

ELECTRON RESONANCE IN ANTIFERROMAGNETIC NiCl_2

M. O. KOSTRYUKOVA and I. L. SKVORTSOVA

Moscow State University

Submitted to JETP editor June 29, 1964

J. Exptl. Theoret. Phys. (U.S.S.R.) **47**, 2069-2072 (December, 1964)

Electron resonance in NiCl_2 is investigated at a frequency of 9.2 Gc/s between 300 and 4.2°K. Resonance absorption in NiCl_2 at temperatures below the antiferromagnetic transformation point is connected with the existence of a low-frequency antiferromagnetic resonance branch in nickel chloride.

ANHYDROUS nickel chloride NiCl_2 belongs to the class of layered antiferromagnets, the antiferromagnetism of which was first predicted by Landau^[1].

NiCl_2 has a layered crystalline structure of the type D_{3d}^5 . The nickel ions are arranged in layers which alternate with the halide layer. The principal symmetry axis C_3 is perpendicular to the layers. The point of antiferromagnetic transformation of NiCl_2 is 52.3°K according to calorimetric data^[2,3], and the susceptibility measured in a field ~ 3 kOe has a maximum at $T = 51^\circ\text{K}$ ^[4].

Neutron diffraction investigations^[5] have shown that some anhydrous halides of the iron group have magnetic ordering, wherein the magnetization of the sublattices lies in the basal plane of the crystal, i.e., it is directed perpendicular to the principal axis C_3 . Inside each layer, the spins are ordered ferromagnetically, while in the neighboring layers they are mutually antiparallel.

For antiferromagnetic NiCl_2 , there are no neutron diffraction data and it is possible to judge the orientation of the spins only from the results of investigations of the magnetic susceptibility of single crystal NiCl_2 ^[4]. NiCl_2 is completely isotropic both above and below the transition point. In this connection, we can assume that the spins lie in the basal plane, the anisotropy in which is small and therefore the sublattice magnetization is established perpendicular to the field for arbitrary field directions.

For ordinary uniaxial antiferromagnets with compensated antiferromagnetism, in which the magnetization of the sublattices is perpendicular to the principal axis, the spectrum of the antiferromagnetic resonance, as shown by calculations, has a low-frequency branch whose frequency is determined by the magnitude of the external field^[6].

The low-frequency branch of the antiferromagnetic resonance, which was theoretically predicted^[7,8] for weak-ferromagnetism rhombohedral

antiferromagnets of the MnCO_3 type, in which the sublattice magnetization is perpendicular to the principal axis, was recently observed experimentally^[9,10].

Proposing to observe the low frequency branch in the spectrum of layered antiferromagnets, we have undertaken an investigation of antiferromagnetic resonance in NiCl_2 .

The NiCl_2 single crystal was grown from a melt of anhydrous nickel chloride by passing a quartz ampoule containing liquid NiCl_2 slowly through a heated oven. The anhydrous substance was obtained from $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ by drying in vacuum at $\sim 200^\circ\text{C}$ with subsequent sublimation at $\sim 1000^\circ\text{C}$.

The investigated sample in the form of an oval disc with transverse dimensions 3×5 mm and thickness ~ 1 mm was split off the grown single crystal. The plane of the disc coincided with the basal plane of the crystal. The sample was transparent and had good layer delineation. Since NiCl_2 absorbs water, the single-crystal sample was placed in a thin-wall glass ampoule filled with heat-exchange helium and sealed off.

The absorption measurements were made at 9.2 Gc/s in a rectangular cavity tuned to the H_{101} mode. The klystron frequency was automatically adjusted to the resonant frequency of the cavity. The constant magnetic field and the high-frequency field were mutually perpendicular during the measurements. The absorption in the sample was registered by determining the change in the signal from the detector, and the line width was obtained by plotting the derivative of the absorption curve. In the latter case, low-frequency modulation of the magnetic field was used, and the alternating signal from the detector was amplified with a narrow band amplifier and measured with a cathode voltmeter.

The absorption in NiCl_2 was investigated by us

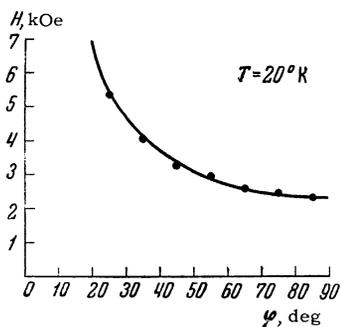


FIG. 1

at room temperatures, at temperatures obtained by pumping on nitrogen and hydrogen vapor, and also at 4.2°K.

From the position of the resonant line at room temperature we estimated the *g*-value which was found to be isotropic and equal to 2.23. The paramagnetic absorption line at *t* = 300°K is sufficiently symmetrical and its width is 720 Oe. The paramagnetic line barely shifts when the temperature is reduced from 300 to 53°K, but on approaching the Curie point the line broadens noticeably. The *g*-value we obtained agrees with the results obtained with powdered NiCl₂ by Leech and Manuel^[11], and the line width which we observed in the single crystal at 300°K is approximately 1.6 times as small as for the powdered sample.

Measurements of absorption in antiferromagnetic NiCl₂ were made by us between 4 and 20°K. We observed a sharply pronounced resonance absorption, and the magnitude of the resonant field depends in this case on the orientation of the field relative to the crystal axis. This dependence is represented for *T* = 20°K in Fig. 1. It can be seen that the experimental points fit well on the curve (solid line in the figure), which is described by the formula

$$H_{\varphi} = H_{\perp} / \sin \varphi, \quad (1)$$

where H_{\perp} —value of the resonant field applied to the basal plane and φ —angle between the *c* axis and the direction of the field. Thus, when the resonant line is excited, the effective field component is the one lying in the basal plane. The resonance absorption lines for different temperatures below 20°, for a field oriented at an angle $\varphi = 50^{\circ}$ relative to the principal axis, are shown in Fig. 2. The ordinates of Fig. 2 represent the ratio of the signal from the detector for various values of *H* to the signal at the maximum employed magnetic field, of the order of 6800 Oe. The dashed curve on the same figure shows the paramagnetic absorption line near the Curie point at *T* = 53°K.

Figure 3 shows, in coordinates $H_{\text{res}}/(\omega/\gamma)$ and

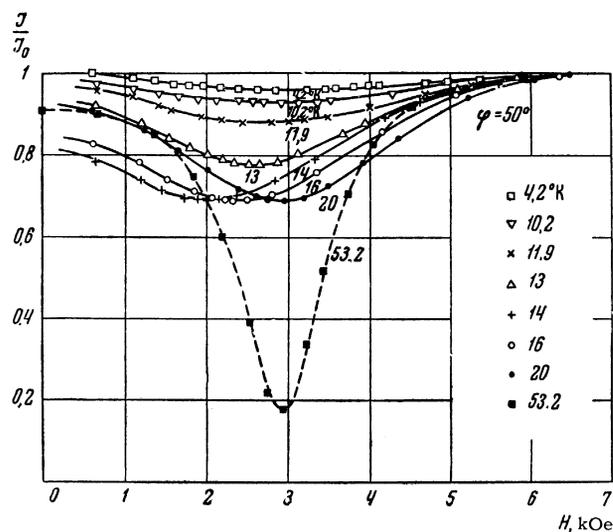


FIG. 2

T, the magnitude of the resonant field as a function of the temperature for $\varphi = 50^{\circ}$. At this orientation of the sample in the field (and analogously, for other orientations for which φ is close to 90°), resonance is observed at liquid-hydrogen temperatures in fields for which $H_{\text{res}}/(\omega/\gamma)$ is of the order of unity. The resonant field, however, varies with the temperature: the field first decreases in the interval from 20 to 14°K, and with further decrease in temperature to $\sim 10^{\circ}$ K it increases sharply. We see also (Fig. 2) that the height of the maximum of the resonance line does not change between 20 and 14°K, and then decreases rapidly (to almost one-fifth at 10°K). Below 10°K, the resonance line is not very pronounced.

The integral intensity of absorption at liquid-hydrogen temperatures (from 20 to 14°K) is large and absorption in antiferromagnetic NiCl₂ cannot be attributed to the influence of the impurity. The good agreement between the experimental data and the theoretical dependence of the position of the antiferromagnetic resonance line on the field orientation (1) allows us to assume, apparently, that in NiCl₂ at hydrogen temperatures we actually observe the low-frequency branch of antiferromag-

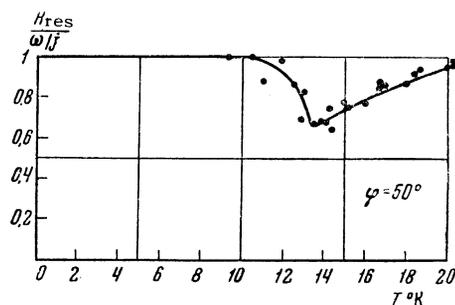


FIG. 3

netic resonance, the frequency of which is of the order of γH , when the field lies in the basal plane.

The vanishing of the resonant absorption below 10°K can be attributed to the presence in NiCl_2 of a phase transformation into a different antiferromagnetic state. This is apparently accompanied by a change in the picture of magnetic ordering. A similar transformation was observed, for example, in antiferromagnetic MnCl_2 ^[12].

In conclusion we thank A. I. Shal'nikov for interest in the work and take the opportunity to thank A. S. Borovik-Romanov for interest in the work and a discussion of the results and L. A. Prozorov for valuable methodological advice.

¹L. D. Landau, *Sov. Phys.* **4**, 675 (1933).

²Trapeznikov, Shubnikov, and Milyutin, *Sov. Phys.* **9**, 237 (1936).

³R. H. Busey and W. F. Giaque, *J. Am. Chem. Soc.* **74**, 4443 (1952).

⁴Bizette, Terrier, and Tsai, *Compt. rend.* **243**, 1295 (1956).

⁵Wilkinson, Cable, Wollan, and Koehler, *Phys. Rev.* **113**, 497 (1959).

⁶E. A. Turov, *Fizicheskie svoïstva magnitoporyadochennykh kristallov* (Physical Properties of Magnetically Ordered Crystals), AN SSSR, 1963.

⁷A. S. Borovik-Romanov, *JETP* **36**, 766 (1959), *Soviet Phys. JETP* **9**, 539 (1959).

⁸E. A. Turov, *JETP* **36**, 1254 (1959), *Soviet Phys. JETP* **9**, 890 (1959).

⁹Borovik-Romanov, Kreïnes, and Prozorova, *JETP* **45**, 64 (1963), *Soviet Phys. JETP* **18**, 46 (1964).

¹⁰M. Date, *J. Phys. Soc. Japan* **15**, 2251 (1960).

¹¹J. W. Leech and A. J. Manuel, *Proc. Phys. Soc.* **B69**, 210 (1956).

¹²D. H. Douglass, Jr. and M. W. P. Strandberg, *Physica* **27**, 1 (1961).

Translated by J. G. Adashko
302