NMR of two-dimensionally-magnetically-ordered compounds containing graphite and $CoCl_2$ or $NiCl_2$

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The magnetic properties of layered graphite compounds (LGC) with $CoCl_2$ or $NiCl_2$ with various stages (graphite layers) are investigated at $T< 20$ K by a pulsed chlorine NMR technique in a zero external field. It is found that beginning from the first stage ($CoCl_2$) or the second stage ($NiCl_2$) the magnetization in these compounds varies linearly with temperature and can be satisfactorily described by the Narath approximation for a two-dimensional ferromagnetic substance at $H_A = 0.24$ kOe for LGC containing $NiCl_2$ and $H_A = 0.97$ kOe for LGC with $CoCl_2$. By comparing the experimental NMR data for pure and graphitized compounds it is concluded that interlayer interaction plays a decisive role in the appearance of magnetic anisotropy in pure $NiCl_2$ and $CoCl_2$, whereas for graphitized structures the effective intralayer contribution H_{AT} to the magnetic anisotropy H_A may be considered as predominant. The relaxation times T_2 and T_1 are measured. From the fact that the quadrupole coupling constants e^2Qq_{zz}/h are greater in graphitized structures than in nongraphitized ones it is concluded that an additional covalent chlorine-graphite *p*-bond is formed.

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INTRODUCTION

The investigated layered graphite compounds (LGC) with $CoCl_2$ and $NiCl_2$ are obtained by introducing layers of the paramagnetic salt in the crystalline state into the graphite lattice. The technology of sample preparation is described in[1,2]. The salt layers, which constitute chlorine—metal—chlorine sandwiches, are separated by n layers of a carbon grid (n = 1, 2, 3, ... is the number of the compartment of the compound). In the study of the magnetic properties of LGC with $MeCl_2$ (Me is a divalent ion of the iron group) it becomes possible to eliminate the influence of the interlayer exchange interaction that exists in pure salts. At the same time, LGC with chlorides of transition metals are in themselves an interesting research object. The distinguishing features of the magnetic properties in LGC with $NiCl_2$ and $CoCl_2$ are reported in[2-4].

The NMR method was used earlier to investigate both $NiCl_2$ and $CoCl_2$ themselves[5], as well as LGC with $NiCl_2$ with two compartments[6]. In the present study we used the NMR method to investigate LGC with $NiCl_2$ at n = 3 and LGC with $CoCl_2$ at n = 1, 2, and 3. It was assumed that the difference in n will be connected with the different approaches to ideal two-dimensional behavior in the interaction of the magnetic ions. The direct object of the investigation was the chlorine nuclei, which carried information concerning the magnetization of the magnetic ions $\langle S_z \rangle$, as is clear from the formula

$$h\nu_{\text{NMR}} = \sum_i A_i \langle S_z \rangle_T = \gamma_{\text{Cl}} H_{\text{eff}}. \quad (1)$$

where A_i is the constant of the hyperfine interaction of the chlorine nucleus with the electron spin **S** of the i-th magnetic ion.

We investigated polycrystalline samples synthesized at the Scientific Institute for Hetero-organic Compounds of the USSR Academy of Sciences, where the agreement between their structures was established by x-ray diffraction. The temperature ranged from 1.65 to 20° K and was maintained accurate to ~ 0.05° K. In the analysis of the NMR spectra in LGC with $NiCl_2$ and $CoCl_2$ we have assumed, by starting from the data of[2], that in the case of magnetic ordering the spins of the 3d-metal ions lie in the plane of the layer. This was confirmed by the large value of the amplification of the radio-frequency field in the samples (signals were observed at minimally short pulses), which is characteristic of ordering of the easy-plane type. In this case, the NMR signal of each of the two isotopes of Cl (nuclear spin I = 3/2) will contain, besides the line determined by Eq. (1), quadrupole satellites at the frequencies $\nu_{\text{NMR}} \pm \nu_Q/2$, which form, jointly with the fundamental line, a quadrupole triplet.

EXPERIMENTAL RESULTS AND DISCUSSION

a) Layered graphite compounds with $NiCl_2$. In LGC with $NiCl_2$ at n = 3, the spin-echo spectrum (Fig. 1a) coincides in form almost completely with the NMR spectrum in LGC with $NiCl_2$ at n = 2[6]. The slight difference between the frequencies is almost within the limits of experimental error (the accuracy in the determination of the frequencies, owing to the superposition of the individual lines, can be estimated at ± 0.15 MHz). Just as in[6], this spectrum can be resolved into a sum of two spectra, in each of which there are two quadrupole triplets (two chlorine isotopes) plus low-intensity low-frequency lines that seem to be connected with the defects of the structure of LGC with $NiCl_2$[6]. The quadrupole triplets at T = 1.75° K are 47.2, 43.2, 40.2 MHz and 45.2, 41.4, 38.8 MHz for Cl^{35} and 37.5, 35.9, 33.3 MHz and 36.7, 34.5, 31.2 MHz for Cl^{37}. The reason for the doublet splitting appears to be, just as for n = 2, the nonequivalent disposition of the chlorine ions in the layer adjacent to the layer of the magnetic Ni^{2+} ions. Thus, from the doublet spectrum of Cl^{35} we obtain $|\nu_Q| = 7.0$ MHz $H_{\text{eff}}(0) = 108$ kOe and $|\nu_Q| = 6.4$ MHz, $H_{\text{eff}}(0) = 103.5$ kOe. The signal intensity decreases with increasing temperature, the lines broaden and can no longer be resolved above 13° K, and at T > 15° K they cannot be distinguished from the noise. Figure 2 shows the temperature dependence of the frequencies at the maxima of the intense spectral lines, from which it is seen that even the third compartment is characterized by a linear dependence of the frequency $\nu_{\text{NMR}}(T)$. For the central lines of the Cl^{35} triplet (lines 1 and 2), $d\nu_{\text{NMR}}/dT = 0.82$ and 0.86 MHz/deg, as against 0.68 and 0.62 MHz/deg for Cl^{37} (lines 3 and 4), whereas for n = 2

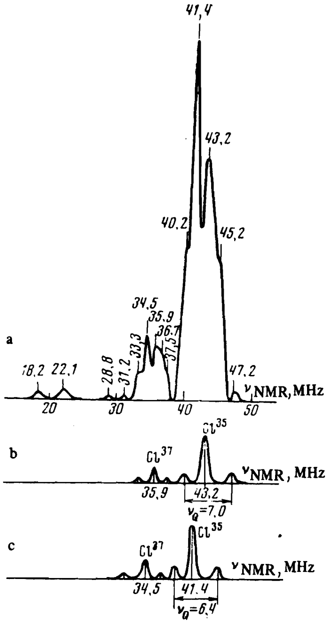

FIG. 1

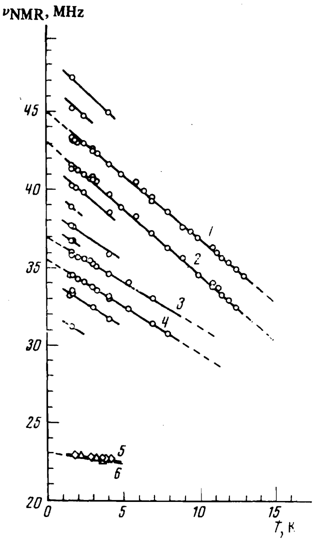

FIG. 2

FIG. 1. a—NMR spectrum in LGC with $NiCl_2$ ($n = 3$) at $T = 1.75°K$; b and c—symbolic resolution of the fundamental part of the spectrum into quadrupole triplets corresponding to distorted (b) and undistorted (c) arrangements of the Cl^- ions relative to the Ni^{2+} ions in comparison with pure $NiCl_2$.

FIG. 2. Temperature dependence of the NMR transition frequencies of the chlorine nuclei in LGC with $NiCl_2$ at $n = 3$ (lines 1 and 2 are the central components of the quadrupole triplets for Cl^{35}, and lines 3 and 4 are the same for Cl^{37}) and of the central component of the quadrupole triplet of Cl^{35} in LGC with $CoCl_2$ (line 5—case $n = 1$, line 6—cases $n = 2$ and 3).

the values of $d\nu_{NMR}/dT$ of the two components of the doublet were ~0.83 and ~0.67 MHz/deg for Cl^{35} and Cl^{37}, respectively.

A feature of the behavior of the NMR spectrum in the third compartment is a certain bending of the $\nu_{NMR}(T)$ lines at $T < 3°K$. However, as seen from Fig. 2, its value and the small temperature interval in which it is registered (1.7—3°K) do not allow us to examine this deviation from linearity of $\nu_{NMR}(T)$ with sufficient reliability. Experiments with superposition of an external constant magnetic field ($H_0 \parallel h_{HF}$ and $H_0 \perp h_{HF}$), performed in analogy with [6], show that the observed signals are not due to domain walls.

The character of the dependence of the relaxation times T_2 and T_1 on the temperature is the same as for $n = 2$, namely, with increasing temperature the time T_2 decreases sharply (Fig. 3), and T_1 decreases practically linearly at a rate ~60 μsec/deg. For different isotopes, the times are different, although the character of the dependence is the same: thus, for example at $T = 4.21°K$ the relaxation times for Cl^{35} amount to T_2 ~ 40 μsec and T_1 ~ 1000 μsec, and for Cl^{37} they are equal to T_2 ~ 70 μsec and T_1 ~ 2000 μsec. The temperature dependence of T_2 can be expressed analytically in the form $1/T_2 = T^{1.37}$.

b) Layered graphite compounds with $CoCl_2$. The NMR spectrum in LGC with $CoCl_2$ is practically the same for all three investigated compartments, and its form for $n = 1$ at $T = 1.75°K$ is shown in Fig. 4. This spectrum is also made up of a superposition of a large number of NMR lines, many of which cannot be resolved even at $T = 1.75°K$. This prevents us from interpreting this spectrum in the same detail as for LGC with $NiCl_2$ and, in particular, from determining $|\nu_Q|$ with the same accuracy (it can be assumed that $|\nu_Q| = 5-6$ MHz). Two maxima at frequencies 22.5 and 18.7 MHz at $T = 4.21°K$ are distinctly registered. The ratio of these frequencies, ≈ 1.2, agrees with the ratio of the magnetic moments of Cl^{35} and Cl^{37}, so that they can be identified with the central components of the quadrupole triplets. There is no clearly pronounced doublet character of the spectra in this case, although the maximum at 21.5 MHz and the unresolved line in the region of 18 MHz can be regarded as attributes of this character. To obtain reliable results, the observations were performed beyond the maximum at the frequency 22.5 MHz (at $T = 4.21°K$) corresponding to the central transition ($-1/2 \leftrightarrow +1/2$) of the isotope Cl^{35}. The temperature dependence of the frequency of this line is shown in Fig. 2 for all three investigated compartments. Lines 5 and 6, plotted from the experimental data for the three compartments, are straight with $d\nu_{NMR}/dT$ equal to 0.11 (first compartment) and 0.13 MHz/deg (second and third compartments). These differences lie almost entirely within the measurement errors, so that it can be concluded that a two-dimensional magnetic structure with small anisotropy field H_A is realized in LGC with $CoCl_2$, starting with the first compartment; this structure leads to a linear temperature dependence of the magnetization.

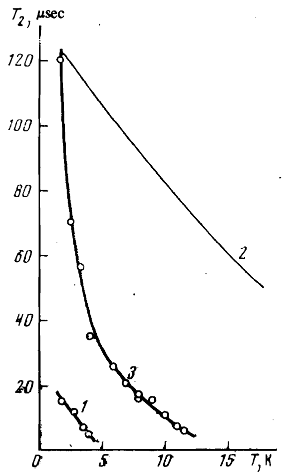

FIG. 3

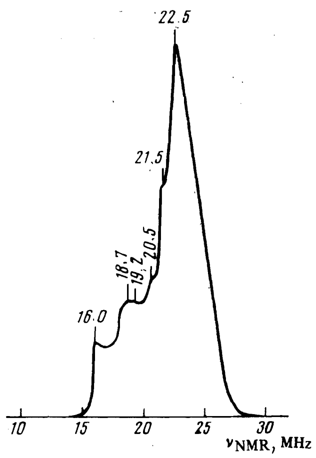

FIG. 4

FIG. 3. Dependence of the spin-spin relaxation time T_2 on the temperature: 1—in LGC with $CoCl_2$ ($n = 1, 2, 3$); 2—in LGC with $NiCl_2$ ($n = 2, 3$); 3—in pure $CoCl_2$.

FIG. 4. NMR spectrum of chlorine nuclei in LGC with $COCl_2$ at $T = 1.75°K$ for $n = 1$.

The relaxation times for all three compartments are practically the same, and their values at $T = 4.21$ K and for Cl^{35} are T_2 ~ 5 μsec and T_1 ~ 1500 μsec. The temperature dependence of T_2 in the interval 1.7—4.21°K is shown in Fig. 3 (curve 1). In contrast to pure $CoCl_2$ (curve 2), the spin-spin relaxation time T_2 becomes so short here that at $T > 5°K$ the pulse method of observing the NMR signal ceases to be effective. We note that according to Karimov [3], the macroscopic spontaneous magnetization in LGC with $CoCl_2$ becomes manifest for all three compartments at $T < 8.1°K$.

c) Two-dimensional character of the magnetic properties of layered graphite compounds with $NiCl_2$ and $CoCl_2$. To analyze the properties of quasi-two-dimensional layered compounds of the $MeCl_2$ type, it is convenient to use for the magnetization a formula [7,8] in which account is taken of the effective anisotropy field H_A:

$$M(T)=M(0)[1-CTf(T)], \tag{2}$$

where

$$f(T)=\sum_{n=1}^{n=\infty}\frac{1}{n}\exp\left\{-\frac{ng\beta H_A}{kT}\right\}, \tag{3}$$

and C is a constant that depends on the type of magnetic structure and on the intralayer exchange. If account is taken of the interaction in the layer only between the nearest neighbors, J_T, this constant for the $NiCl_2$ and $CoCl_2$ structures is equal to

$$C=\frac{\sqrt{3}}{24\pi}\frac{k}{J_TS^2}. \tag{4a}$$

Lindgard et al.[9] introduced two exchange integrals for $NiCl_2$ in a layer: J_{Tnn} and J_{Tnnn} for exchange between nearest neighbors and J_{Tnnn} for exchange between the next-nearest neighbors in the layer. In this case we have

$$C=\frac{\sqrt{3}}{24\pi}\frac{k}{(J_{Tnn}+3J_{Tnnn})S^2}. \tag{4b}$$

Calculation by the molecular-field theory with allowance for the intralayer interaction of only the nearest neighbors yields J_T = 7.37°K and 10.4°K for $NiCl_2$ and $CoCl_2$ respectively. These values were also used in the analysis of the magnetic properties of $NiCl_2$ and $CoCl_2$ [10-12]. They lead to the following values of C (Eq. (4a)): $C = 3.12 \times 10^{-3}\ \mathrm{deg}^{-1}$ for $NiCl_2$ and $C = 2.21 \times 10^{-3}\ \mathrm{deg}^{-1}$ for $CoCl_2$. At these values of C, Eq. (2) accounts satisfactorily for our experimental results (the linear $\nu_{NMR}(T)$ dependence for LGC with $NiCl_2$ and $CoCl_2$), with H_A equal to 0.24 and 0.97 kOe, respectively (in the calculation we used the values of $g_\perp$ known for the pure chlorides, namely $g_\perp = 2.23$ for $NiCl_2$ [13] and $g_\perp = 5.86$ for $CoCl_2$ [14], which agree with EPR measurements in LGC with $NiCl_2$ [6] and $CoCl_2$ 1)). The values of $\nu_{NMR}(0)$ should in this case be somewhat smaller than those obtained by linear extrapolation of $\nu_{NMR}(T)$. For example, at n = 2 their values for LGC with $NiCl_2$ and $CoCl_2$ are 41.80 and 22.95 MHz, respectively (deviation ≤ 1.5%).

The exchange constants J_{Tnn} = 21.9°K and J_{Tnnn} = −4.9°K obtained for $NiCl_2$ from the spin-wave dispersion by measuring inelastic neutron scattering [9] lead, using formula (4b), to the value $C = 3.19 \times 10^{-3}\ \mathrm{deg}^{-1}$ and practically to the same values of H_A and $\nu_{NMR}(0)$ in LGC with $NiCl_2$ as in the earlier estimates. Thus, the NMR data cannot differentiate between the model proposed in [9] and the molecular field theory in which only one exchange constant is taken into account.

In the case of layered antiferromagnets, the effective anisotropy field H_A may contain, in addition to other terms, also a small interlayer interaction J_L [8]. However, simple summation with H_A in the cases with $NiCl_2$ and $CoCl_2$ leads to appreciable discrepancies between the model proposed in [8] and the experimental results. The apparent reason is that J_L/J_T in these compounds is not as small as in $CrCl_3$, for which the Narath method was developed [8]. On the other hand, in samples with graphite, where the requirement $J_L \ll J_T$ is satisfied, H_A turns out to be much smaller than the values of H_A in pure weakly-three-dimensional $NiCl_2$ and $CoCl_2$, as obtained from measurements of the AFMR frequencies and of the exchange fields H_E in them [13,14]. This is evidence of the decisive role played by interlayer interaction in the appearance of magnetic anisotropy in pure $NiCl_2$ and $CoCl_2$.

The temperature dependence of the frequencies and of the relaxation times in LGC with $NiCl_2$ and $CoCl_2$ agrees with the assumption [6] that magnetic ordering in these structures proceeds via destruction of the long-range magnetic order while a stable short-range order is maintained—an effect accompanied by fluctuations that shorten the relaxation times sharply.

d) Comparison of the experimental results in two-dimensional and three-dimensional layered bichlorides. For a number of reasons, and primarily because the ratio J_L/J_T for pure salts is not too small, the function f(T) in the form (3) does not characterize the deviations from the weakly-anisotropic two-dimensional model, which appear already in the strongly-anisotropic three-dimensional model, and the experimental results [5] agree poorly with Eq. (2). The function f(T) can be expressed in various forms, depending on the approximation in which the eigenvalues of the interaction Hamiltonian are obtained and on the manner in which the spin-wave energy is taken into account. In a theoretical analysis of $NiCl_2$ and $CoCl_2$, Yoshimori [15] took into account two spin-wave modes and actually obtained two values of f(T): $f(T) \propto T$ for the low-temperature region (the "three-dimensional" contribution of the low-frequency branch of the spin waves comes into play here), and $f(T) \propto \ln(T/\Theta)$ for the high-temperature region (this dependence is the high-temperature approximation of the Narath function [8]). In LGC with $NiCl_2$, it was found experimentally that

$$\nu_{NMR}(T)=\nu_{NMR}(0)(1-C'T), \tag{5}$$

where $\nu_{NMR}(0)$ = 42.500 MHz, $C' = Cf(T) = 1.93 \times 10^{-2}\ \mathrm{deg}^{-1}$, C is a coefficient of the form (4a) or (4b), and f(T) is a function of the type of (3). Comparing (5) with the results of [5], we found that the contribution of the three-dimensional behavior in pure $NiCl_2$ can be taken into account in (2), within the limits of experimental accuracy, by replacing f(T) by the function

$$f'(T)=\frac{C'}{C}\left[1-\left(\frac{\Delta}{kT}\right)^{\alpha}\right]=\left[1-\left(\frac{\Delta}{kT}\right)^{\alpha}\right]f(T), \tag{6}$$

where α is a dimensionless quantity ($\alpha = 0.196$ for $NiCl_2$) and Δ is a parameter that appears when the results of [5] are compared with the results on LGC with $NiCl_2$. According to our estimates Δ/k = 6.77°K. We can then use for the NMR frequencies in $NiCl_2$ (pure or containing graphite) a modification of Eq. (2), i.e.,

$$\frac{\nu_{NMR}(0)-\nu_{NMR}(T)}{\nu_{NMR}(0)}=-CT\left[1-\left(\frac{\Delta}{kT}\right)^{\alpha}\right]\sum_{n=1}^{n=\infty}\frac{1}{n}\exp\left\{-\frac{ng\beta H_A}{kT}\right\}. \tag{7}$$

It can be assumed that Δ characterizes the degree of three-dimensionality of the pure salt, and depends on the interlayer exchange and on the anisotropy ($\Delta = 0$ in the case of LGC with $NiCl_2$). It is necessary here to consider two fields H_A, one in the exponential of (7), H_A = 0.24 kOe, which was obtained for LGC with $NiCl_2$ and can probably be regarded as an effective intralayer contribution to the anisotropy field H_{AT}, and another entering into the equations for the AFMR frequencies and resulting, apparently, from the effective interlayer contribution H_{AL} to the anisotropy.

For pure $CoCl_2$, the behavior of M(T), according to Yoshimori [15], is determined over the entire temperature region in which the two-dimensional system was investigated by the contribution of the quasi-three-dimensional low-frequency spin-wave branch and $\Delta M(T)/M(0) \propto T^2$, so that a comparison of this type is meaningless.

COVALENT p-BOND IN $NiCl_2$ AND $CoCl_2$ IMPLANTED IN THE GRAPHITE LATTICE

The weak three-dimensionality of $NiCl_2$ and $CoCl_2$ practically vanishes when the interacting layers are separated by merely one ($CoCl_2$) or two ($NiCl_2$) layers of a carbon grid. Introduction of additional layers of graphite has practically no influence on the microscopic magnetization of the magnetic-ion layers $\langle S_z \rangle_T$; the same holds true also for the macromagnetization in $CoCl_2$ [3]. This confirms the indirect character of the exchange between the Me^{2+} ions in adjacent layers. An antiferromagnetic coupling can result from indirect exchange via the covalent bridges $Me^{2+}—Cl^-—Cl^-—Me^{2+}$. On the basis of nuclear-quadrupole resonance data, Barns, Segel, and Jones [16] have shown that in compounds of the $MeCl_2$ type, besides a high degree of ionicity of the $Me^{2+}—Cl^-$ bond (50—80%), the chlorine ions participate in a covalent, almost pure p-bond with the Me^{2+} ions. The magnitude of this bond determines the number U_{pz} of uncompensated 3p electrons oriented along the z axis, which participate in the production of the electric-field gradient (EFG) at the Cl^- nucleus. In these structures, according to [16], the covalence determines almost completely the value q_{zz} of the EFG, i.e., the experimental parameter $|\nu_Q|$. The ionic bond in the case of $NiCl_2$, $CoCl_2$, $FeCl_2$, and $MnCl_2$ accounts for only 2—5% of the experimental value of this parameter. The s-hybridization of the p-bond leads to an increase of the EFG tensor q_{zz} and to the appearance of an isotropic hyperfine interaction between the 3d ion and the halide nucleus, and this is indeed the cause of the NMR in these samples [5]. If the parameter q_{zz} (or $|\nu_Q|$) is known, then the degree of s-hybridization can be estimated from the formula [16]

$$S = \frac{1}{3} \frac{1-3\beta\varepsilon}{1-\beta} \frac{q_{zz}}{q_{n10}}, \qquad (8)$$

where q_{n10} is the field gradient for one excess p electron on the z axis, with a value $q_{n10} = 20 \times 10^{15}$ cgs esu [17] for Cl^{35}; ϵ is the correction for the change in the gradient as a result of the ion charge of Cl^-, with $\epsilon = 0.15$ for Cl^- [17]; β is the degree of ionicity of the bond.

Parameter		LGC with $NiCl_2$			LGC with $CoCl_2$		$FeCl_2$
		n ***$=0$	$n=2$	$n=3$	n **$=0$	$n=1, 2, 3$	
Hyperfine interaction constant for chlorine, $A_s \times 10^4$, cm^{-1}.		4.775	4.72	4.80	3.455	2.72	2.375
Quadrupole-coupling constant, MHz	Calculation*	—			0.11	—	0.24
	Experiment**	6.496	13.2	14.0	5.254	10—12	4.74
β, %		60			68		68
S, %		3,42			3.3		2,97
$\gamma_s^2 = (1-\beta)S$		0,0137			0.0106		0,0095
U_{pz}		0.325	0,66	0,70	0.263	0,5—0,6	0.238

*Calculated value—for pure ionic model [16] $e^2Qq_{zz}h^{-1}(1 - \gamma_\infty)$.
**Experimental value of e^2Qq_{zz}/h.
***n = 0 corresponds to $MeCl_2$ without graphite.

If the ion is a 3d metal, then the hyperfine constant A_i in (1) contains information on the transfer of the density of the 3d electrons of Me^{2+} to the chlorine s-orbits that take part in the hybridization (the parameter α_s), and when the p-bond s-hybridization increases, the value of α_s, and consequently also A_i and the NMR frequency, will increase. In [5], the values of α_s for $NiCl_2$, $CoCl_2$ and $FeCl_2$ were obtained from NMR data. For these three compounds they turned out to be practically the same at ≈0.65%. The table lists data characterizing the quadrupole-coupling constant e^2Qq_{zz}/h, the degree β of the ionicity of the $Me^{2+}—Cl^-$ bond, obtained from the difference of the electronegativities [17], the degree S of s-hybridization of the covalent p-bond $Me^{2+}—Cl^-$ in the pure salts, obtained from the values of $|\nu_Q|$ and β by formula (8), and the number $U_{pz} = q_{zz}/q_{n10}$ of the uncompensated p-electrons. It is seen from the table that the degree S of s-hybridization in pure chlorides of Ni, Co, and Fe is of the order of 3% (S = 4.1% for $CdBr_2$ and S = 6% for $CrCl_3$), corresponding to bond valence angles θ close to 90° ($S = \cos\theta/(\cos\theta - 1)$ [17]). This quantity can be set in correspondence with the value of α_s obtained in [5] and due precisely to s-hybridization of the covalent bond. According to [5] we have

$$\alpha_s = \lambda_s^2/3N_e, \quad \lambda_s = \gamma_s + S_s,$$
$$N_e = 1 + 2\gamma_s S_s + \gamma_s^2.$$

Here S_s is the overlap integral and γ_s is a parameter characterizing the covalence, with $\gamma_s^2 = (1-\beta)S$. Substitution of the values of S were obtained from $|\nu_Q|$ and β, determined from the difference of the electronegativities, leads to acceptable agreement with α_s [5], even if the overlap integral S_s of the 3d orbits of Me^{2+} with the 3s orbit of the Cl^- ion is neglected.

Introduction of graphite into the samples leads to an increase of the quadrupole-coupling constant e^2Qq_{zz}/h by almost a factor of 2. This can be attributed either to the appearance of an additional covalent p-bond with graphite or to an increase of s-hybridization of the existing p-bond with Me^{2+} due to the change of the valence angles of the bond. However, the degree of s-hybridization when graphite is introduced changes negligibly in comparison with the change of q_{zz}, as indicated by the small change of H_{eff} at the chlorine nucleus (or of the hyperfine interaction constant $A_s^{(1)}$), which is of the order of 0.1% and 20% for LGC with $NiCl_2$ and $CoCl_2$, respectively. Consequently, the increase of q_{zz} is due to the fact that the p electrons of the graphite form a covalent bond with the p electrons of the chlorine (the electronic structures of chlorine and graphite are $3s^23p^5$ and $1s^22s2p^3$), thereby increasing the total covalence of the chlorine bonds. Owing to the directivity of the covalent p bond, the resulting chlorine-graphite bond should be smallest in LGC with one compartment (one layer of graphite for two layers of chlorine). With increasing n, an increase should take place in the chlorine-graphite bonds, followed by saturation. A certain increase of $|\nu_Q|$ in LGC with $NiCl_2$ for n = 3 in comparison with n = 2 (3—6%) favors this argument. The data for U_{pz} (see the table) illustrate the foregoing.

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(1) At T ≲ 11° K, we observed EPR in LGC with $CoCl_2$ of the first compartment in the form of a broad asymmetric line that agrees with $g_\parallel \sim 3$ and $g_\perp \gtrsim 6$.

[1] R. C. Croft, Australian J. Chem. 9, 184, 1956.
[2] Yu. S. Karimov, M. E. Vol'pin, and Yu. N. Novikov,

ZhETF Pis. Red. **14**, 217 (1971) [JETP Lett. **14**, 142 (1971)].

[3] Yu. S. Karimov and Yu. N. Novikov, ibid. **19**, 268 (1974) [**19**, 159 (1974)].

[4] Yu. S. Karimov, Zh. Eksp. Teor. Fiz. **66**, 1121 (1974) [Sov. Phys.-JETP **39**, 547 (1974)].

[5] F. V. Bragin and S. M. Ryabchenko, Fiz. Tverd. Tela **15**, 1050 (1973) [Sov. Phys.-Solid State **15**, 721 (1973)].

[6] F. V. Bragin, Yu. N. Novikov, and S. M. Ryabchenko, Zh. Eksp. Teor. Fiz. **66**, 361 (1974) [Sov. Phys.-JETP **39**, 172 (1974)].

[7] A. Narath, Russ. transl. in: Sverkhtonkie vzaimodeĭstviya v tverdykh telakh (Hyperfine Interactions in Solids), Mir, 1970, p. 191.

[8] A. Narath, Phys. Rev. **131**, 1929, 1963.

[9] P. A. Lingard, J. Als-Nielsen, R. J. Birgeneau, and H. J. Guggenheim, Trudy Mezhdunarodnoĭ konferentsii po magnetizmu MKM-73 (Proc. Intl. Conf. on Magnetism, ICM-73), Vol. 5, Nauka (1974).

[10] H. Bizette, T. Terries, and B. Tsai, C. R. (Paris) **243**, 1295, 1956.

[11] M. E. Lines, Phys. Rev. **131**, 540, 1963.

[12] A. F. Lozenko and S. M. Ryabchenko, Fiz. Tverd. Tela **12**, 807 (1970) [Sov. Phys.-Solid State **12**, 624 (1970)].

[13] A. F. Lozenko and S. M. Ryabchenko, Ukr. Fiz. Zh. **18**, No. 10, 1726 (1973).

[14] I. S. Jacobs, S. Roberts, and S. D. Silverstein, J. Appl. Phys. **39**, 816, 1968.

[15] A. Yoshimori, Phys. Rev. **130**, 1312, 1963.

[16] R. G. Barnes, S. L. Segel, and W. H. Jones, Jr., J. Appl. Phys. (1), **33**, 296, 1962.

[17] C. Townes and A. Schawlow, Microwave Spectroscopy, McGraw-Hill, 1955.

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148