Antiferromagnetic resonance in layered $CoCl_2$ and $NiCl_2$ crystals

A. F. Lozenko and S. M. Ryabchenko

Physics Institute, Ukrainian Academy of Sciences

(Submitted February 23, 1973)
Zh. Eksp. Teor. Fiz. 65, 1085–1092 (September 1973)

The dependences of the exchange field $H_E(T)$ in layered $CoCl_2$ and $NiCl_2$ crystals are investigated by the AFMR technique. The $H_E(T)$ dependence in $CoCl_2$ is found to be proportional to the temperature dependence $\langle s_Z\rangle_T^2 \approx (1/2)(\langle s_Z\rangle + \langle s_Z\rangle^3)$. The value of $\langle s_Z\rangle_T$ is measured by the NMR technique. It is suggested that biquadratic interlayer exchange may be involved. The anisotropy field H_A is independent of temperature, a fact which does not correspond to the models employed in the theoretical investigations of the magnetic properties of $CoCl_2$. In $NiCl_2$ the dependence $H_E(T)$ is proportional to $\langle s_Z\rangle$ and $\nu_{\mathrm{h.f.}}(T, H=0)$. This confirms the dipole-dipole mechanism of anisotropy. The strong temperature dependence of H_E in the two crystals is not consistent with the theoretical calculations of Mitsek and Kolmakova, according to which $H_E T = \mathrm{const}$. The isotropic gap observed in the low-frequency AFMR spectrum in $CoCl_2$ is related to the appearance of magnetostriction. Within the accuracy of the experiments, the temperature dependence of the gap magnitude is in accord with the magnetostriction model.

1. INTRODUCTION

$CoCl_2$ and $NiCl_2$ crystals belong to the layered antiferromagnets with anisotropy of the "easy plane" type and without weak ferromagnetism. Their crystal structure is practically identical and is isomorphic to $CdCl_2$, with space symmetry D_{3d}^5. Theoretical investigation of the magnetic properties of these crystals has been the subject of a number of papers[1–4]. According to data on the specific heat[5,6] and the susceptibility[7], the Néel temperature is $T_N = 24.7$°K for $CoCl_2$ and $T_N = 49.6$°K for $NiCl_2$. The magnetic properties of $CoCl_2$ and $NiCl_2$ have been investigated experimentally by Starr et al.[8]

Jacobs et al.[9] investigated antiferromagnetic resonance (AFMR) in $CoCl_2$ in the far infrared region (10–20 cm^{-1}) at T = 4.2°K. It was found that the high-frequency AFMR frequency $\nu_{HF}(H = 0) = 19.0 \pm 0.2\ cm^{-1} = 570 \pm 6$ GHz. From the frequency-field dependence, $\nu_{HF}(H)$, was found the value $H_E(T = 4.2°K) = 32$ kOe. From measurements of the magnetization[9] was found $g_\perp = 5.86$. The same authors determined the intraplane and interplane contributions to the axial anisotropy. The value of $g_\perp$ in[9] is about 20% larger than $g_\perp$ as found from investigation of the electron paramagnetic resonance of Co^{2+} in $CdCl_2$. A number of authors[9,10] attribute these differences to exchange shift of the g-factor. The temperature dependence of the hf AFMR[11] does not agree with that expected theoretically on the assumption that the sublattice magnetization M(T) corresponds to a Brillouin function.

Earlier[12], an investigation was made of the temperature dependence of the nuclear magnetic resonance of the Cl^- nucleus in the internal field of antiferromagnetic $CoCl_2$ and $NiCl_2$. The NMR frequency in this case is proportional to $\langle s_Z\rangle_T$. The $\langle s_Z\rangle_T$ found experimentally[12] for $CoCl_2$ does not correspond to a Brillouin function but agrees with $\nu_{HF}(T)$ in zero magnetic field[11]; this may indicate that the anisotropy is not of single-ion nature.

AFMR in $NiCl_2$ has been investigated in a number of papers[13–16]. In investigation of the hf AFMR in zero magnetic field[14], a breaking up and shifting of the hf AFMR line from specimen to specimen were detected. It was assumed that these phenomena were due to defectiveness of the crystal. For this reason it was actually not possible to make a reliable comparison with the results of measurement of the temperature dependence of the NMR frequency of Cl^- in $NiCl_2$, which is proportional to $\langle s_Z\rangle_T$[12].

In the present paper, in order to determine in more detail the nature of the anisotropy field, and also in order to test the deductions in the paper of Kolmakova and Mitsek[17] on the basis of the temperature dependence of H_E, a measurement of $H_E(T)$ was undertaken in $CoCl_2$ and $NiCl_2$. In addition, the present paper undertakes to make more precise the temperature dependence of the hf AFMR in $NiCl_2$; for these measurements, specially grown specimens, of higher quality than those investigated earlier[14], were used.

In easy-plane antiferromagnets, the low-frequency (lf) AFMR can have a very small anisotropic gap, due to anisotropy within the plane; and there can also be observed an isotropic contribution to the value of the gap from magnetostriction[18,19]. The lf AFMR in $NiCl_2$ was investigated earlier[13,15]. A practically isotropic gap in its spectrum was detected, amounting to 3.5 kOe at 4.2°K. In an investigation of $CoCl_2$ at low frequencies (< 40 GHz), no LF AFMR was observed. EPR was not seen above T_N. Therefore, in order to study the size and nature of the gap in the LF AFMR spectrum in $CoCl_2$ and to test the assumption of an exchange shift of the g-factor, we carried out an investigation of the temperature dependence of the LF branch of the AFMR.

2. EXPERIMENTAL RESULTS

The apparatus used for the measurements was similar to that described earlier[14,15]; it operated over the range 50 to 78 GHz, at temperatures from 4.2 to 50°K. The accuracy of measurement of the temperature of the thermistor was ±0.01°K, and the temperature of the specimen could differ from the temperature of the thermistor by no more than ±0.25°K. As was shown by Turov[20], the lf and hf branches of the AFMR spectrum must be observed with different polarizations of the radiofrequency field h, so that for $\mathbf{h} \perp \mathbf{H}_0 \perp C_3$ the lf branch of the spin-wave spectrum must be excited, with frequency

$$\nu_{LF} = g_\perp \beta h^{-1} [H^2(1 + a/A) + \Delta^2]^{1/2} \tag{1}$$

(Δ may include isotropic and anisotropic parts), whereas for $h \parallel H \perp C_3$ it is the hf branch of the AFMR, with frequency

$$\nu_{HF} = g_\perp \beta h^{-1} H_{EA} (1 - H^2/H_E^2)^{1/2}, \qquad (2)$$

where $H_{EA} = (H_A H_E)^{1/2}$. The notation in the formulas corresponds to that adopted in Turov's book[20].

Our simultaneous observation of both branches of the AFMR for arbitrary polarization, both in $CoCl_2$ and in $NiCl_2$, is perhaps due to the fact that the specimen dimensions were large in comparison with the wavelength.

A. AFMR in $CoCl_2$

According to Jacobs et al.[11], in the temperature range T < 24°K the value of $\nu_{HF}(H = 0) \geq 400$ GHz. Hence according to (2), at frequencies 60–80 GHz, amounting to 0.15 to 0.2 of $\nu_{HF}(H = 0)$, the value of $H_{res} \approx H_E$ with an accuracy better than ~ 1.5%, which exceeds our accuracy of determination of H_{res}. Since we made measurements in fields close to the saturation field H_E, it would in general be necessary to take into account the contribution from the demagnetizing fields of the specimen; but estimates of this contribution showed that it should be ≤ 500 Oe, which has no important effect on the conclusion about the temperature dependence of H_E; furthermore, measurements on specimens of appreciably different shapes, for which the contribution from the demagnetizing factor should be different, revealed no differences in the values of H_E within the limits of our experimental accuracy (±200 Oe). Therefore the actual values of the demagnetizing fields do not exceed these values. In accordance with formula (2) and with the results of Jacobs et al.[11], this allowed us to identify the field in which the hf AFMR is observed with the saturation field H_E and to investigate its temperature dependence directly.

To the x-coordinate of an xy-recorder was fed a signal proportional to the current in the winding of a superconducting solenoid; and at a number of fixed frequencies from our frequency range, families of curves were recorded for the microwave power reflected from a short-circuited waveguide with the specimen, for various temperatures from helium to T_N. The values of $H_E(T)/H_E(0)$ obtained from such an experiment are shown in Fig. 1. Besides the values of $H_E(T)$, shown on the graph by circles, also presented here for comparison is the normalized temperature dependence of the NMR frequency, proportional to $\langle s_z \rangle_T$[12] (the solid line on the graph), which coincides with $\nu_{HF}(T, H = 0)/\nu_{HF}(T = 0, H = 0)$[11]. The measurements of $H_E(T)$ made on different specimens agree with each other. From Fig. 1 it is evident that the temperature dependences of H_E and of $H_{EA} \sim \nu_{HF}(T, H = 0)$ differ strongly.

In the investigation of the lf branch of the AFMR, we observed a temperature-dependent gap in the spin-wave energy. There are noticeable differences in the position of the lf resonance in different specimens. The experimental dependence of the position of the lf resonance on frequency for one of the specimens, at various temperatures, is shown in Fig. 2.

On plotting ν^2 as a function of H^2 (these graphs are not shown), we find for each temperature the corresponding values of $g_\perp(1 + a/A)^{1/2}$ and $g_\perp\Delta$. It turned out that for a given specimen, $g_\perp(1 + a/A)^{1/2}$ is independent of temperature to within ±5%, whereas $g_\perp\Delta$ varies strongly with temperature. The dotted curves in Fig. 2 correspond to equation (1) with different $g_\perp\Delta$ for different temperatures but with a single $g_\perp(1 + a/A)^{1/2} = 9.4 \pm 0.3$. The temperature dependence of $g_\perp\beta\Delta/h$ is shown in Fig. 3. We give the temperature dependence of $g_\perp\beta\Delta/h$ rather than of $\Delta(T)$ in order to eliminate a possible contribution from a temperature dependence of the g-factor. If we use for $g_\perp$ the value 5.86 [9], $\Delta(T \rightarrow 0) \approx 8$ kOe. Other values of $g_\perp(1 + a/A)^{1/2}$ and of Δ are obtained for different specimens and in measurements at individual frequencies. The accuracy of determination of $g_\perp\beta\Delta/h$ from measurements on a single specimen lies within the limits shown in Fig. 3, whereas the spread of values of Δ from specimen to specimen amounts to ~13%. The value of $g_\perp(1 + a/A)^{1/2}$ obtained by us from the data shown in Fig. 2 differs from that found by Jacobs et al. [9], 11.6 ± 0.2. We observed that this parameter changes appreciably from specimen to specimen, and this may explain the observed difference.

No measurements were made with rotation of the magnetic field in the plane of the specimen, but the measurements made on different specimens were carried out with random orientation of the magnetic field in the plane of the crystal. Therefore the spread in the value of Δ from specimen to specimen may be due to an anisotropic contribution to the value of the gap. Since the value of $H_E(T \rightarrow 0)$ (including A) that we measured on different specimens remains the same, and since there is no basis for supposing that $g_\perp$ changes from specimen to specimen, the reason for the spread in $g_\perp(1 + a/A)^{1/2}$ must be considered to be differences in the parameter a, which is the difference between the intraplane and interplane contributions to the axial anisotropy.

Measurements at different frequencies show an anomalous behavior of the LF AFMR in the range where the sublattices turn perpendicularly to the external field. The large line-width of the lf branch of the AFMR, however, prevented us from investigating this phenomenon in detail. The line-width remains unchanged (≈ 3 kOe) in the temperature range 4.2–14°K but then increases abruptly (to 6 kOe at 24°K) with approach to T_N.

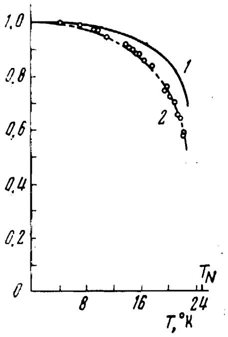

FIG. 1

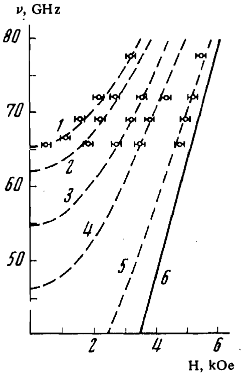

FIG. 2

FIG. 1. Temperature dependences $H_E(T)$, $\langle s_z \rangle_T \sim \nu_{hf}(T, H = 0)$, and $\langle s_z \rangle_T^2$, normalized by the corresponding values at T = 0°K, in $CoCl_2$. ○, experimental points $H_E(T)$; curve 1, $\langle s_z \rangle_T/\langle s_z \rangle_0 \sim \nu_{HF}(T, H = 0)/\nu_{HF}(T = 0, H = 0)$; curve 2, $(\langle s_z \rangle_T/\langle s_z \rangle_0)^2$.

FIG. 2. Frequency-field relation for LF AFMR in $CoCl_2$ at various temperatures. ○, experimental points; dotted curves, calculation by equation (1) with various Δ: 1, $\Delta = 7.9$ (T = 4.2°K); 2, $\Delta = 7.5$ (T = 12°K); 3, $\Delta = 6.6$ (T = 16°K); 4, $\Delta = 5.6$ (T = 20°K); 5, $\Delta = 3$ (T = 24°K); 6, $\Delta = 0$. $g_\perp(1 + a/A)^{1/2}$ for all curves is 9.4 ± 0.3.

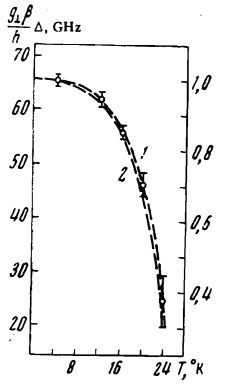

FIG. 3

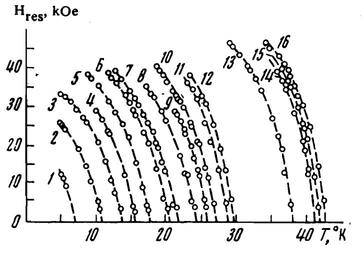

FIG. 4

FIG. 3. Temperature dependence of $g_\perp\beta\Delta/h$ in $CoCl_2$. O, experimental results according to equation (1); curves 1 and 2, reduced temperature dependences $H_E(T)$ and $[H_E(T)]^{1.25}$.

FIG. 4. Temperature dependences of H_{res} for HF AFMR in $NiCl_2$ for the following frequencies (in MHz): 1, 76 290; 2, 75 010; 3, 73 920; 4, 72 665; 5, 71 570; 6, 70 075; 7, 69 515; 8, 68 010; 9, 66 650; 10, 66 130; 11, 64 240; 12, 63 840; 13, 57 170; 14, 53 090; 15, 52 655; 16, 52 540.

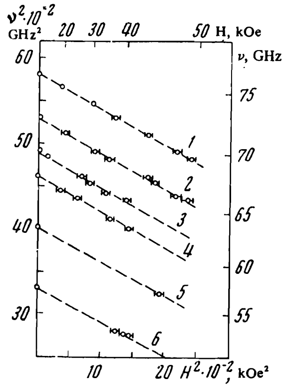

FIG. 5

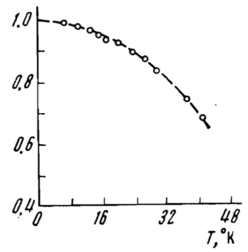

FIG. 6

FIG. 5. Frequency-field relation for HF AFMR in $NiCl_2$ in squared coordinates, for various temperatures (in °K): 1, 7; 2,15; 3, 20; 4, 24; 5, 29.5; 6, 37.7.

FIG. 6. Reduced temperature dependences $H_E(T)$ (O) and $\langle s_z\rangle_T \sim \nu_{HF}(T, H = 0)$ (dotted curve) for $NiCl_2$.

B. AFMR in NiCl$_2$

With the same apparatus, over the frequency range 50–78 GHz and the temperature range 4.2–44°K, measurements were made of the temperature dependence of the resonance field H_{res} for HF AFMR in $NiCl_2$ at fixed frequencies; see Fig. 4. The families of curves in Fig. 4 enable us to construct the temperature dependence of the exchange field, $H_E(T)$.

As is seen from Fig. 5, the frequency-field relations corresponding to various temperatures, in squared coordinates, are a set of straight lines; that is, equation (2) is satisfied. The intersection of the straight line with the H^2 axis gives us the value of H_E^2 for the corresponding temperature. The parallelism of these lines indicates that the temperature dependence of $H_E(T)/H_E(0)$ coincides with the temperature dependence of the ratio $\nu_{HF}(T, H = 0)/\nu_{hf}(T = 0, H = 0)$, which can also be obtained from Fig. 4.

Figure 6 gives the mutually compatible temperature dependences $H_E(T)/H_E(0)$ and $\nu_{HF}(T)/\nu_{hf}(0)$ in zero field (circles), and for comparison the temperature dependence $\langle s_z\rangle_T/\langle s_z\rangle_0$[12] (dotted curve). Thus the discrepancy noted earlier[12] between $\langle s_z\rangle_T$ and $\nu_{HF}(T)$ was due to the assumed role of deformations and defects in the crystals used in the experiments[14], and comparison of the temperature dependence of the sublattice magnetization with the theory of Yoshimori[2] is more proper.

DISCUSSION

If the hyperfine constant is independent of temperature, the temperature dependence of the NMR frequency should correspond to the temperature dependence of $\langle s_z\rangle$, as was also assumed earlier[12]; and in the model of a molecular field H_E due to exchange interaction of the type As_1s_2, it should depend on the temperature as $\langle s_z\rangle/g_\perp$.

From the model of exchange shift of the g-factor for $CoCl_2$[10], it could be expected that $g_\perp$ would decrease by ~ 25% with increase of temperature from 0°K to T_N, though our finding that $g_\perp(1 + a/A)^{1/2}$ is independent of temperature does not agree with this assumption. At the same time, the more rapid diminution of H_E with increase of temperature, in comparison with $\langle s_z\rangle$, that we have found could be due only to strong increase of the g-factor with temperature.

If we assume, on the basis of the temperature independence of the value of $g_\perp(1 + a/A)^{1/2}$, that $g_\perp$ is independent of temperature (the independence of $(1 + a/A)^{1/2}$ follows from equations of the paper of Jacobs et al.[9]), then evidently the stronger temperature dependence of H_E as compared with $\langle s_z\rangle$ can be attributed to a specific interplane exchange interaction in $CoCl_2$.

Curve 2 in Fig. 1 corresponds to the temperature dependence of $\langle s_z\rangle^2$. As is seen, in the high-temperature range (T > 15°K) it describes well the temperature dependence of H_E. The observed temperature dependence of H_E can also be described on the assumption that

$$H_E \sim \alpha_1\langle s_z\rangle + \alpha_2\langle s_z\rangle^3$$

by suitable choice of the coefficients. The accuracy of our experiment does not allow us to obtain accurate values of α_1 and α_2, but for a suitable approximation they must be within the limits ($0.4 < \alpha_1$; $\alpha_2 < 0.6$; $\alpha_1 + \alpha_2 = 1$), The term in $\langle s_z\rangle^3$ will appear in the molecular-field model in the case of biquadratic exchange.

The Brillouin function for s = 1/2 also lies satisfactorily on the experimental points $H_E(T)$, but this is most probably an accidental coincidence. Since $H_E(T)$ is approximately proportional to $\langle s_z\rangle^2 \sim \nu_{hf}^2 = (g_\perp\beta/h)^2H_AH_E$, it follows that H_A is independent of temperature over this range. Such a behavior of H_A does not correspond to the models used in previous papers[4,9].

In contrast with this, in the case of $NiCl_2$, as follows from Fig. 6, $\nu_{HF}(T, H = 0)$, $\langle s_z\rangle_T$, and $H_E(T)$ agree, and this supports the dipole-dipole mechanism of anisotropy in this compound. Apparently the interplane exchange H_E in $NiCl_2$ lacks the peculiarities noted for $CoCl_2$. Such a difference between the two crystals can be understood if, in the latter case, orbital degeneracy of the ground state of the Co^{2+} plays an important role. The result obtained on strong temperature dependence of H_E in both crystals contradicts the theoretical calculation of Mitsek and Kolmakova[17], from which it follows that $H_E(T)$ = const. Evidently this is due to the fact that Mitsek and Kolmakova[17] considered the case of a uniaxial antiferromagnet with anisotropy of the "easy axis" type, or else their results are invalid in the temperature range that we investigated and useful only for $T_N >> T \to 0$.

According to data from neutron diffraction investigations, there exists in the basal plane of $CoCl_2$ anisotropy that leads to domain formation[21]. This anisotropy is very small and is overcome in weak magnetic fields of 2 kOe (the field for turning of the sublattices, spin-flop). The spread of the values of Δ that we found does not exceed 2 kOe. Thus the indicated spread can be due to both defectiveness of the crystals and to the manifestation of an anisotropic part of the gap.

As a result of measurements made on a large number of specimens (> 10), it can be asserted that the value of the gap for $CoCl_2$ amounts to $\Delta = 8 \pm 1$ kOe; or in frequency units, $g_\perp \beta \Delta / h = 65.5 \pm 8$ GHz. Thus the isotropic contribution to the gap amounts to 8 kOe and considerably exceeds a possible anisotropic contribution.

The most probable mechanism leading to an isotropic gap in the lf resonance spectrum is magnetostriction[18,19]. An analogous, practically isotropic gap is observed in $NiCl_2$[13,15]. According to Turov and Shavrov [18], the value of the gap is determined by the formula

$$\Delta^2 = H_{ms} H_E, \tag{3}$$

where H_{ms} is the magnetostriction field, expressed in terms of the magnetostrictive and elastic constants of the specimen. From the values found, it follows that at T = 4.2°K the field H_{ms} for $CoCl_2$ is 2 kOe, whereas for $NiCl_2$ at the same temperature $H_{ms} = 0.1$ kOe.

Stevenson's[22] compressibility measurements for the isomorphic crystals $CoCl_2$ and $NiCl_2$ are practically identical, and this permits us to assume equality of the elastic coefficients that enter in H_{ms}. Consequently, the difference in H_{ms} for these crystals can be due only to a difference in the magnetostrictive constants. The possibility that magnetostrictive constants may be appreciably larger for $CoCl_2$ than for $NiCl_2$ seems natural, because of the orbital degeneracy of the ground state of Co^{2+}.

In the model of Turov and Shavrov[18], $H_{ms}(T)$ is proportional to the cube of the antiferromagnetism vector $l(T)$; that is, $H_{ms} \sim \langle s_z \rangle_T^3$. On using the fact that we found $H_E \sim \langle s_z \rangle_T^2$, we get

$$\Delta = (H_E H_{ms})^{1/2} \sim (\langle s_z \rangle^5)^{1/2} \sim (H_E)^{1,25}.$$

Figure 3 shows the experimentally found dependence $\Delta(T)$ and gives the dependences $H_E(T)/H_E(0)$ and $[H_E(T)/H_E(0)]^{1.25}$. It is seen that within the limits of accuracy of our experiment, it is impossible to choose between these two approximations, and one can speak of a satisfactory agreement with theory[18].

In this paper, the temperature dependences found for the crystal parameters have not been compared with Yoshimori's[2] theory, because such an analysis was made earlier[12].

---

[1] J. Kanamori, Prog. Theor. Phys. **20**, 890 (1958).

[2] A. Yoshimori, Phys. Rev. **130**, 1312 (1963).

[3] H. B. Shore, Phys. Rev. **131**, 2496 (1963).

[4] M. E. Lines, Phys. Rev. **131**, 540 (1963); **133**, A841 (1964).

[5] O. N. Trapeznikova, L. V. Shubnikov, and G. Milyutin, Phys. Z. Sowjetunion **9**, 237 (1936).

[6] R. C. Chisholm and J. W. Stout, J. Chem. Phys. **36**, 972 (1962).

[7] H. Bizette, T. Terrier, and B. Tsai, C. R. Acad. Sci. (Paris) **243**, 1295 (1956).

[8] C. Starr, F. Bitter, and A. R. Kaufmann, Phys. Rev. **58**, 977 (1940).

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

[10] S. D. Silverstein, Phys. Rev. Lett. **14**, 140 (1965).

[11] I. S. Jacobs, S. Roberts, and P. E. Lawrence, J. Appl. Phys. **36**, 1197 (1965).

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

[13] M. O. Kostryukova and L. M. Kashirskaya, Zh. Eksp. Teor. Fiz. Pis'ma Red. **9**, 400 (1969) [JETP Lett. **9**, 238 (1969)].

[14] A. F. Lozenko, V. I. Malinovskiĭ, and S. M. Ryabchenko, Zh. Eksp. Teor. Fiz. **60**, 1387 (1971) [Sov. Phys.-JETP **33**, 750 (1971)].

[15] A. F. Lozenko and S. M. Ryabchenko, Zh. Eksp. Teor. Fiz. Pis'ma Red. **16**, 332 (1972) [JETP Lett. **16**, 234 (1972)].

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

[17] I. P. Kolmakova and A. I. Mitsek, Izv. Akad. Nauk SSSR Ser. Fiz. **34**, 1011 (1970) [Bull. Acad. Sci. USSR Phys. Ser. **34**, 901 (1970)].

[18] E. A. Turov and V. G. Shavrov, Fiz. Tverd. Tela **7**, 217 (1965) [Sov. Phys.-Solid State **7**, 166 (1965)].

[19] A. S. Borovik-Romanov and E. G. Rudashevskiĭ, Zh. Eksp. Teor. Fiz. **47**, 2095 (1964) [Sov. Phys.-JETP **20**, 1407 (1965)].

[20] E. A. Turov, Fizicheskie svoĭstva magnitouporyadochennykh kristallov (Physical Properties of Magnetically Ordered Crystals), Izd. Akad. Nauk SSSR, 1963 (Translation, Academic Press, 1965).

[21] M. K. Wilkinson, J. W. Cable, E. O. Wollan, and W. C. Koehler, Phys. Rev. **113**, 497 (1959).

[22] R. Stevenson, Can. J. Phys. **44**, 281 (1966).

Translated by W. F. Brown, Jr.
110