Nuclear magnetic resonance of chlorine in the internal field of a magnetically ordered layered compound of graphite with NiCl$_2$

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The NMR method in conjunction with spin echo is used to investigate the behavior of the spontaneous magnetization $\langle S_z \rangle_T$ in a layered compound in which NiCl$_2$ layers are separated by two layers of graphite. It is shown that the microscopic magnetization of the layers of the magnetic ions does not correspond to the macroscopic magnetization of such a compound, although it does depend on the temperature linearly, thus confirming the two-dimensional character of the magnetic system. The point $T = 18.1$ °K, in which the macromagnetization sets in, is not the temperature at which $\langle S_z \rangle_T \to 0$, but there are observed at this point certain singularities that are apparently connected with the establishment of long-range order in the system, whereas $\langle S_z \rangle_T \neq 0$ in the macroscopically paramagnetic region. The presence of graphite atoms does not change H_{eff} at the chlorine nuclei significantly in comparison with the antiferromagnetic NiCl$_2$, thus indicating that the electron density on the 3*s* orbit of Cl$^-$ is not sensitive to the possible transport of the graphite *p* electrons. At the same time, this presence makes it necessary to place the Cl$^-$ ions in the NiCl$_2$ layers in two nonequivalent positions, a fact manifest by the presence of a doublet in the NMR spectrum.

SUBJECT AND METHOD OF INVESTIGATION

When NiCl$_2$ is introduced into the graphite lattice, a compound is produced with a layered structure and with new magnetic properties. The production of such compounds is described in[1,2], and the first investigations of the magnetic properties of the layered graphite compound (LGC) with NiCl$_2$ (and also with CoCl$_2$ were published in[2,3]. The magnetic properties of analogous structures with MoCl$_5$, FeCl$_3$, and FeCl$_2$ were investigated in[4,5]. According to[2,3], the LGC with NiCl$_2$ behaves like a two-dimensional paramagnet with $T_c = 18.1$°K. At $T < 18.1$°K this compound reveals ferromagnetic properties that differ from those of ordinary ferromagnets.

The present paper is devoted to nuclear magnetic resonance (NMR) in second-degree polycrystalline LGC with NiCl$_3$.[1)] The investigation was carried out with the IS-3 spin-echo installation in the temperature interval 1.75 to 20°K. The temperature was maintained accurate to ~0.01°K.

The NMR frequency in a zero external field is determined by the magnetization of the sublattice whose magnetic ions are coupled by the hyperfine interaction with the investigated nuclei:

$$h\nu_{\text{NMR}} = \gamma_n H_{\text{eff}} = \sum_i A_i \langle S_z \rangle_T .$$

Here A_i is the hyperfine interaction constant of the investigated nucleus with the electron spin of the i-th magnetic ion. We were thus able to measure exactly the temperature dependence of $\langle S_z \rangle_T$ and compare it with the results of an investigation of the macroscopic magnetization[3].

The spin-echo spectrum from the chlorine nuclei in the investigated sample is a superposition of a large number of NMR lines. The plot of this spectrum at T = 1.75°K is shown in Fig. 1a. We investigated the temperature dependence of the frequencies of the maxima of the NMR spectra (Fig. 2). To illustrate the behavior of the intensities, we constructed a graph in three dimensions (Fig. 3). As the temperature is raised, the spin-spin relaxation time T_2 decreases abruptly, the lines broaden, and the signals decrease in intensity and become practically unobservable at T > 17°K. The NMR frequency decreases, but does not vanish as T → 18°K, with $\nu_{\text{NMR}}(T) \approx 0.65\, \nu_{\text{NMR}}(0)$. The NMR spectrum is the same for the investigated samples with different NiCl$_2$ contents.

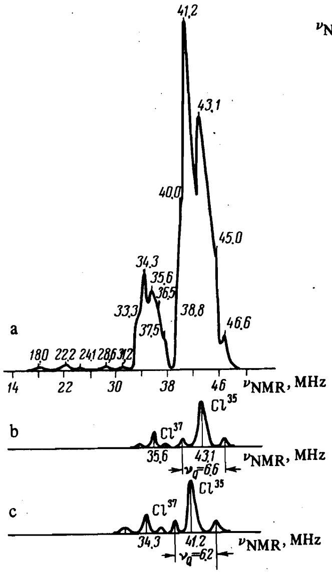

FIG. 1

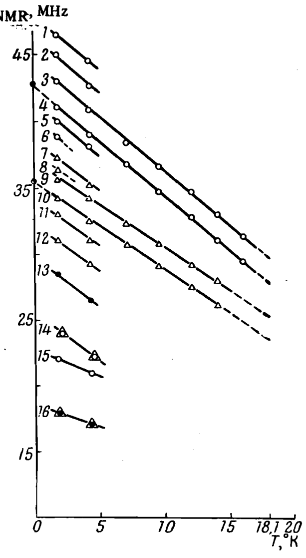

FIG. 2

FIG. 1. a) NMR spectrum in LGC with NiCl$_2$ at T = 1.75°K. b and c) Symbolic resolution of the main part of the spectrum into quadrupole triplets corresponding to distorted (b) and indistorted (c) arrangement of the Cl$^-$ ions relative to the Ni^{3+} ions as compared with pure NiCl$_2$.

FIG. 2. Temperature dependence of the NMR transition frequencies of the chlorines in LGC with NiCl$_2$. The dark symbols correspond in the frequency scale to $\nu_n(0)$ in pure antiferromagnetic NiCl$_2$.

Experiments were performed also with a constant external magnetic field superimposed, at $H_0 \parallel h_{HF}$ and $H_0 \perp h_{HF}$. If the signal were determined by the domain walls, then it would decrease with increasing H_0 regardless of the direction of H_0. At $H_0 \parallel h_{HF}$ the signal intensity decreased to approximately one-half at H_0 = 500 Oe

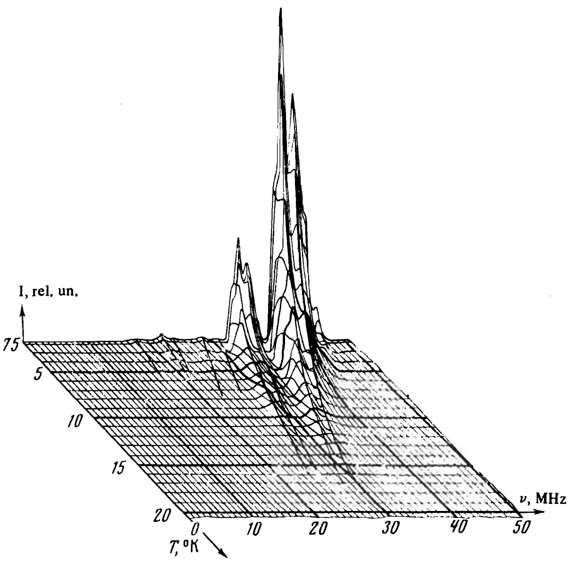

FIG. 3. Temperature dependences of the chlorine NMR signal intensity and frequency in LGC with $NiCl_2$. The intensity scale is relative.

and the signal vanished completely at $H_0 \geq 1000$ Oe. At $\mathbf{H}_0 \perp \mathbf{h}_{HF}$ the signal intensity increased and the signal became noticeable even at T = 17.5°K. In a field ~1 kOe and at T = 12°K the signal intensity increased approximately 1.3 times. These experiments allowed us to conclude that the observed signals do not pertain to the domain walls. They also indicate that the ordering is ferromagnetic in character.

We estimated the relaxation times of the Cl^{25} nuclei to be $T_2 \approx 100$ μsec and $T_1 \sim 2000$ μsec at T = 4.21°K. The time T_1 varies little with temperature, and T_2 decreases abruptly with increasing temperature. The optimal setting of the apparatus for undistorted observation of the NMR spin-echo signals corresponded to minimal pulse durations for the IS-3 spectrometers ($t_1 = 1$ μsec, $t_2 = 2$ μsec) and to a maximum tank-circuit voltage (~0.5 kV); the product of the RF pulse amplitudes by their duration was smaller by one order of magnitude than for pure $NiCl_3$, thus indicating a large amplification of the RF field in the samples.

RESULTS AND DISCUSSION

The main part of the NMR spectrum shown in Fig. 1a can be obtained by superimposing two parts of quadrupole triplets from the nuclei Cl^{35} and Cl^{37}, connected with the two values of H_{eff} at the chlorine nuclei (a symbolic resolution of such a spectrum is shown in Figs. 1b and 1c. The lines 1—12 (Fig. 2) cluster about two $(-1/2 \leftrightarrow +1/2)$ transition frequencies for Cl^{35} (lines 3 and 4) and two frequencies for Cl^{37} (lines 9 and 10). The ratios ν_3/ν_9 and ν_4/ν_{10} correspond, within the limits of the measurement accuracy, to the ratio of the nuclear magnetic moments for Cl^{35} and Cl^{37}, equal to 1.201. At T = 1.75°K the quadrupole triplets are 46.6, 43.1, 40.0 MHz and 45.0, 41.2, 38.8 MHz for Cl^{35} and 37.5, 35.6, 33.3 MHz and 36.5, 34.3, 31.1 MHz for Cl^{37}. The central lines of the two triplets, 4 and 10, when extrapolated to 0°K, lead to frequency values that almost coincide with $\nu_n(0)$ for pure $NiCl_2$[6], and $H_{eff} = 102$ kOe ($H_{eff} = 103$ kOe for pure $NiCl_2$). It is obvious that the chlorine ions responsible for these lines occupy the same positions relative to the Ni^{2+} ions as in the pure $NiCl_2$. Lines 3 and 9 are the central components of the triplets for another arrangement of the chlorines, and for them $\nu^{35}(0) = 44.5$ MHz, $\nu^{37}(0)$, and $H_{eff} = 107$ kOe. The frequency distance between the doublets does not vary with temperature. The dependence of the echo amplitude on the distance between the 90° and 180° pulses is oscillatory, thus indicating that there is one more splitting in the spectrum, on the order of several kilohertz. The frequencies of lines 15 and 16 are equal to half the frequencies of lines 3 and 9, possibly as a result of nonlinear effects, while the frequencies of lines 13 and 14 amount to 2/3 of the frequencies of the principal lines 3 and 9, and can be connected with the chlorine lines that have only two rather than three Ni^{2+} ions in their immediate surrounding.

It is shown in[2] that the magnetic moments of the Ni^{2+} ions lie in the planes of the layers, and then we have $|\nu_Q| = 6.6$ MHz for the first triplet and 6.2 MHz for the second triplet of Cl^{35}, approximately double the value of $|\nu_Q|$ in pure $NiCl_2$[7].

The dependence of $\nu_{NMR}(T)/\nu_{NMR}(0)$ on the temperature is linear within the limits of experimental accuracy and is the same for all lines (Fig. 1), in accord with the expected ratio for a two-dimensional ferromagnetic layered structure, under the condition that the anisotropy energy (and also the energy of the interlayer temperature dependence) is much less than kT even for the lowest temperature in the experiment[8]. If the obtained temperature dependence is extrapolated to high temperatures, then we have for the principal lines $\nu_{NMR}(T) \to 0$ at one point T ≈ 53°K (for pure $NiCl_2$ we have $T_N = 49.6$°K and the maximum of the specific heat of $NiCl_2$ occurs at 52.4°K).

When the sample was placed in a weak external magnetic field, besides the change in the NMR signal intensity, a rise took place also in the resonant frequency. The lines corresponding to Cl^{35} shifted by an amount $0.25[\text{MHz/kOe}]H_0$ at T = 4.21°K and $0.60[\text{MHz/kOe}]H_0$ at T = 12°K, while $\gamma_n = 0.417$ MHz/kOe. The shift can be either the result of the direct action of the external magnetic field on the nuclear spins (in the case of ferromagnetic ordering and under the condition that the direction of the hyperfine field at the Cl^- nuclei coincides with the direction of the electronic magnetization of Ni^{2+}), or else as the result of the change in the magnetization of the two-dimensional ferromagnetic layer. The former effect is independent of temperature and the shift cannot exceed γH. The latter effect depends on the temperature, and in our case it is this effect which determines in the main the dependence of the frequency (intralayer magnetization) on the external magnetic field. However, the large widths of the spectral lines did not enable us to separate completely the contribution of the direct action of the magnetic field on the nuclear spin, and to find the constants in the equations used in[8].

A comparison of our results with those of Karimov[3] shows that the macroscopic magnetization of GLC with $NiCl_2$, measured by him, does not correspond to the microscopic magnetization of the Ni^{2+} layers, which is responsible for the NMR frequency. One of the possible causes of this disparity may be the two-dimensional character of the investigated system. Indeed, in order for a macroscopic magnetization to appear it is necessary that a long-range magnetic order exist, and this is possible in a two-dimensional system only in the presence of a definite anisotropy[9] or weak three-dimensionality (interlayer interaction). At the same time,

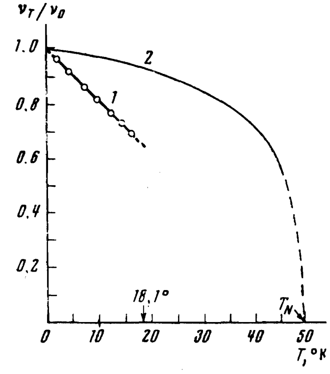

FIG. 4

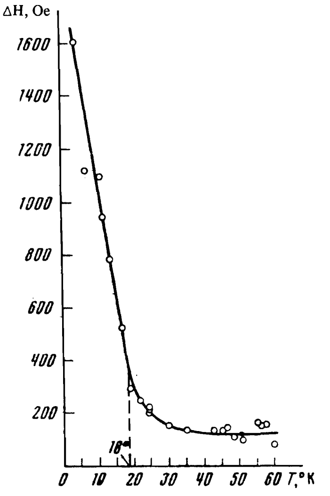

FIG. 5

FIG. 4. Temperature dependence of $\nu_{NMR}(T)/\nu_{NMR}(0)$ for all frequencies of the NMR spectrum: 1—straight line drawn through the experimental points for LGC with $NiCl_2$, 2—magnetization curve of sublattice in pure antiferromagnetic $NiCl_2$ [6].

FIG. 5. Temperature dependence of the EPR line width in LGC with $NiCl_2$.

each chlorine ion is coupled by hyperfine interaction to only the three nearest ions of the 3d metal, and the effective field at the chlorine nucleus differs from zero if the mutual orientation of the electron spins of these ions is preserved as a result of the presence of short-range order. Thus, in the temperature region where there is only short-range order (in this case, at $T \geq 18$°K), the NMR frequency of the Cl^- nuclei will differ from zero, but the NMR lines will be greatly broadened by short-range order fluctuations, and become unobservable. The presence of short-range order in the 18—50°K region agree with the broad susceptibility maxima obtained in[2] and stretching into the region of high temperatures. Another possible explanation may be a situation wherein the two-dimensional ordering in each layer of Ni^{2+} is realized at $T \approx 50$°K, but up to $T = 18.1$°K the magnetic moments of the individual layers are not correlated, and the sample behaves macroscopically like a paramagnet (in analogy with the superparamagnetism phenomenon). Such a model should lead to singularities in the spin specific heat at $18 < T < 50$°K.

We investigated also the temperature dependence of the electron spin resonance line width of GLC with $NiCl_2$ in the temperature interval 4.2—60°K.2) At $T < 18$°K, the electron resonance line consists of two lines superimposed on the other, one quite broad and shifted towards weaker fields (this line vanishes at $T \gtrsim 18$°K), and another, with $g \approx 2.23$, that becomes narrower with rising temperature. The first line is most probably due to ferromagnetic resonance, and the second to EPR. In the region where short-range fluctuations are produced, the EPR line width should increase in conformity with the increasing dimensions of the fluctuations[10]. There is no advantage in comparing in detail measurements made on powder with the theory of EPR broadening of short-range fluctuations, but the temperature dependence of the EPR line width (Fig. 5) shows that such fluctuations do take place at $T > 18$°K, thus confirming our assumption.

The appearance of two values of H_{eff} acting on the chlorine nuclei indicates that the positions of the Cl^- ions are not equivalent (if the distance between the magnetic ions coupled by strong interaction in the Ni^{2+} layers remain unchanged) in the layers adjacent to the Ni^{2+} layer in such a compound. Thus, for $FeCl_3$ introduced in graphite, it was shown that the preferable positions of the chlorine ions relative to the graphite layers are such that the carbon atoms are located at the centers of chlorine triangles (Fig. 4 of[11]). On the other hand, the chlorine ions tend to preserve normal (for the pure salt) distances between themselves and the third ion (Cl^-). Cowley and Ibers[11] regard as an equilibrium (but nevertheless distorted) state wherein half of all the chlorine ions are aligned as "wanted" by the graphite, having in mind each individual chlorine layer. No order whatever is observed in this case. That the structure of the $MoCl_5$ layer introduced in graphite is distorted is indicated also by the data of Syme-Johnson.

What remains unclear is whether the proximity of the graphite leads only to structural distortion, or whether the graphite electrons take part in the production of the field at the Cl^- nucleus. Croft[13] suggests that conduction electrons are transferred from the graphite to the cation, and the experimental data[12,14] favor this hypothesis. It can be concluded from our data that the indicated transport effects are in any case not strong enough to change the density of the 3s electrons of Cl^-, which determines via the fine-structure constant A_i the value of H_{eff} at the chlorine nucleus[6] (H_{eff} in LGC with $NiCl_2$ differs from H_{eff} in pure $NiCl_2$ by 1—3%).

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1)The number of the degree shows the number of graphite carbon grids per layer.

2)The authors are grateful to D. L. Lyfar' for the EPR measurements.

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