HIGH-FREQUENCY ANTIFERROMAGNETIC RESONANCE IN ANHYDROUS $NiCl_2$

A. F. LOZENKO, V. I. MALINOVSKIĬ, and S. M. RYABCHENKO

Institute of Physics, Ukrainian Academy of Sciences

Submitted September 10, 1970

Zh. Eksp. Teor. Fiz. 60, 1387–1392 (April, 1971)

The high-frequency branch of antiferromagnetic resonance (AFMR) in anhydrous $NiCl_2$ is investigated in the 79–52-GHz frequency range at temperatures between 4.2 and 40°K. A value D = 0.5 cm^{-1} for the anisotropy constant is found by using the value of the exchange constant between layers, B = 3.5 cm^{-1}, obtained by Kanamori on the basis of $\chi_\perp$ measurements. This value of D corresponds to the dipole-dipole contribution to anisotropy. The temperature dependence of the AFMR frequency agrees with the values of the constants presented above provided that in the given temperature range the sublattice magnetization is determined by the two-dimensional ferromagnetic sublattice.

1. INTRODUCTION

THE properties of layered antiferromagnets were investigated in a number of papers.[1-9] In these crystals there is a strong ferromagnetic exchange interaction in the plane of the layer and a relatively weak antiferromagnetic interaction between layers.[1] This causes the magnetic properties of the two-dimensional ferromagnetic structure to turn out to be decisive in a number of cases[2] for the magnetization behavior of the sublattices. The $NiCl_2$ crystals have a symmetry of the type D_{3d}^5. Judging from measurements of the magnetic susceptibility[3] and from the presence in these crystals of a practically gapless low-frequency branch of antiferromagnetic resonance (AFMR),[4,5] the antiferromagnetism vector in them lies in the basal plane of the crystal. Kostryukova and Kashirskaya[5] have shown also that there is an insignificant anisotropy of sixth order in the basal plane.

Kanamori[6] and Yoshimori[7] considered the spin-wave theory of magnetic properties of $FeCl_2$, $NiCl_2$, and $CoCl_2$ crystals. Yoshimori,[7] who considered in greatest detail the properties of $NiCl_2$, used a semicontinuous model, i.e., the spin density was assumed to be continuously distributed in the basal plane (naturally, the anisotropy in the basal plane was disregarded in this case). He obtained expressions for the energy of the spin-wave branches in the crystal and asymptotic expressions for the sublattice magnetization.

The behavior of EPR near the point of transition to the antiferromagnetic state (T_N = 49.6°K) was investigated in [8]. It was shown that the EPR line width agrees well with the notion of fluctuations of the spin short-range order, and the anisotropy of the EPR spectrum is due entirely to the contribution of the magnetic dipole-dipole interaction.

For the purpose of a more detailed study of the magnetic properties of this crystal, we investigated the high-frequency AFMR branch in $NiCl_2$ in a zero external magnetic field. The results of the investigations are the subject of the present article.

2. APPARATUS

The high-frequency AFMR was investigated by us in the frequency interval 78.5–52 GHz at temperatures from 4.2 to 40°K. The experimental setup used for the registration of the AFMR is shown in Fig. 1. Samples of single-crystal $NiCl_2$ in the form of parallelepipeds or disks were glued to a short-circuiting plunger in such a way that the magnetic microwave field was applied in the basal plane of the sample. ($H_{UHF} \perp C_3$). A tube containing a semiconducting thermistor was soldered to the outside of a waveguide, made of internally-silvered German silver tubing, alongside the location of the sample. A bifilar heating coil (R ≈ 150 ohm, not shown in Fig. 1) was wound on the end part of the waveguide and on the tube with the thermistor and was covered from the outside by a heat-insulating sheath of teflon film with layers of cotton. The German-silver waveguide with the sample, thermistor, heating coil, and heat-insulating sheath were mounted on the axis of a sealed tube filled with heat-exchange helium gas.

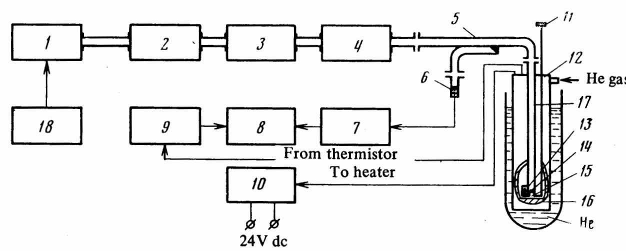


FIG. 1. Block diagram of setup for the observation of AFMR: 1–klystron, 2–attenuator, 3–wave meter, 4–matching device, 5–directional coupler, 6–detector, 7–F-116/2, 8–x-y recorder; 9–bridge, 10–rheostat, 11–rotating device for the sample, 12–sealed insert in cryostat, 13–thermistor, 14–sample, 15–plunger, 16–thermostating packing, 17–round waveguide, 18–klystron power supply.

Such a construction ensured the possibility of establishing any value of temperature in the range 4.3–55°K. The good thermal contact between the thermistor and the sample should have ensured equality of the temperatures of the sample and the thermistor, as was verified by the reproducibility of the AFMR signal under different heating regimes and at different pressures of the heat-exchange helium.

After emerging from the cryostat, the round waveguide was adapted to a rectangular one. The frequency was measured with a resonant wave meter accurate to ±10 MHz.

The microwave power reflected from the short-circuited plunger with the sample passed through a directional coupler with a cross-talk attenuation ~10 dB to a crystal detector. The detector current, amplified by an F-116/2 photogalvanic amplifier, was fed to the y coordinate of a PDS-021 x-y plotter.

The x-coordinate of the PDS-021 was connected to the unbalance voltage of the bridge, to the input of which the thermistor was connected. The voltage of the battery supplying the bridge was chosen such that the measuring current did not heat the thermistor. By setting the bridge to definite values of the resistance, we obtained several overlapping measurement bands. The heater was energized by voltage from a manual rheostat, and the rate of heating in the region of greatest interest was slow enough to reproduce the absorption lines. The AFMR was measured in the following manner: a definite frequency of the klystron generator was set (several klystrons of different types were used to cover the entire frequency range), after which the microwave section was matched at a temperature far from resonance. The entire temperature interval was then covered smoothly and the AFMR absorption line was recorded on the automatic plotter in the form of a decrease of the reflected power.

The fact that the klystron was not frequency-stabilized led to a mismatch of the microwave section and in final analysis to errors in the determination of the temperature at which the absorption of a given frequency is maximal. The same effect resulted from the impossibility of separating the absorption from the dispersion in this particular scheme.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The measurements were made on several samples with different dimensions, different geometric shapes and quality (cracks and strata), since the samples were grown by sublimation and from the melt. Differences exceeding the experimental errors were observed in the frequency of the AFMR at low temperatures in different samples. On the low-temperature side, in addition to the main absorption line, there were observed in practically all the samples additional lines similar to the additional lines in MnF_2.[10] One of the additional lines was present in the spectra of almost all the samples and the others did not repeat regularly. Some of these lines were obviously of apparatus origin and depended on the tuning conditions of the microwave section. In the "high-temperature" region (T ~ 25–35°K) there were no additional lines, but a temperature-hysteresis effect was observed. An effect analogous to temperature hysteresis was noted for $NiCl_2$ in [9]. The magnitude of the temperature hysteresis exceeded the possible contribution due to the difference between the temperatures of the sample and the thermistor. The results of the measurements are shown in Fig. 2, which gives data on the temperature dependence of the AFMR frequency of the fundamental line for several samples and a curve for the repeating additional line. In the high-temperature region, it shows points obtained when the sample was heated and when the sample was cooled after superheating to a temperature above 50°K ($> T_N$). When the sample was cooled from another lower value

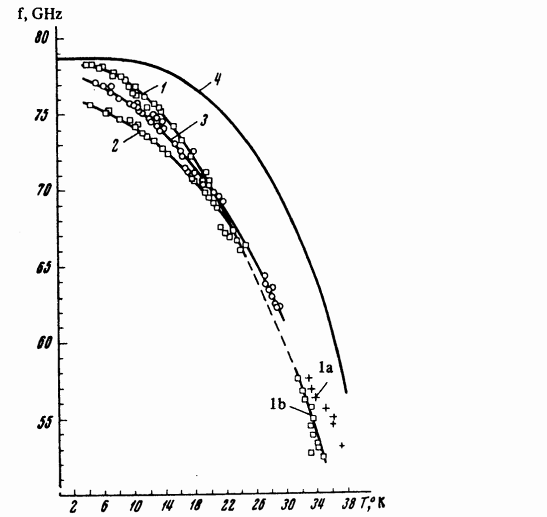
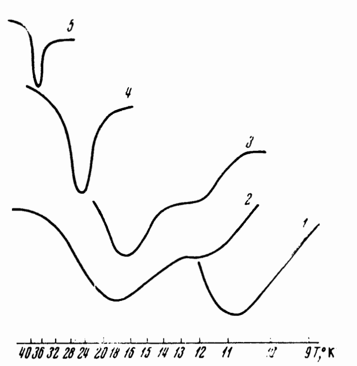


FIG. 2. Temperature dependence of the AFMR frequency: 1—fundamental line for sample No. 1 and sample No. 3; 1a—heating of sample; 1b—cooling of sample from T = 50°K; 2—additional line for sample No. 1; 3—fundamental line of sample No. 2; 4—dependence of the reduced spontaneous magnetization on the temperature in the molecular-field approximation.

FIG. 3. Plots of AFMR signals 1–76 230 MHz—sample No. 1; 2–73 560 MHz—sample No. 1, 3–74 560 MHz—sample No. 3; 4–67 110 MHz—sample No. 2; 5–54 740 MHz—sample No. 1.



of the temperature, one could obtain a curve for practically any of the intermediate points. The rather considerable scatter of the points is due to the large width of the AFMR line, to apparatus imperfections, and also to the fact that the additional lines, superimposed on the fundamental line, cause an apparent shift of the latter. Several typical AFMR plots obtained by us are shown in Fig. 3.

The AFMR line width could be determined from the width of the lines in terms of temperature and from the slope of the $\nu(T)$ curves. In view of the poor accuracy with which the width is determined in this manner, we do not present here a plot of $\Delta\nu(T)$. We note only that the line width increases with increasing temperature from 1200 ± 200 MHz at 8°K to 4000 ± 700 MHz at 32°K.

According to [7], the frequency of the high-frequency AFMR at T = 0 should equal

$$h\nu(0) = 2(BD)^{1/2}, \tag{1}$$

where $B = J_2 z_2$, J_2 is the exchange integral between the nearest nickel ions in the neighboring layers, $H_{ex} = -2 \sum_{i>j} J_{ij} S_i S_j$, $z_2 = 6$ is the number of nearest ions in the neighboring layers, and D is the anisotropy constant at the term of the form $DS^2_{z_i}$ in the spin hamiltonian.

According to estimates by Kanamori,[6] the measured values of $\chi_\perp$ in [3] lead to $B \simeq 3.5$ cm^{-1}.

As seen from Fig. 2, extrapolation of the $\nu(T)$ curves for different samples to T = 0 give different values of $\nu(0)$, from 78 500 to 75 200 MHz. Accordingly, the value of D can range from 0.488 to 0.448 cm^{-1}. Taking into account the approximate character of B, we must assume $D \approx 0.5$ cm^{-1}. Kanamori estimated the effective dipole-dipole contribution to the value of D. According to his calculations, the anisotropy due to the dipole interaction makes a contribution $D_{dip} = 0.5$ cm^{-1}. Consequently, the anisotropy field, which is effective in the high-frequency branch of the antiferromagnetic resonance, just like the anisotropy of the EPR of a crystal near the Neel temperature,[8] can be explained practically fully as being due to the dipole-dipole interaction.

The appearance of the slight anisotropy of sixth order in the basal plane[5] can likewise be attributed to dipole-dipole interaction.

The temperature dependence of the anisotropy field connected with the dipole-dipole interaction, as well as that of the exchange field, should be proportional to the sublattice magnetization, and consequently the temperature dependence of the AFMR frequency should in our case be proportional to M(T). As seen from Fig. 2, the temperature dependence of the AFMR frequency does not correspond to the temperature dependence of the reduced magnetization of the sublattice in the molecular-field model (curve 4).

According to Yoshimori's calculation,[7] the following relation should be satisfied for the temperature dependence M(T) near $T \ll 4$°K

$$M(0) - M(T) \sim T^2, \tag{2}$$

and for the region $T \gg 10$°K

$$M(0) - M(T) \sim T \ln [kT / (2B + {}^1/_2 D)]. \tag{2a}$$

Expression (2a) is connected with the properties of the two-dimensional ferromagnetic structure. (This relation is close to linear.) The temperature region of our measurements does not correspond to the region of applicability of (2) and (2a), but (2a) is the high-temperature expansion of a relation of the type

$$M(0) - M(T) = -cT \ln (1 - e^{\Delta/kT}), \tag{3}$$

which was used by Narat[2] to approximate the behavior of M(T), which is connected with the two-dimensional ferromagnetic sublattice in $CrCl_3$.

The temperature dependence obtained by us for the AFMR frequency can be satisfactorily described by a relation of the type (3), but the differences in the low-temperature parts of the curves (Fig. 2), and also the large scatter of the experimental points, do not make it possible to determine the value of Δ with sufficient accuracy. The point is that for different values it is possible to choose the proportionality coefficient in (3) in such a way that the calculated curves lie in the region of the scatter of the experimental points. We find the limits of the possible scatter of the values of Δ by determining the coefficient of proportionality from the experimental points at two values of the temperature and then calculating the value of the frequency as $T \to 0$. It is possible to obtain the values of $\nu(0)$ within the limits of the scatter of the experimental points for all values of Δ/k in the range from 8 to 20°K. For example, if we determine c from the values of the AFMR frequency at 20 and 35°K, then the corresponding value of $\nu(0)$ for $\Delta/k = 10$ and 20°K will be 79.7 and 77.1 GHz, and the calculated curves for all values of the temperature will pass within the limits of the scatter of the experimental points. The values of B and D, obtained from extrapolation of the AFMR frequency to T = 0, lead to $\Delta/k \approx 10$°K, which agrees with the obtained limits of the possible value of Δ from $\nu_{AFMR}(T)$. Attempts were made to explain the additional low-frequency lines and the variation of $\nu(0)$ from sample to sample. To this end, an investigation was made of the dependence of the AFMR frequency on the rotation of the microwave magnetic field in the basal plane and on the angle between the microwave magnetic field and the C_3 axis of the crystal (this angle ranged from 60 to 90°). We also sought a correlation between the shape of the sample and the value of $\nu(0)$. None of these tests led to affirmative results. Apparently the most probable cause of the scatter of $\nu(0)$ and of the appearance of additional low-frequency lines is the imperfection of the employed samples (cracks and inclusions of hydrated $NiCl_2$). This assumption agrees with the fact that $\nu(0)$ was largest for the most perfect samples, for which the number of additional lines was minimal.

A discussion of the observed temperature hysteresis of the AFMR frequency in the high-temperature part of the curve cannot be carried out, in view of the insufficient accuracy of this experiment.

A clarification of the noted features of the AFMR in $NiCl_2$, and also an investigation of the dependence of the AFMR on the external magnetic field for the purpose of refining the values of the exchange field and the anisotropy field is an interesting problem for further experiments.

The authors are grateful to L. I. Zarubin (Semiconductor Institute, Ukrainian Academy of Sciences) for supplying the thermistor and to L. A. Kupriyanova, V. S. Frolova, and A. A. Motuz for supplying the samples.

[1] L. D. Landau, Sow. Phys. **4**, 675 (1933).

[2] A. Narat, Phys. Rev. **131**, 1929 (1963).

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

[4] M. O. Kostryukova and I. L. Skvortsova, Zh. Eksp. Teor. Fiz. **47**, 2069 (1964) [Sov. Phys.-JETP **20**, 1390 (1965)].

[5] M. O. Kostryukova and L. M. Kashirskaya, ZhETF Pis. Red. **9**, 400 (1969) [JETP Lett. **9**, 238 (1969)].

[6] J. Kanamori, Progr. Theor. Phys. **20**, 890 (1958).

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

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

[9] J. W. Leech and A. J. Manuel, Proc. Phys. Soc. **B69**, 210 (1956).

[10] F. Johnson and A. Nethercot, Phys. Rev. **114**, 705 (1959).

Translated by J. G. Adashko
152