Investigation of the $BaMnF_4$ phase diagram by the antiferromagnetic resonance technique

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The phase diagram of $BaMnF_4$ in a magnetic field parallel to the antiferromagnetism axis is investigated by the AFMR technique at 27.3, 33.7, 38.3, and 40.9 GHz. The boundary curve of sublattice flipping is determined on basis of orientation resonance. AFMR and EPR are found to coexist in the region adjacent to the transition from a state with flipped sublattices to a paramagnetic state. Both AFMR and EPR disappear at 2 °K on going from the antiferromagnetic state with non-flipped sublattices to the paramagnetic state. This can be attributed to "overlapping" of the spectral branches. The effect of critical fluctuations of short-range order on the AFMR and EPR linewidths is considered.

It was shown earlier[1] that $BaMnF_4$ is an antiferromagnet with a clearly pronounced two-dimensional magnetic order, wherein the strong exchange interaction occurs only between Mn^{2+} ions lying in a single layer. As indicated in[2], the crystal structure of $BaNiF_4$, and consequently of the isomorphic $BaMnF_4$, is such that an interaction between the nearest layers should not become manifest, at least in the static properties, in the case of antiferromagnetic order in the layer. Therefore weak interaction between layers occurs only every other layer. Lines has shown[3] that in such substances the transition to the ordered state has a number of peculiarities and is possible only in the presence of weak anisotropy and (or) weak interaction between layers. The results of[4] also give grounds for assuming the presence of a very weak interaction between layers, which is apparently responsible for the low-frequency magnetoelectric resonances.

Investigations of magnetic properties of $BaMnF_4$, including one by the AFMR method, are of great interest for the study of the features of two-dimensional magnetic ordering in phase states of matter. The magnetization curves of $BaMnF_4$ along the easy axis b were investigated by Holmes, Eibshutz, and Guggenheim[5]. They determined from the jumps of the magnetic moment the value of the sublattice flipping field at several temperatures. They have shown that the flipping field H_c^* increases with temperature. The largest value, 14.5 kOe, was attained at T = 20°K. In addition, they noted that the AFMR line vanishes at T = 21°K. The antiferromagnetic resonance spectrum of $BaMnF_4$ was investigated by Petrov, Popov, and Prozorova[6] at 45–100 GHz. In the helium temperature region, no spectrum singularity is connected with two-dimensional ordering or observed. However, the temperature dependence of the gap of the hf branch at $H \parallel c$ has revealed in the temperature region above T_N tails connected with the existence of long-lived short-range-order regions. No detailed investigations were made of the temperature dependence of AFMR at $H \parallel a$ and $H \parallel b$.

Our purpose was to investigate AFMR near the limiting H(T) curves at $H \parallel b$ on the phase diagram, which was simultaneously determined, and to investigate the singularities connected with the two-dimensional magnetic ordering of $BaMnF_4$. Preliminary information, in the form of the phase diagram, was obtained by plotting the temperature dependence of the flipping field from the data of[5,6]. These results enable us to assume that $H \approx 14.5$ kOe at $T \approx 20$°K corresponds to the triple point of the diagram, and to choose the optimal experimental conditions.

The working frequency range was chosen such that the resonant fields of the AFMR and of the EPR overlapped as fully as possible with the region of the "orientation" resonance and the region in the vicinity of the triple point. To this end we chose the mode[7]

$$(\nu/\gamma)^2 = H^2 - 2H_{A1}H_E \qquad (1)$$

at $H \parallel b$ and $H > H_c^*$, with

$$H_c^* = (2H_{A1}H_E/\alpha)^{1/2}, \qquad (2)$$

where $\alpha = 1 - \chi_\parallel/\chi_\perp$ and γ is the gyromagnetic ratio.

EXPERIMENTAL PROCEDURE

The measurements were performed in the frequency range 27.3–40.9 GHz with a direct-amplification bridge-circuit microwave spectroscope. The power compensation in the absence of a signal was effected with an attenuator and a phase shifter, by adjusting the degree of damping and the phase in one of the arms of the bridge. The use of the bridge circuit has also made it possible to tune to the absorption signal or to the dispersion signal, and ensured sufficient sensitivity in the intermediate regions of the field and temperature, where the AFMR and EPR signals are weak. The reflex-type resonator construction has made possible tuning over a wide frequency range, and also adjustment of the coupling with the waveguide channel. The microwave power sources were standard klystron generators. The frequency measurement error was $\pm 2 \times 10^{-3}$. The magnetic field was produced by a superconducting solenoid having an additional coil for field modulation. The modulation frequency was 900 Hz. The reference marker for the magnetic field of the solenoid was the narrow line of the EPR signal from a DPPH standard. The possibility of performing measurements at helium temperatures and higher was ensured by a vacuum-cryostat setup. The sample temperature was measured with a thermocouple of gold-iron alloy coupled with copper, calibrated against standard platinum and germanium thermometers. The accuracy with which the temperature was measured and regulated was not worse than 0.1°K.

The $BaMnF_4$ single crystals were grown and kindly furnished by S. V. Petrov. To ensure accurate mounting, the sample was made in the form of a disc of 3 mm diameter and 1 mm thickness, from a single crystal with a large cleavage plane perpendicular to the b axis,

and was then glued to the polished bottom of the cylindrical resonator. The condition H ∥ b was satisfied in this case with accuracy not worse than 1°.

RESULTS AND DISCUSSION

The AFMR following application on a magnetic field along the easy axis b was investigated at four frequencies, $\nu_1 = 27.3$ GHz, $\nu_2 = 33.7$ GHz, $\nu_3 = 38.3$ GHz, and $\nu_4 = 40.9$ GHz. The temperature dependences of the resonant fields are plotted in Fig. 1 in coordinates H^2 and T.

1. Sublattice Flipping Line H_c^*

The H_c^* near the triple point was determined from the orientational resonance (OR) at the frequencies ν_1 and ν_2, wherein the resonant field coincides with the sublattice-flipping field. Below T = 15°K, the H_c^* line was obtained by calculation. Following the proposed calculation of Nagamiya, Yosida, and Kubo[7], we obtained also the temperature dependences of the frequency regions in which the OR should be observed. The lines A, B, and C in Fig. 2 are the temperature dependences of the values of the characteristic frequencies in the AFMR spectrum at H ∥ b, and the frequency intervals from zero to C and between A and B constitute the OR region. It should be noted that at the frequencies ν_3 and ν_4 the OR should be observed in the regions between the lines A and B also at T > 22.5°K. However, we did not observe any OR at these frequencies in the indicated temperature region. Figure 1 shows the H_c^* line and part of the line $C = 2H_{A1}H_E(\alpha^{-1} - 1)$, and the temperatures at which the AFMR mode should go over into the OR mode are marked for the frequencies ν_1 and ν_2. The experimental results show good agreement with the calculated data.

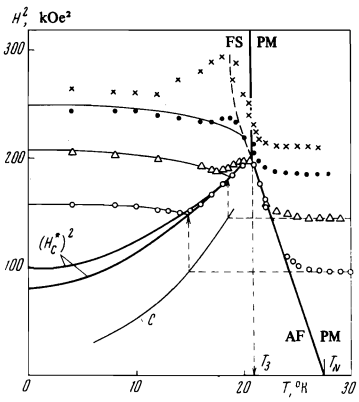

FIG. 1. Temperature dependence of the resonant AFMR and EPR fields: ○–ν_1 = 27.3 GHz, △–ν_2 = 32.7 GHz; ●–ν_3 = 38.3 GHz; X–ν_4 = 40.9 GHz. For the frequencies ν_1, ν_2, and ν_3 the figure shows the theoretical temperature dependences of the resonant fields, calculated using the Brillouin function [6].

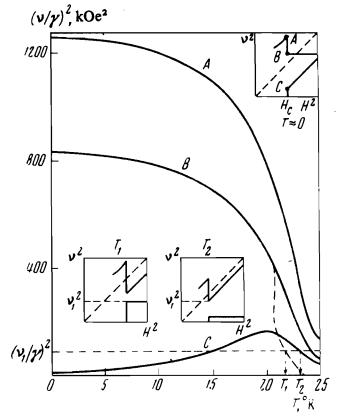

FIG. 2. Calculated temperature dependence of the characteristic frequencies of the AFMR spectrum at H ∥ b, which determine the region of the orientational resonance. The inserts in the figure show the form of the AFMR spectrum at T ≈ 0, T_1, and T_2.

The temperature dependence of H_c^* was calculated by formula (2) in two ways. In the first case (upper curve of Fig. 1) we used the susceptibility data from[5] and the value of $2H_{A1}H_E$ at 4.2°K from[6]. In place of the temperature dependence of $2H_{A1}H_E$ we used the temperature dependence of the gap $2H_{A2}H_E$[6], assuming in accordance with the results of[7] that the ratio of the anisotropy constants in a rhombic crystal is independent of the temperature. In the second case (lower curve of H_c^* in Fig. 1) we used in the calculation the values obtained by us for $2H_{A1}H_E$, and also the unpublished data on the susceptibility, obtained earlier with a sample from one and the same $BaMnF_4$ single crystal as in the AFMR investigation.

The two curves diverge appreciably at $T \ll T_N$, but the divergence vanishes gradually as $T \to T_N$. Besides the different degree of perfection of the crystals, one of the possible causes of the divergence of the data on the values of H_c^* and $2H_{A1}H_E$ for T < 14°K may be the fact that the type of the phase transition on the H_c^* line depends on the angle between the direction of the magnetic field and the easy axis, a dependence considered theoretically by Chepurnykh[8]. For $BaMnF_4$ at T = 4.2°K, the transition should be of first order, since the condition $H_c^* < H_{a2}^2 - H_a^2$[9] is satisfied if the AFMR data from[6] are used: H_{A2} = 30.1 kOe, H_A = 28.4 kOe, and H_c = 9.8 kOe. Substitution of the value H_c = 10.4 kOe from[5] reverses the sign of the inequality, and the transition should be of second order.

The value H_c = 9.3 kOe obtained by us corresponds to a first-order transition if the angle between H and the b axis is equal to zero. When the direction of the magnetic field does not coincide with the easy axis, there should exist a critical angle at which the phase transition becomes of second order and the turning of the sublattices proceeds gradually. The critical angle, as found in[8] is equal to the ratio of the anisotropy and exchange-interaction constants. For two-dimensional $BaMnF_4$ this value is of the order of 10^{-4} at T = 4.2°K[5]. It is difficult in practice to mount the sample with such an accuracy, and it appears that this explains the discrepancy between the experimental data. Gradual rotation of the sublattices in the case of inaccurate setting of the crystal axis relative to the direction of the magnetic field was observed also in the two-dimensionally-ordered crystals K_2MnF_4 and Rb_2MnF_4[10] and in $(CH_3NH_3)_2MnCl_4$[11]. With increasing temperature, as will be shown below, the ratio of the anisotropy to exchange increases in $BaMnF_4$, the requirements imposed on the accuracy of the setting of the crystal when determining H_c^* become less stringent, and the agreement between the experimental data is improved.

2. Line of Transition of an Antiferromagnet with Flipped Sublattices into the Paramagnetic State (FS–PM)

The FS-PM line was determined from the abrupt decrease of the resonant field to the EPR field and from the maximum of the line width ΔH at the frequencies ν_3 and ν_4. When this maximum was approached with increasing temperature the intensity of the signal decreased smoothly and the signal at the maximum did not differ from the noise. The intensity increased sharply with further increase of the temperature. Averaging curves were drawn through the values of the resonant fields at the temperatures close to the maxima

of ΔH for the frequencies ν_3 and ν_4, and the temperatures of the line-width maximum were marked on these curves. The values of the transition temperatures were made more accurate by using the intersection of the straight lines $\Delta H = f(\epsilon)$ for $T < T_N$ and $T > T_N$, which were plots of expression (3) below in logarithmic coordinates. The FS-PM line shown in Fig. 1 was drawn through the obtained $T_N(H)$ points.

Figure 3 shows the temperature dependence of the resonance line width at 48.9 GHz. At the frequency 38.3 GHz, the dependence of the line width is qualitatively similar, but at lower temperatures the dependence is weaker, and the maximum is somewhat narrower. Mori and Kawasaki[13], and also Kondo and Mori[14] considered the influence of the critical fluctuations of the short-range order on the width of the EPR and AFMR lines, and have shown that the critical slowing down of the decay of the correlations of the moments leads to a singularity on the temperature dependence of the line width at the transition point, the width for weakly-anisotropic antiferromagnets being

$$\Delta H \sim |\varepsilon|^{-\delta}, \qquad (3)$$

where $\epsilon = (T - T_N)/T_N$, and the value of T_N depends on the magnetic field.

The value 0.24 calculated by us for the exponent δ at 40.9 GHz in the interval of ϵ from −0.015 to 0.05 is close to the value 0.25 determined for a weakly-anisotropic uniaxial antiferromagnet at $T < T_N$[12]. At the same time, the obtained value $\delta = 0.36$ for $\epsilon = 0.015$ to 0.04 differs strongly from the theoretical value (0.75 for "pure" EPR[13]) and from the value 1.25 for the AFMR mode that can be observed at temperatures below T_N[14]. The discrepancy between the values of δ at $T > T_N(H)$ points to a more complicated influence of the short-range-order correlation in $BaMnF_4$ with two-dimensional exchange interaction and with low symmetry.

In the vicinity of the FS-PM line we observed two essential singularities of the AFMR. The first is that at the frequency 40.9 GHz there is an anomalous growth of the resonant field at $T \approx 18°K$, possibly connected with the splitting of the AFMR modes due to the inaccurate orientation of the magnetic field relative to the easy axis b. The splitting of the AFMR modes in $BaMnF_4$ was investigated in[6]. We used a formula from[15], which is suitable at $T \geq 0$:

$$\frac{H_z^2}{2H_{A_1}H_E + (\nu/\gamma)^2} - \frac{H_y^2}{2\alpha H_E(H_{A_2} - H_{A_1}) - (\nu/\gamma)^2} = 1,$$

where H_z and H_y are the projections of the resonant field on the axes b and c, respectively, and calculated the dependence of the resonant field on the frequency at $T = 17°K$. The best agreement with the experimental values is obtained at an angle 1° between the field and the b axis.

The other singularity pertains to the line shape of the resonant signal at the frequency 40.9 GHz and at $T = 18°K$, registered in the case of slow passage over the field and at a stable temperature. The accompanying distortion of the line shape is typical of simultaneous observation of two overlapping resonances. The resolution of the total signal was improved by tuning the bridge to the dispersion signal. One of the plots of such a signal is shown in Fig. 4, where the left-hand large

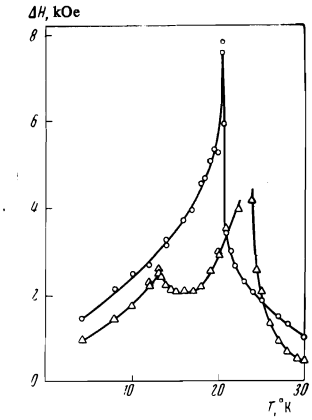

FIG. 3. Dependence of the AFMR and EPR line width on the temperature. △–27.3 GHz, ○–40.9 GHz. Solid lines–averaging curves corrected in accordance with expression (3). The minimum of ΔH at the frequency 27.3 GHz is due to the transition of the AFMR into orientational resonance [12].

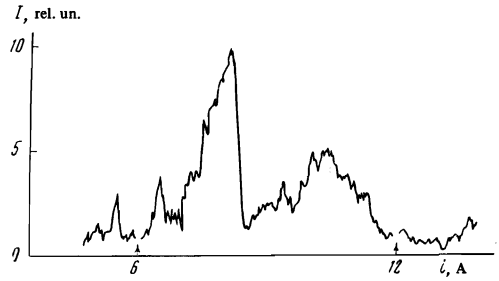

FIG. 4. Experimental plot of the dispersion curve of the mixed EPR and AFMR signals at $\nu = 40.9$ GHz and $T = 18°K$; the arrows mark the solenoid current.

peak corresponds to the EPR field. However, the registered low-intensity total signal was not always reproducible, and in some cases the total signal was observed only when the magnetic field was decreased or increased. When the temperature was increased or when the FS-PM line was approached, the resonant field decreased (Fig. 1) and the separation of the signal became difficult. A similar phenomenon was observed at 38.3 GHz and was manifest in a slight deformation of the absorption line and dispersion, observed in the temperature interval $T = 19.3–20°K$. Figure 1 shows alongside the FS-PM line a dashed line joining the points in which the indicated singularity of the line shape is noticeable.

Whereas the growth of the resonant field at 40.9 GHz is possibly connected with the splitting of the modes, the results listed below suggest that the existence of a mixed signal is due to other factors. Within the limits of the measurement error, we did not observe in the investigated temperature and frequency region the decrease of the resonant field below the EPR field for the corresponding frequency, which should have occurred in the case of AFMR mode splitting, as observed in[6]. The distance between the observed additional low-intensity peaks (Fig. 4) corresponds to the splitting of the fine-structure level in crystalline compounds of manganese, including antiferromagnetic ones[16,17]. We therefore believe that it is more correct to attribute the mixed signal to the coexistence of ferromagnetic and antiferromagnetic states in the FS-PM transition region, owing to the influence of the short-range order. On the other hand, the splitting of the modes helps make the difference between the resonance EPR and AFMR fields at 40.9 GHz and $T \approx 18°K$ maximal, and contributed to a more pronounced separation of the total signal. The coexistence of paramagnetic and antiferromagnetic states, resulting from the influence of the short-

range order, was observed by Spence and El Saffar[18] in the ordinary three-dimensional antiferromagnet $LiCuCl_3 \cdot 2H_2O$, and the interval of the coexistence temperatures was found to be 0.02°K. In two-dimensional antiferromagnets, as shown in[3], the influence of the short-range correlations should be much stronger. Therefore the interval between the dashed and solid FS-PM lines can be arbitrary regarded as the mixed-state region.

3. Line of Transition of an Antiferromagnet with Nonflipped Sublattices to the Paramagnetic State (AF–PM)

The determination of the AF-PM line did not differ in principle from the determination of the FS-PM line. The obtained AF-PM line in the temperature 20.5–24°K at the frequencies ν_1 and ν_2 is close to a straight line when plotted in terms of the coordinates H^2 and T (Fig. 1), as for an ordinary uniaxial antiferromagnet[19]. The intercept of this line with the T axis yields a value $T_N = 27.2$°K, which agrees with T = 27°K determined in[1]. The temperature dependence of the resonant fields and the line width of the frequencies ν_1 and ν_2 have near the AF-PM line a singularity connected with the fact that there is a considerable temperature interval between the vanishing of the AFMR signal and the appearance of the EPR signal. For the frequency ν_1 = 27.3 GHz, the interval amounts to approximately 2°K.

The observed vanishing of the resonance can be explained if account is taken of the dependence of the AFMR frequency, marked B in Fig. 2, on the ratio of the magnetic field to the exchange field in accordance with spin-wave theory[9]. Using the formula

$$(\nu/\gamma)^2 = H_a(1 - H^2/H_E^2),$$

it is possible to refine the temperature dependence of the line B, the form of which changes significantly in the temperature region in which the resonant and exchange fields have close values. The dashed curve in Fig. 2 shows the correct line B with allowance for the phase-diagram lines obtained by us. The calculation was carried out for the fields corresponding to the resonant fields at the frequency ν_1 = 27.3 GHz. It is seen from Fig. 2 that at the frequencies between the lines B and C, past their intersection point, no resonance should be observed, since a "spillover" of the modes takes place at this point. As a result, when AFMR is observed with a spectrometer at a fixed frequency, the value of which is lower than the intersection point of B and C, there exists a temperature interval T_1 and T_2 (Fig. 2) where there is no resonance. At the frequency ν_1, the resonance signal should vanish at $T_1 = 22$°K, which agrees with experiment. The possible existence of the "spillover" of the modes in $CuCl_2 \cdot 2H_2O$ was demonstrated in[15].

It is seen from Fig. 2 that the lines C and A do not intersect at T_N as in the case of $CuCl_2 \cdot 2H_2O$[7], and thus, there is a formal possibility of the existence of orientational resonance (OR), meaning also of a sublattice-flipping field at $T > T_N$. This possibility agrees also with the results of[1], where it is noted that anisotropy exists at $T > T_N$, as does a field H_C in which the magnetization along the b axis changes jumpwise. We observed no OR above T_N, but established that the resonant fields differ from the EPR field. Thus, at 27.3 GHz this difference is noticeable up to 80°K, and the value $\delta = 0.92$, determined from the dependence of the line width on the temperature at $T > T_N$, lies between $\delta = 0.75$ for EPR[13] and $\delta = 1.25$ for the AFMR mode that can be observed above T_N[14]. Like the authors of[6], we arrive at the conclusion that the results should be connected with the existence of long-lived regions of short-range order at temperatures much higher than T_N in two-dimensional antiferromagnets.

The parameters of the triple points, $T_t = 20.6 \mp 0.3$°K and $H_t = 14.4 \mp 0.2$ kOe, were determined from the intersection of the obtained phase-diagram lines H_C^*, FS-PM, and AF-PM. The continuation of the FS-PM line to the intercept on the T axis on the phase diagram (Fig. 1) yields another parameter, $T_3 \approx 21$°K. According to theoretical considerations[7,20], the difference between T_N and T_3 is determined only by the anisotropy. The anisotropy-field value calculated from $T_N - T_3$ turns out to be much larger than the 100 Oe obtained at T = 1.4°K in[5].

To explain this fact, we calculated the temperature dependence of the anisotropy field H_{A1} from the data on the dependence of the resonant AFMR fields on the temperature and the phase-transitions lines. The $H_{A1}(T)$ curve has a maximum T = 20°K, where H_{A1} is equal to 1.6 kOe. This unusual dependence of the anisotropy field on the temperature may be due to the influence of the crystal field of the liquid on the magnetic ions, which leads to single-ion anisotropy. This assumption is corroborated by the splitting of the EPR into fine-structure components, observed in the temperature region close to T_t (Fig. 4). Since the magnetic ion $BaMnF_4$ is in the S state, the ratio of the distances to the Mn^{2+}-ion nearest neighbors in the deformed layers is equal to 1.05[21] and it can be assumed that the anisotropy of the obtained interaction is small, while the main contribution to the anisotropy is made by dipole interactions, as in the case of K_2MnF_4 and Rb_2MnF_4[10], and the influence of the crystal field of the ligands. If the dipole and the single-ion anisotropy are of approximately the same order, say at T = 0°K, and the anisotropy-constant tensors have different principal axes (which is perfectly feasible for $BaMnF_4$, since the lattice-magnetization vector is parallel to the b axis and the polarization vector P is directed along the twofold axis a[22]), the total anisotropy will be small in this case. With increasing temperature, the dipole and the single-ion anisotropy vary in different fashions[7,20], and the value of the resultant uncompensated anisotropy field can increase. It appears that this is the situation in $BaMnF_4$.

[1] R. V. Zorin, B. I. Al'shin, D. N. Astrov, and A. V. Tishchenko, Fiz. Tverd. Tela 14, 3103 (1972) [Sov. Phys.-Solid State 14, 2661 (1973)].
[2] D. E. Cox, M. Eibshütz, H. U. Guggenheim, and L. Holmes, J. Appl. Phys., 41, 943 (1970).
[3] M. E. Lines, J. Phys. Chem. Sol., 31, 101 (1970).
[4] B. I. Al'shin, D. N. Astrov, and R. V. Zorin, Zh. Eksp. Teor. Fiz. 63, 2198 (1972) [Sov. Phys.-JETP 35, 1161 (1972)].
[5] L. Holmes, M. Eibshütz, and H. J. Guggenheim, Solid State Commun., 7, 973 (1969).
[6] S. V. Petrov, M. A. Popov, and L. A. Prozorova, Zh. Eksp. Teor. Fiz. 62, 1884 (1972) [Sov. Phys.-JETP 35, 981 (1972)].
[7] T. Nagamiya, K. Yosida, and R. Kubo, Adv. Phys., 4, 1 (1955).

[8] G. K. Chepurnykh, Fiz. Tverd. Tela **10**, 1917 (1968) [Sov. Phys.-Solid State **10**, 1517 (1968)].
[9] V. G. Bar'yakhtar, A. A. Galkin, S. N. Kovner, and V. A. Popov, Zh. Eksp. Teor. Fiz. 58, 494 (1970) [Sov. Phys.-JETP **31**, 264 (1970)].
[10] D. U. Breed, Physica, **37**, 35 (1967).
[11] W. D. van Amstel and L. J. de Jongh, Solid State Commun., **11**, 1423 (1972).
[12] H. J. Gerritsen, M. Garber, and W. J. Drewes, Physica, **22**, 213 (1956).
[13] H. Mori and K. Kawasaki, Progr. Theor. Phys., 28, 971 (1962).
[14] Y. Kondo and H. Mori, Phys. Lett., **30A**, 230 (1969).
[15] H. J. Gerritsen, Physica, **21**, 639 (1955).
[16] S. A. Al'tshuler and B. N. Kozyrev, Elektronnyĭ paramagnitnyĭ rezonans soedineniĭ élementov promezhutochnykh grupp (Electron Paramagnetic Resonance of Compounds of Intermediate-Group Elements), Nauka, 1972.
[17] D. C. Fowlis and C. V. Stager, Canadian J. Phys., **50**, 2681 (1972).
[18] R. D. Spence and M. El Saffar, J. Phys. Soc. Japan, **17**, 244 (1962).
[19] A. S. Borovik-Romanov, Itogi nauki fiz.-matem. nauki, 4, Antiferromagnetizm (Science Summaries, Phys.-Math. Sciences, 4, Antiferromagnetism), AN SSSR, 1962.
[20] K. W. Blazey, H. Rohrer, and R. Webster, Phys. Rev. **B4**, 2287 (1971).
[21] L. J. de Jongh, P. Blombergen, and H. P. Colpa, Physica, 58, 305 (1972).
[22] E. T. Keve, S. C. Abrahams, and J. L. Bernstein, J. Chem. Phys., **51**, 4928 (1969).

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