ANTIFERROMAGNETIC RESONANCE IN $NiCO_3$ *AND INVESTIGATION OF ANTIFERROMAGNETIC ORDERING IN THE VICINITY OF THE NEEL POINT*

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Submitted July 7, 1969

Zh. Eksp. Teor. Fiz. 57, 1967–1972 (December, 1969)

The low frequency branch of antiferromagnetic resonance of $NiCO_3$ is investigated at frequencies between 50 and 190 GHz. At 4.2°K the dependence of the resonance frequency ν on magnetic field H can be satisfactorily described by the formula $(\nu/\gamma)^2 = H(H + H_D) + H_\Delta^2$ with the following values of the constants: $\gamma = 3.07 \pm 0.1$ GHz/kOe, $H_D = 120 \pm 6$ kOe, and $H_\Delta^2 = 55.6 \pm 9.2$ kOe^2. The dependence of the resonance frequency and width of the resonance curve ΔH on temperature is investigated. For $T > T_N$ the resonance line continues to shift with the temperature. The explanation of this is that the resonance observed is due to collective motion of spins which, under the action of the magnetic field, produce an antiferromagnetic structure.

1. INTRODUCTION

NICKEL carbonate is isomorphous to the well investigated carbonates of manganese and cobalt, which are antiferromagnets with weak ferromagnetism. However, in view of the difficulties in synthesizing and growing single crystals of $NiCO_3$, its properties have not been well investigated until recently. Bizette and Tsai[1] observed at temperatures 4 and 20°K a rather appreciable ferromagnetic moment in polycrystalline samples of $NiCO_3$. Alikhanov[2] has shown that below 25°K there is produced in $NiCO_3$ an antiferromagnetic structure which admits, according to the Dzyaloshinskiĭ theorem[3], the existence of weak ferromagnetism. Kalinkina[4] observed a maximum on the heat-capacity curve at T = 22.2°K. The purpose of the present work was to study, in a wide range of frequencies the temperatures, the low-frequency branch of antiferromagnetic resonance (AFMR) in $NiCO_3$ and to observe antiferromagnetic ordering by the field above T_N.

2. MEASUREMENT METHOD AND SAMPLES

The AFMR in $NiCO_3$ was investigated with a millimeter-band radio spectrometer[5]. The measurements were performed in the frequency range from 50 to 190 GHz.

The $NiCO_3$ samples were placed in a short-circuited segment of a copper waveguide with a cross section 3.6 × 1.8 mm, making it possible to carry out the measurements in a wide frequency range for the same setting of the investigated sample. The reflected signal was detected with a silicon detector and was fed after amplification to the Y coordinate of an automatic recording potentiometer PDS-021. The voltage$_{\mathrm{GHz}}{}^{2}$ied to the X-coordinate of the potentiometer was proportional to the current in the superconducting solenoid. The resonant-absorption line was recorded at fixed frequencies while the magnetic field was varied continuously. The microwave signal frequency was measured with standard wave meters accurate to 0.02%.

The magnetic field was produced by a superconducting solenoid made of 65 BT wire with a maximum field value 50 kOe. The magnetic field of the solenoid was calibrated by antiferromagnetic resonance in $MnCO_3$. The field measurement accuracy was determined mainly by the errors of the automatic potentiometer and amounted to ±100 Oe over the entire range.

To obtain temperatures above 4.2°K, a vacuum cryostat was used[6]. The temperature was measured with a carbon resistance thermometer calibrated at the points 4.2, 14, 20.39, and 27.25°K. The accuracy with which the temperature was measured and maintained with not worse than 0.2°C.

The $NiCO_3$ crystals were produced by A. A. Shternberg by a hydrothermal method at the Crystallography Institute of the USSR Academy of Sciences. They were rhombohedral and green in color. The principal measurements were made on one of the larger crystals, the principal diagonal of which was approximately 0.3 mm. The samples were secured with BF-4 adhesive in such a way that the static field was in the basal plane of the crystal accurate to 3°.

3. RESULTS OF EXPERIMENT

1. At a temperature of 4.2°K, we investigated in detail the dependence of the resonant-absorption frequency on the applied static field H (Fig. 1). It was established that the value of the resonant field does not depend on the field orientation in the basal plane. The results of the experiment were reduced by least squares with the aid of an M-20 computer. It turned out that they are well approximated by the expression

$$\nu^2 = a_0 + a_1 H + a_2 H^2 \quad (1)$$

with the following coefficients:

$a_0 = 529 \pm 88$ GHz^2, $a_1 = 1142 \pm 15$ GHz^2/kOe, $a_2 = 9.46 \pm 0.55$ GHz^2/kOe^2.

2. The resonant-absorption line for single crystals was symmetrical in form. At a temperature T = 4.2°K and a frequency 130 GHz, its half-width was $\Delta H \approx 3$ kOe.

In preliminary experiments, the resonance was observed on a small-crystallite sample synthesized by

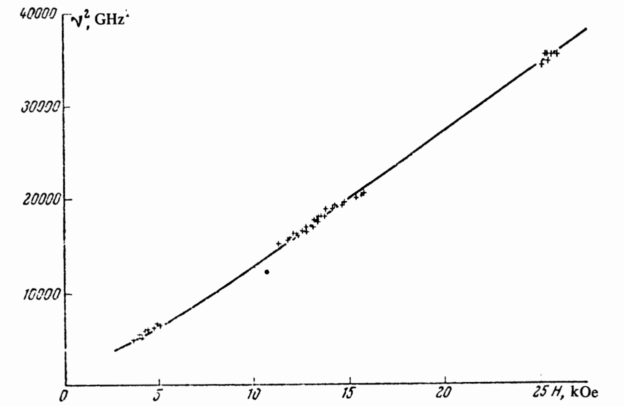

FIG. 1. Dependence of the antiferromagnetic resonance frequency for $NiCO_3$ on the static magnetic field at T = 4.2°K.

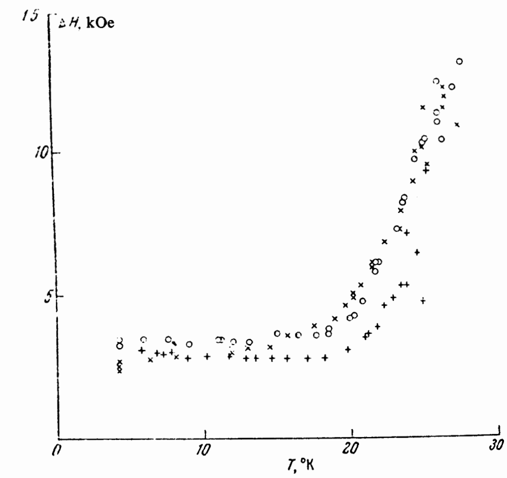

FIG. 2. Dependence of the resonant absorption line half-width on the temperature at 161 GHz (X), 130.7 GHz (O), and 99.7 GHz (+).

Yu. F. Orekhov, the crystallites of which oriented themselves in the field. In this case the width of the resonance line was also ≈ 3 kOe. The line broadened with increasing temperature (Fig. 2). No investigation was made of the influence of the method of securing and orienting the sample on the value of ΔH.

3. For several frequencies we investigated the temperature dependence of the resonant field. The results of the experiment are shown in Fig. 3. The upper limit of the temperature at which the measurements were performed at each of the frequencies was determined by the broadening of the resonance-absorption line. The temperature of the transition into the antiferromagnetic states for $NiCO_3$, according to recent static measurements of Kreĭnes and Shal'nikova[7], is $T_N = 25.0$°K. This agrees with an estimate given by Alikhanov[2], and is somewhat higher than the value obtained from measurements of the specific heat[4]. It is seen from Fig. 4 that above this temperature the value of the resonant field continues to increase strongly. But, at $T > T_N$, the resonant absorption observed in $NiCN_3$ is not the usual paramagnetic resonance.

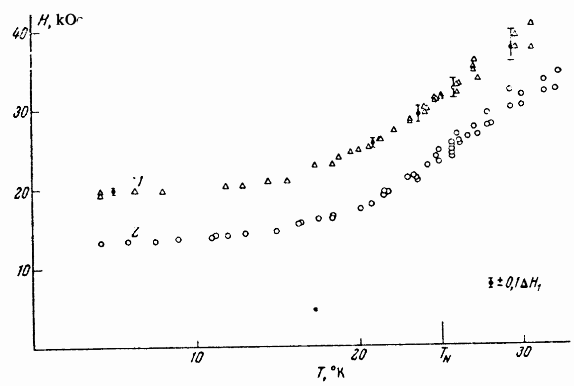

FIG. 3. Temperature dependence of the resonant field at 161 GHz (1) and 130 GHz (2).

4. DISCUSSION OF RESULTS

The theoretical dependence of the AFMR frequency on the magnetic field H for rhombohedral crystals (group D_{3d}^6) in the case of an isotropic g-factor was obtained by Borovik-Romanov[8] and Turov[9]. For the low-frequency branch of the AFMR spectrum, which was investigated in the paper this dependence is given by

$$(\nu/\gamma)^2 = H(H + H_D), \tag{2}$$

where γ is the gyromagnetic ratio and H_D is the Dzyaloshinskiĭ field, which can be determined independently from static measurements. The formula (1) obtained by us can be reconciled with formula (2) by assuming that an energy gap H_Δ^2 is present in the low-frequency branch of the AFMR. Such an energy gap can be the result either of residual stresses in the crystal, or of magnetostriction[10]. We did not, however, investigate the nature of H_Δ^2. Comparing the experimental data with the theoretical formula

$$(\nu/\gamma)^2 = H(H + H_D) + H_\Delta^2, \tag{3}$$

we obtain the following values for the constants:

$\gamma = 3.07 \pm 0.09$ GHz/kOe $H_D = 120 \pm 6$ kOe, $H_\Delta^2 = 55.6 \pm 9.2$ kOe^2.

It must be emphasized that this is the largest value of H_D in the series of antiferromagnetic carbonates.

As shown by Borovik-Romanov and Ozhogin[11], for antiferromagnetic structures admitting a tilting of the sublattices, antiferromagnetic ordering can be induced above the Neel point in a strong magnetic field. Allowance for this effect explains the anomalies of the susceptibility near T_N in $MnTO_3$, $CoCO_3$, $NiCO_3$, NiF_2, and other antiferromagnets. With the aid of this effect it is possible to explain also the anomalous temperature dependence of the resonant field observed by us at $T > T_N$.

In his dissertation, Ozhogin[12] considered the influence of inducing the magnetic ordering by a field on the AFMR, and he showed that the frequency is determined as before by formula (2), in which the field $H_D = \beta l$ (l—antiferromagnetic moment) should be determined by the equation

$$BCl^3 + B\lambda[T - T_N]l - \beta H = 0, \tag{4}$$

which is obtained by minimizing the thermodynamic potential near T_N

$$\Phi = \tfrac{1}{2}Al^2 + \tfrac{1}{2}Bm^2 + \tfrac{1}{2}al_z^2 - \beta(l_y m_x - l_x m_y) + \tfrac{1}{4}Cl^4 - mH, \quad A = \lambda(T - T_N). \tag{5}$$

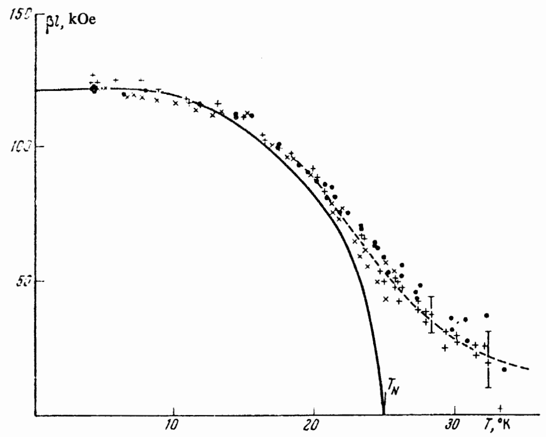

FIG. 4. Temperature dependence of the antiferromagnetic moment of 161 GHz (●) 130.7 GHz (+), and 99.7 GHz (X). Curves – theoretical dependences.

It is seen from (4) that if $T > T_N$ but $H \neq 0$, then l, and consequently also H_D, differs from zero and depend on H and T.

From the experimental data given in Fig. 3, neglecting the presence of the energy gap (which leads to an error not larger than 5%), we have calculated the temperature dependence of H_D. The results of the calculation are shown in Fig. 4. The solid line shows the Brillouin curve for s = 1, calculated for $T_N = 25°K$. The dashed line shows the theoretical curve obtained from formulas (3) and (4), with the following values of the constants: $\beta^4/BC = 5.4 \times 10^3$, $\beta^2\lambda/C = 1.2 \times 10^3$, and $\nu = 130$ GHz. It is seen from the figure that within the limits of errors the experimental points coincide well with the dashed curve.

Thus, in $NiCO_3$ at temperatures above T_N, the observed resonance is due to the collective motion of the spins that make up the antiferromagnetic structure under the influence of the field.

I am sincerely grateful to P. L. Kapitza for continuous interest in the work, to A. S. Borovik-Romanov for fruitful discussions, to A. A. Shternberg and Yu. F. Orekhov for supplying the samples, and to K. I. Rassokhin for help with the experiments.

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Translated by J. G. Adashko
227