were not set to their best sensitivity at zero bias. When the signal had vanished after extensive contact pressure a short current pulse across the barrier could bring back almost full sensitivity. It is thought that this effect is due to welding of the contact and formation of a depletion layer.

V. FUTURE IMPROVEMENTS

As a result of our measurements, the main limitation for an improvement in NEP seems to be the harmonic-mixing process. The high-harmonic conversion loss cannot be overcome by a further increase in LO power because of LO current noise and burnout of the contact. Higher LO frequencies are necessary to come to low harmonic orders or even to fundamental mixing. It seems unreasonable to use microwave sources like carcinotrons which are extremely expensive and hard to handle at these frequencies. Moreover, the stabilization of LO frequency will become a main problem.

A possible method, now under test at our laboratory, is the use of a second smaller HCN laser as an additional LO delivering some milliwatts at the 311-μm transition. The difference between 337 and 311 μm corresponds to a frequency near 75 GHz from where the spectrum can be converted down by mixing with a stable 4-mm klystron in the same contact. This process needs no harmonic conversion and should lead to sensitivities near the calculated limit. In addition, the development of infrared lasers to higher output powers is still going on. In the near future this should allow FIR collective scattering to become a useful diagnostic for fusion plasmas.

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Submillimeter Spectroscopy of Weak Antiferromagnets in Magnetic Fields Up To 300 kOe

E. G. RUDASHEVSKY, A. S. PROKHOROV, AND L. V. VELIKOV

Abstract—**The dynamic properties of antiferromagnets with Dzyaloshinsky interaction were investigated at wavelengths 0.3–14 mm, in magnetic fields up to 300 kOe and temperature 4.2–400 K. The problems of impurities, field induced phase transitions, types of spin oscillation, etc., for different types of antiferromagnets with Dzyaloshinsky interaction are discussed. Based on the investigation results, a new approach to the physics of magnetic phenomena, using the complete rational basis of invariants and avoiding potential series expansion, has been developed.**

DESPITE the fact that antiferromagnetism has been known for a long time [1] and up to today over 300 antiferromagnetic insulators have been discovered, there is an increasing interest in studying this phenomenon by resonance methods. The main reason for this is that inherent oscillation frequencies of the above classes of materials fall in the submillimeter and the far-infrared ranges of electromagnetic radiation (200 μm–2000 μm). It is worthwhile noting that the interest in these materials is explained by the following two reasons. First, the present active conquest of this range from both superhigh frequencies (vacuum electronics) and from optics (lasers); the sources of coherent radiation of the above range have become available. Second, the necessity of finding substances for practical applications over this range.

A variety of antiferromagnets have greatly differing properties and, as a rule, have nonlinear and very complicated dependences of resonance frequency upon magnetic field, temperature, and orientation. Of special importance is the insight into the fundamental properties of antiferromagnets in order to investigate their use in practice and to predict the properties of newly synthesized crystals.

Though there are many known antiferromagnets, antiferromagnetic resonance (AFMR) has been observed for relatively few of them (about 30), and the number of

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comprehensively studied antiferromagnets by the AFMR is rather low (about 10).

Progress in antiferromagnet studies and in theoretical understanding of their properties is principally due to investigations of the materials with magnetic ions in the S state. This fact makes it possible to apply the well-developed spin-wave theory, the main assumption of which is rigorous conservation of the magnetic-moment magnitude (which is the case for only ions in the S state). But more often the magnetic ion is not in the S state, which provides a greater variety of frequency—field, orientation, and temperature dependences.

Among the best studied antiferromagnets is the class of the so-called antiferromagnets with weak ferromagnetism. The weak ferromagnetism theory, initially suggested and developed by Dzyaloshinsky [2], and based on the thermodynamic theory of Landau, explained that weak ferromagnetism results from slight canting of the antiparallel sublattice magnetizations $\boldsymbol{M}_1$ and $\boldsymbol{M}_2$ ($|\boldsymbol{M}_1| = |\boldsymbol{M}_2|$) (the transversal Dzyaloshinsky interaction); predicted the possibility under certain conditions of the longitudinal Dzyaloshinsky interaction, when $|\boldsymbol{M}_1| \neq |\boldsymbol{M}_2|$. While the transversal Dzyaloshinsky interaction has been experimentally observed and studied for a long time [3], the longitudinal Dzyaloshinsky interaction was experimentally discovered quite recently in static [4] and resonance [5] measurements.

The present work reports some results of extensive studies of antiferromagnets whose paramagnetic space groups are D_{4h}^{14}(CoF_2,NiF_2) and D_{3d}^{6}(α-Fe_2O_3,$FeBO_3$). Such substances are most typical since they exhibit two types of transversal Dzyaloshinsky interaction and various ground states which are determined by sublattice magnetic orientation with respect to crystallographic axis without magnetic field. From the symmetry viewpoint, a thermodynamic potential for the substances can be expanded in a series of components of magnetization vectors $\boldsymbol{M} = \boldsymbol{M}_1 + \boldsymbol{M}_2$ and $\boldsymbol{l} = (\boldsymbol{L}/2M_0) = \boldsymbol{M}_1 - \boldsymbol{M}_2$, and within an accuracy up to the second-order terms is

$$\Phi = \tfrac{1}{2}B\boldsymbol{M}^2 + \tfrac{1}{2}al_z^2 + d_\perp^{\pm}(M_x l_y \pm M_y l_x) - \boldsymbol{MH} \quad (1a)$$

where constants B,a,$d_\perp^{\pm}$ can be derived by means of the effective fields of exchange, anisotropy, and transversal Dzyaloshinsky interaction, respectively; axis Z is just the highest order axis (C_4 for D_{4h}^{14} and C_3 for D_{3d}^{6}); and axis X coincides with [100] for D_{4h}^{14} and with U_2 for D_{3d}^{6}.

Despite the slight formal difference in the thermodynamic potentials for the above spacial groups, there is a principal difference in the physical nature of $d_\perp^-$ and $d_\perp^+$ (antisymmetric exchange and single-ion anisotropy, respectively) [6]. A slight formal difference between the two types of Dzyaloshinsky interaction will give rise to principally different formulas of the AFMR spectra. The calculations were carried out on the standard assumption of the spin-wave theory:

$$\left.\begin{aligned} \boldsymbol{M}^2 + \boldsymbol{L}^2 &= \text{const} \\ (\boldsymbol{ML}) &= 0 \end{aligned}\right\} \quad (1b)$$

$$\left.\begin{aligned} \nu_1/\gamma &= [H(H + H_D^-) + H_{ME}H_E]^{1/2} \quad (D_{3d}^{6}) \\ \nu_1/\gamma &= [(H + H_D^+)(H + 4H_D^+)]^{1/2} \quad (D_{4h}^{14}) \end{aligned}\right\} \quad \begin{aligned} \boldsymbol{H} &= \{H00\} \\ \boldsymbol{l} &= \{0l0\} \end{aligned} \quad (2a),\ (2b)$$

$$\nu_2/\gamma = [2H_AH_E + H_D^{\pm}(H + H_D^{\pm})]^{1/2} \quad (D_{3d}^{6},\ D_{4h}^{14}) \quad (3)$$

$$\left.\begin{aligned} \nu_1/\gamma = [2H_AH_E - (H_D^{\pm})^2]^{1/2} \cdot \left\{1 - \frac{H_A^2 + (H_D^{\pm})^2}{[2H_AH_E - (H_D^{\pm})^2]^2} H^2\right\}^{1/2} \quad (D_{3d}^{6},\ D_{4h}^{14}) \end{aligned}\right\} \quad \begin{aligned} \boldsymbol{H} &= \{H00\} \\ \boldsymbol{l} &= \{0l_yl_z\} \end{aligned} \quad (4)$$

$$\left.\begin{aligned} \nu_{1,2}/\gamma &= [2H_AH_E - (H_D^-)^2]^{1/2} \pm H \quad (D_{3d}^{6}) \\ \nu_{1,2}/\gamma &= \{[(2H_AH_E)^{1/2} \pm H]^2 - (H_D^+)^2\}^{1/2} \quad (D_{4h}^{14}) \end{aligned}\right\} \quad \begin{aligned} \boldsymbol{H} &= \{00H\} \\ \boldsymbol{l} &= \{00l\}. \end{aligned} \quad (5a),\ (5b)$$

It is important that the above formulas are derived from the same potential (1a) written only up to second powers on magnetization components with model assumption (1b), valid rigorously only in the case of magnetic ions with quenched orbital motion. One can also introduce higher order terms into potential (1a), but this will make the calculations so complicated that it is not clear how and to what extent higher order invariants will change formulas (2a)–(5b), how many invariants should be taken into account for the accurate solution, etc.

Addition of further invariants into potential (1a) becomes very important in connection with the problems of magnetic-field-induced phase transitions. There are 38 fourth-order invariants for group D_{4h}^{14} and 18 for group D_{3d}^{6}. Naturally, it is practically impossible to derive formulas such as (2a)–(5b) with so great a number of invariants (constants). Moreover, there is no sense in writing out the solutions with this enormous number of constants, since there are very few feasible experiments and, consequently, very few phenomenological constants to be measured. This problem is discussed at the end of the present paper in connection with the CoF_2 investigation.

Formulas (2a)–(4) and (5b) were verified experimentally over an electromagnetic radiation range (14 mm–300 μm) at 4.2–400 K in a continuous magnetic field up to 150 kOe [7] and in a pulsed magnetic field up to 300 kOe. Fig. 1(a) shows the experimental setup for measurements in a continuous magnetic field [8]. Fig. 1(b) represents the part of the setup for measurements at 4.2–80 K. The radiation was detected by n-InSb at $T = 4.2$ K. In case of a pulsed magnetic field ($\lambda = 4$ mm–1000 μm) quartz dielectric waveguide were employed [9]. The radiation sources were backwave oscillators [10], wavelengths were measured by a Fabry–Perot interferometer with metallic-wire grids [11]. The measurement accuracy was not less than 1 percent.

The experimental results corresponding to formulas

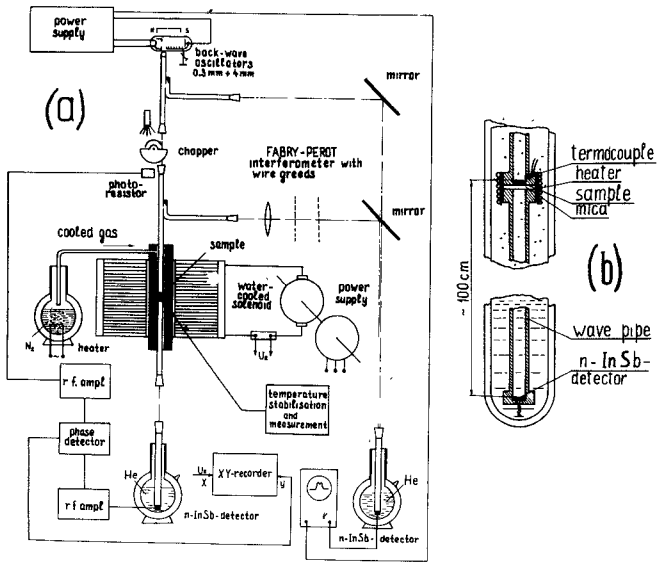

Fig. 1. (a) Experimental setup for measurements in continuous magnetic fields up to 150 kOe. (b) Part of dewar with n-InSb detector and wave pipe for measurements at 4.2–80 K.

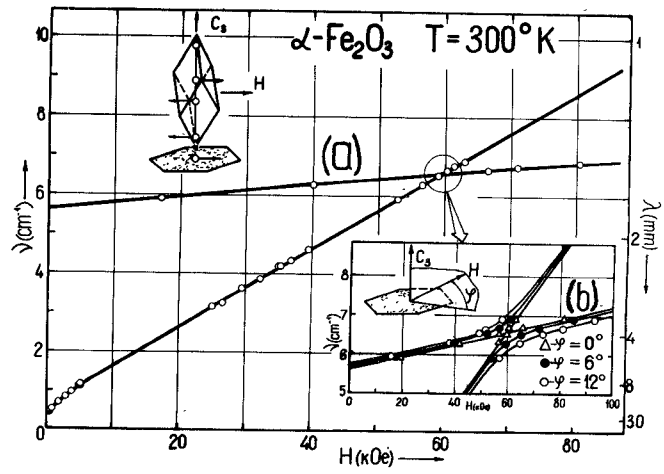

Fig. 2. (a) Experimental results and theoretical curves corresponding to formulas (2a) and (3) for α-Fe_2O_3 ("low-frequency" AFMR branch and "high-frequency" AFMR branch). (b) Experimental results for the region of intersection of branches and theoretical curves corresponding to formulas (6)–(7b) for α-Fe_2O_3.

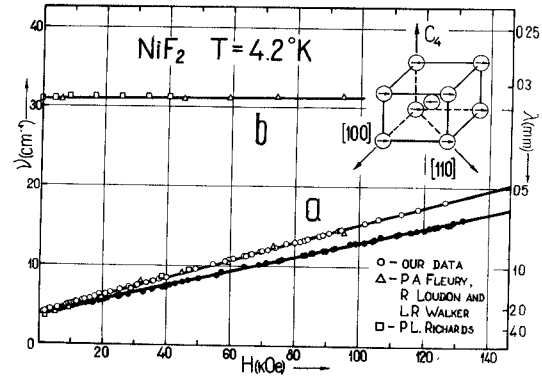

Fig. 3. Field dependence of the AFMR frequencies at 4.2 K for NiF_2. ○—$H_\parallel$ [100]; ●—$H_\parallel$ [110] [24].

(2a)–(3) for α-Fe_2O_3 and NiF_2 are given in Figs. 2 and 3, respectively. The difference in the physical nature of Dzyaloshinsky interaction for NiF_2 and α-Fe_2O_3 leads to the following: a) for NiF_2 $\nu_1(H = 0)$ depends on Dzyaloshinsky interaction, but for α-Fe_2O_3 the value of $\nu_1(H = 0)$ is low and results from magnetoelastic interaction [12]; b) in NiF_2 the experiments reveal a well-defined dependence of ν_1 upon the magnetic-field direction in the basal plane, while this effect is not observed in α-Fe_2O_3.

Fig. 2(b) gives the results for the region of the intersection of curves (2a) and (3). The correlation of these bound oscillations is described by the formula [13]

$$(\nu^2 - \nu_1^2)(\nu^2 - \nu_2^2) - \gamma^4(\chi_\parallel/\chi_\perp)H_z^2H_x^2 = 0 \quad (6)$$

where $H_z = H \sin \varphi$, $H_x = H \cos \varphi$, and ν_1 and ν_2 are determined by the expressions:

$$\nu_1/\gamma = [(\chi_\perp/\chi_\parallel)H \cos \varphi(H \cos \varphi + H_D^-) + H_{ME}H_E]^{1/2} \quad (7a)$$

$$\nu_2/\gamma = [2H_AH_E + H_D^-(H \cos \varphi + H_D^-) + (\chi_\parallel/\chi_\perp)H^2 \sin^2 \varphi]^{1/2}. \quad (7b)$$

When $\varphi = 0$, (7a) and (7b) correspond to (2a) and (3). By formulas (6)–(7b) the inherent oscillation frequency of antiferromagnets can be calculated for any angle between the basal plane and the magnetic field direction. Formula (6) is a general equation for frequencies of two interacting oscillations. The oscillation binding is due to term $\gamma^4(\chi_\parallel/\chi_\perp)H_z^2H_x^2$ in (6), which is independent of Dzyaloshinsky interaction. As can be seen from (6), crystal symmetry has no influence on the form of (6). Substance symmetry affects (7a) and (7b). This leads to the conclusion that in other symmetry crystals (say, NiF_2 and CoF_2) the inherent frequencies of bound oscillations of electron spins are also determined by an equation like (6).

By studying the field dependence of AFMR frequencies at various temperatures, one can investigate effective fields and, hence, various types of interactions. Fig. 4(a) and (b) shows the plots $\nu_1(H)$ and $\nu_2(H)$ for $FeBO_3$ [8] at various temperatures [see (2a) and (3)].

The study of the AFMR linewidths as a function of temperature and an external magnetic field allows investigation of the relaxation mechanisms. The temperature dependences of linewidths for $FeBO_3$ of branch $\nu_1(H \approx 5$ kOe, circles) and of $\nu_2(H \approx 50$ kOe, triangles) plotted in Fig. 5(a) greatly differ, which seems to indicate a substantially different relaxation mechanism for ν_1 and ν_2 [8]. From Fig. 5(b) (open circles $\nu_1 = 0.79$ cm^{-1}, closed circles $\nu_1 = 2.53$ cm^{-1}) it follows that the temperature broadening of the AFMR line near T_N strongly depends upon the magnetic field which exhibits resonance absorption (at $\nu_1 = 0.79$-cm^{-1} transition to a paramagnetic state occurs in a magnetic field $H_{res} \approx 5$ kOe, at $\nu_1 = 2.53$ cm^{-1} $H_{res} \approx 20$ kOe). This effect seems to be due to a magnetic field which suppresses fluctuations breaking down the magnetic ordering [14] and is expected to enhance in the submillimeter range ($H_{res} \approx 10^5$ kOe).

The resonance properties of antiferromagnets are greatly

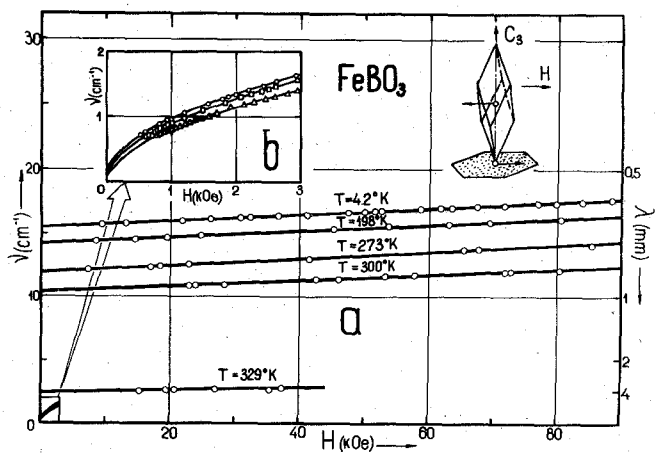

Fig. 4. Field dependences of the AFMR frequencies at various temperatures for $FeBO_3$ $H \perp C_3$.

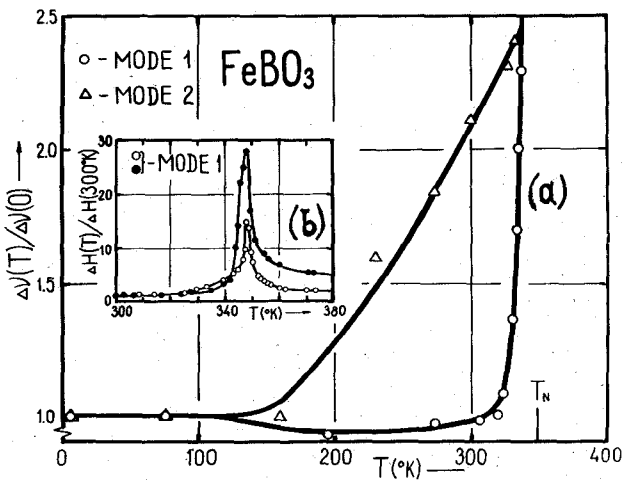

Fig. 5. (a) AFMR line widths versus temperature; ○—results for the "low-frequency" branch; △—results for the "high-frequency" branch. (b) the external magnetic-field effect on AFMR linewidth near T_N.

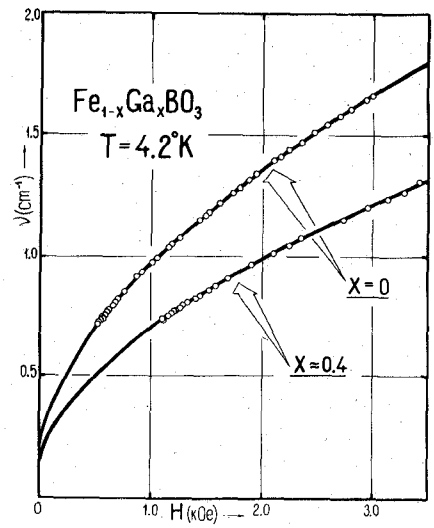

Fig. 6. Field dependences of the AFMR frequencies at 4.2 K for pure $FeBO_3$ and $FeBO_3$ doped with Ga^{+3}.

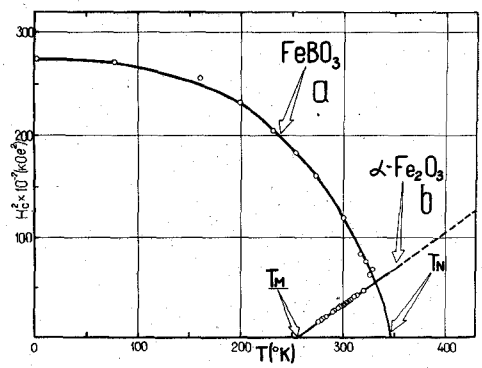

Fig. 7. Temperature dependence of energy gap ($H = 0$) for α-Fe_2O_3 and $FeBO_3$.

influenced by addition of impurities. For example, addition of Fe^{2+} into $MnCO_3$ [15] changes the whole magnetic structure of the crystal. As a consequence, the AFMR frequency dependences should also radically change. Addition of magnetic ions Mn^{2+} (concentration 0.01–0.03 percent) into CoF_2 [16] creates a new oscillation branch in the submillimeter range ($\nu = 28.5$ cm^{-1}). The authors succeeded in observing AFMR in $FeBO_3$ when it was doped with diamagnetic ions of Ga^{3+} even up to Ga^{3+}-ion concentrations of 50 percent and at $T = 4.2$ K (Fig. 6). The dependence of the AFMR frequency is described by formula (2b) with coefficients depending on Ga^{3+}-ion concentration.

The submillimeter spectroscopy method directly provides the values of energy gaps in antiferromagnet spin-wave spectra and the possibility of studying their temperature dependences. These investigations are significant for verifying and establishing applicability of the existing antiferromagnet theories (e.g., the spin-wave theory). Fig. 7 gives two principally different temperature dependences of energy gaps ($H = 0$) [8], [17].

Fig. 8(a) shows the AFMR frequency versus magnetic field for CoF_2. In this case, rather an unusual phenomenon was observed—spin reorientation due to Dzyaloshinsky interaction in a magnetic field normal to the sublattice magnetization orientation [18]. The frequency goes to zero, according to formula (4). The above theory cannot apply to the CoF_2 case, because in a general case condition (1b) is not fulfilled. But in a particular case $\boldsymbol{H} = \{100\}$ formula (4) accurately describes experimental results. In Fig. 8(b) for CoF_2 one can see in the vicinity of $\nu_1 \approx 0$ a cutoff AFMR line due to a step-like phase transition, similar to that observed earlier in α-Fe_2O_3 [19]. This cutoff can be described by taking higher order terms into account, as was mentioned in the foregoing. In case α-Fe_2O_3, in order to elucidate the effect of various invariants allowed by the crystal symmetry, the authors analyzed the effect of all fourth-order invariants upon the kind of phase transition. The essential features of this phenomenon are independent of the field orientation in the basal plane. So, for its correct interpretation, it is sufficient to take into consideration only those fourth-order invariants which are isotropic in the basal plane: l_z^4, $(l_xM_y - l_yM_x)\cdot l_z^2$, $M^2l_z^2$, $M_z^2l_z^2$, etc.

In some works [20], [21] this phenomenon was de-

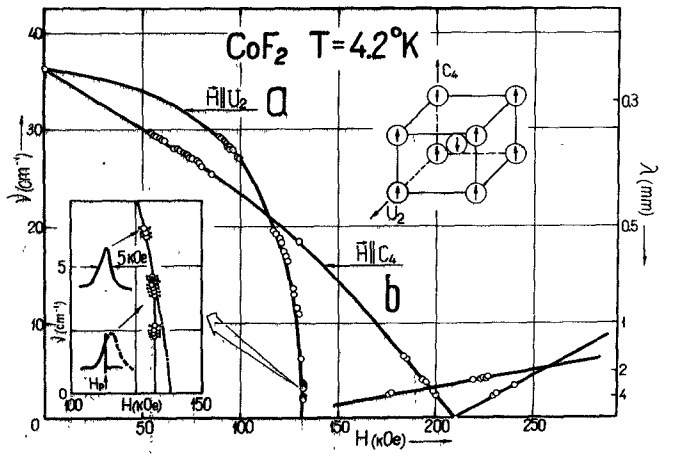

Fig. 8. AFMR frequency versus magnetic field for CoF_2.

scribed with due reference only to one fourth-order invariant l_z^4 ("second constant of anisotropy"). But our analysis [22] of thermodynamic potential with due reference to all the invariants has shown that consideration of any one of them leads to a step-like phase transition. The experimental results available do not allow us to conclude whether any one of the fourth-order invariants isotropic in the basal plane will be predominant in describing the observed phase transition. Note that invariant l_z^4 is least effective in describing the change of the transition kind since l_z^4 decreases near the phase transition.

Description of essential features of this effect in CoF_2 seems to require a greater number of invariants than in the case of α-Fe_2O_3. This is because the magnitudes of the exchange and of the anisotropic interactions in CoF_2 are comparable.

At magnetic-field orientation $H = \{00H\}$, CoF_2 exhibited an unusual field dependence of the AFMR frequency, which cannot be principally accounted for in terms of the ordinary spin-wave theory [formula (1b)] and without due reference to all types of interaction allowed by the symmetry.

Based on the investigation results, a new approach to the physics of magnetic phenomena has been developed using the complete rational basis of invariants (CRBI) [23] and avoiding potential series expansion. Therefore, the experimental and theoretical results obtained will be considered in more detail [5]. In the case $H = \{00H\}$ nonlinearity in the dependence $\nu_1 = \nu_1(H)$ associated with the transverse Dzyaloshinsky interaction in the form $(M_x l_y + M_y l_x)$ was experimentally observed. As $\nu_1 \to 0$, $\partial\nu_1/\partial H$ goes to a finite value $\partial\nu_1/\partial H\,|_{\nu_1=0} = (4.4 \pm 0.2) \cdot 10^{10}$ $(\mathrm{kOe \cdot s})^{-1}$, which contradicts the spin-wave theory prediction $\partial\nu_1/\partial H\,|_{\nu_1=0} = 0$. The theoretical analysis shows that the finite value $\partial\nu_1/\partial H$ is principally connected with the correlation between the transversal Dzyaloshinsky interaction $(M_x l_y + M_y l_x)$ and the longitudinal Dzyaloshinsky interaction $(\boldsymbol{Ml})l_x l_y, (\boldsymbol{Ml})M_x M_y$ at $\chi_{zz} \mid T \to 0\ \mathrm{K} \neq 0$, which was observed experimentally. The correlation between the longitudinal and the transversal Dzyaloshinsky interactions means that the previously mentioned fourth-power term of magnetization in the thermodynamic potential follows from the bilinear spin Hamiltonian which determines the transversal Dzyaloshinsky interaction as well, while the contribution of the averaged products of the fourth-power components of spin operator is negligibly small which is in the correlation with the spin 3/2 of Co^{2+}. The theoretical consideration proceeds from the total potential with reference to all the invariants allowed by the symmetry without series expansions. As a result of the analysis, we suggest the simplest potential which completely describes the experimental and contains only six phenomenological parameters. Any allowed by the symmetry invariants added to this potential will affect neither the spectrum-type nor the number of experimentally found parameters [5].

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Low Frequency Excitations in Antiferromagnetic Tungstates ($NiWO_4$, $CoWO_4$)

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***Abstract*—Absorption spectra of biaxial antiferromagnets have been studied from 7.5 to 500 cm^{-1}. Ordering directions and the g tensor are determined. A new spin-wave branch and spin–phonon interaction will be described.**

I. INTRODUCTION—PROBLEM FORMULATION AND EXPERIMENTAL TECHNIQUE

THE transition metal tungstates have a low (monoclinic) symmetry crystalline lattice. They belong to the C_{2h}^4 space group [1], [2]. Under magnetic ordering they become biaxial collinear antiferromagnets [3] and have the sufficiently high Néel temperature (T_N = 67 K for $NiWO_4$ [4] and T_N = 55 K for $CoWO_4$ [4], [5]). It is important to remember that the ground state of Ni^{2+} is $^3F_4$, and that of Co^{2+} is $^4F_{9/2}$.

According to the results of measuring magnetic, resonance, and optic properties of $NiWO_4$ [6], [10], $CoWO_4$ [5], [7], and isostructural $ZnWO_4$ containing cobalt or nickel [6], [8], [9], the crystal field potential at the magnetic ion site possesses considerable axial and orthorhombic components. This along with the fact that magnetic ion spin exceeds 1/2 (S = 1 for Ni^{2+} and S = 3/2 for Co^{2+}) permits the excitation of both antiferromagnetic resonance (AFMR) modes and a higher frequency spin branch. This follows from the recent theoretical work [11].

The frequencies of AFMR modes and the new high frequency branch should lie within far IR since both the anisotropy energy and exchange interaction are high in this crystal. Thus the estimate of the effective exchange interaction field H_{eff} from the magnetic susceptibility $\chi_\perp$ which was measured along the direction perpendicular to the spontaneous ordering is ~600 kOe for $NiWO_4$ [10]. In this connection the absorption spectra of nickelous and cobaltous tungstates were studied in the far IR (7.5–500 cm^{-1}). The spectrometer [12] composed of an evacuated grating monochromator, cryostats for cooling the sample and detector, and an electric magnet or superconducting solenoid, permitted the measurement resolution of 0.1 cm^{-1} in the vicinity of the long wavelengths and of about 1 cm^{-1} near the short wavelengths, the magnetic field being $H_0 \leq 50$ kOe. The sample temperature could vary from 5 to 300 K.

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II. EXPERIMENTAL RESULTS AND DISCUSSION

A. Antiferromagnetic Resonance

We identify the lowest frequency absorption bands in the $CoWO_4$ and $NiWO_4$ as AFMR modes [13], [14]. Their characteristics are listed in Table I and the spectrum type is shown (for $NiWO_4$) in Fig. 1. The bands observed are polarized, and the polarization character is indicative of their magnetic dipolar nature. In the external magnetic field the AFMR frequencies are shifted. The frequency shift in the external magnetic field is anisotropic [Fig. 2(a)]. When the field is oriented along the monoclinic twofold axis $b(Y)$ and along the direction