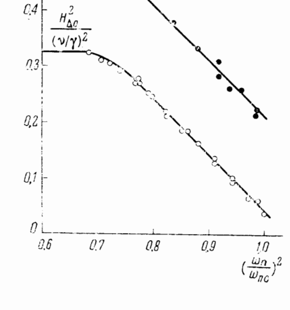


FIG. 9. Dependence of the power required for NMR saturation (p_{cr}) on the relative NMR frequency at which saturation appears.

FIG. 10. Dependence of the relative magnitude of the gap in the AFMR spectrum on the relative frequency of saturation (solid circles—data of Fink and Shaltiel[9]; open circles—data of this work).



fine interaction at the nucleus. Thus

$$h_1 \sim \chi_{\perp e} = \chi_{\perp 0} \frac{\gamma_e^2 (H + H_{\mathrm{D}})^2}{\omega_{e1}^2},$$

where $\gamma_{\perp 0}$ is the static susceptibility of the electronic antiferromagnetic system, and $\gamma_e^2 (H + H_D)^2/\omega_{e1}^2$ is the dependence of the rf magnetic susceptibility on the magnitude of the dc magnetic field for the case of $MnCO_3$ (for $\omega \ll \omega_{e1}$).

There are two possibilities for the relaxation time T_1. As our experiments on determining the relaxation time by double resonance showed, T_1 is independent of the applied dc magnetic field within experimental error in fields of about 1.5 kOe. However, in low fields, where a rapid decrease of the nuclear relaxation time is possible due to interaction with the antiferromagnetic system, there can be a dependence of T_1 on magnetic field. This dependence can be obtained by differentiating Eq. (3) (see Turov and Kuleev[10]):

$$\frac{1}{2T_{1n}} = \Delta\omega_n = \frac{\omega_n^2}{\omega_{n0}} \frac{\omega_{en}^2}{\omega_{e0}^3} \Delta\omega_e. \tag{13}$$

Substituting (11), (13), and the expression for h_1 into (12), we obtain the dependence of absorption in the nuclear system on the magnitude of the applied magnetic field for sufficiently high power:

$$v \sim \frac{[1 - \alpha H (H + H_{\mathrm{D}})] \sqrt{H (H + H_{\mathrm{D}})}}{(H + H_{\mathrm{D}})^2}, \tag{14}$$

where $\alpha = 1/H_0 (H_0 + H_D)$, and H_0 is the field in which NMR is observed at frequency ω at a temperature of the the nuclear system equal to the lattice temperature.

For the case of T_1 independent of the dc magnetic field, we have

$$v \sim \frac{[1 - \alpha H (H + H_{\mathrm{D}})] H (H + H_{\mathrm{D}})}{(H + H_{\mathrm{D}})^2}. \tag{15}$$

The absorption curves observed in the experiment (Fig. 5) can be described using both (14) and (15). In fields greater than 1 kOe, the absorption can be described by (15), and in low fields, by (14). In intermediate fields, one has the sum of contributions from (15) and (14) with variable weights. To confirm the validity of these considerations, an investigation of the dependence of the spin-lattice relaxation time of the nuclear spin system on the magnitude of the applied magnetic field is required.

The processes associated with the establishment and disappearance of saturation in the NMR in the presence of a coupling between the electron and nuclear spin systems have been discussed by de Gennes et al.[6] These authors made estimates of the critical values of the amplitude of the rf magnetic field as a function of the detuning $(\omega - \omega_n)$ for the case of an ideal crystal with the appearance of an initial change of magnetization of the nuclear sublattices due to absorption in the wing of a Gaussian line. The amplitude of the rf field necessary to produce saturation of the nuclear spin system obtained in this work depends exponentially on the detuning $(\omega - \omega_n)^2$. But for the case of disappearance of saturation, they give this formula for the dependence of the amplitude of the rf field on frequency:

$$h^2 \sim (\omega - \omega_n) / (\omega_{n0} - \omega). \tag{16}$$

Witt and Portis[4,7] have proposed another mechanism for the appearance and disappearance of saturation on account of nonideality of the crystal. They proposed that there are regions near defects in which the NMR frequency smoothly changes from ω_{n0} to $\omega_n(H, T)$. This mechanism gives values of the critical rf fields necessary for the transition to the saturated state that are very much less at great differences between the frequencies of the working generator and $\omega_n(H, T)$ than the values in[6]. The dependence of critical power on detuning also has a different form:

$$h^2 \sim (\omega^2 - \omega_n^2) / (\omega_{n0}^2 - \omega^2). \tag{17}$$

However, for $(\omega_{n0} - \omega_n) \ll \omega_{n0}$, we find $h^2 \sim (\omega - \omega_n)/(\omega_{n0} - \omega)$, and (17) then agrees with (16), the result of de Gennes et al.[6]

The results of the investigation of the angular dependence of the processes of transition from the saturated to the unsaturated state and vice versa show that these processes are realized by two different mechanisms. The angular dependence of $p_{1/2}$, which characterizes the transition from the saturated to the unsaturated state, is close to $1/\cos^2(H, h_{rf})$. This means that only the component of h_{rf} that is perpendicular to H acts on the nucleus. This orientation corresponds to the maximum rf susceptibility of the antiferromagnetic system, i.e., to the maximum coefficient of NMR amplification. Thus, for this process, the interaction of h_{rf} with the whole crystal is characteristic. The quantity p_{cr} depends more weakly on the angle between the directions of H and h_{rf}, and this dependence becomes particularly weak at frequencies near ω_{n0}.

Hence in this case the component of h_{rf} interacts in the first place with nuclei in the region of distortions of the antiferromagnetic structure near crystal defects. One may think that for each of these defects there is a distinct direction, but these directions are isotropically distributed in the (111) plane in the case of $MnCO_3$.

We return to the results of the investigation of the dependence of p_{cr} on frequency in the transition from the unsaturated to the saturated state (see Fig. 9). We see that the exponential dependence of p_{cr} on $(\omega - \omega_n)^2$ does not occur in every case. The dependence of p_{cr} on $(\omega^2 - \omega_n^2)$ for different frequencies is different; for frequencies close to ω_{n0} it is linear, which confirms the hypothesis about a mechanism associated with the effect of crystal defects (Eq. (17)). At frequencies far from ω_{n0}, this linearity is destroyed, which, possibly, is due to effects occurring in an ideal crystal. A dependence of the amplification coefficient and the relaxation parameters of NMR on the magnitude of the applied magnetic field can lead to the observed difference from a linear dependence of p_{cr} on $\omega^2 - \omega_n^2$.

The process of disappearance of saturation was investigated by Witt and Portis,[7] who studied the dependence of $p_{1/2}$ on the frequency of NMR saturation in double resonance experiments. The experimental results of[17] are insufficient to distinguish between (16) and (17). However, crystal defects affect significantly only the transition to the saturated state. In the reverse process, distortions of the antiferromagnetic structure near defects can only make the transition to the unsaturated state occur in different regions of the crystal at somewhat different power levels (the simultaneous existence of two AFMR lines, shifted and unshifted, when observing double resonance).

Besides the NMR frequencies, the amplification coefficient and also the relaxation parameters of NMR will obviously differ from the usual values in the vicinity of crystal defects. As a result, the emergence of saturation, which is associated with crystal defects, takes place at higher values of the pump power than the disappearance, which is determined by the amplification coefficient and the relaxation parameters of the ideal portion of the crystal. This is a possible explanation of the hysteresis.

CONCLUSIONS

Our results may be summarized as follows:

1. From double resonance experiments we determined the dependence of the gap in the AFMR spectrum of $MnCO_3$ on the frequency of NMR saturation; the results agree with the theoretical calculation; the observed residual gap is $2H_E H_\Delta^* = 0.39 \pm 0.1$ kOe^2.
2. We investigated the angular dependence of the powers p_{cr} and $p_{1/2}$ on the angle between the directions of the dc and rf fields; the results indicate the presence of two mechanisms which are realized, one during appearance of NMR saturation, the other during its disappearance.
3. By using the position of the AFMR line as a nuclear spin thermometer, we determined the nuclear spin-lattice relaxation time T_1, using the pulse saturation method; we found $T_1 = 0.53 \pm 0.1$ ms for $MnCO_3$.
4. We investigated the hyperfine-modified NMR spectrum at a constant nuclear spin temperature; the results agree with theory and show that the oscillations excited at the investigated frequencies are mixed oscillations of the electronic and nuclear magnetic moment systems.
5. We observed a field dependence of absorption in the nuclear system at high powers. The absorption curves at sufficiently high power extend from the resonance field for a given frequency and temperature $H = H(\omega, T)$ to $H = 0$.
6. We investigated the dependence of the critical power at which saturation appears in the nuclear system on the value of detuning $(\omega^2 - \omega_n^2)/\omega_{n0}^2$. The results confirm that the emergence of saturation in the system occurs because of the presence of defects in the crystal.

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