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# Antiferromagnetism of $NiCO_3$

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The investigations carried out by the author confirmed the existence of antiferromagnetism in $NiCO_3$ as observed earlier by H. Bizette and B. Tsai. The observation shows a Néel temperature about 25°K. Reflections (111) and (100) appear simultaneously in diffraction patterns obtained at low temperatures. In accord with the theory of Dzyaloshinsky, this indicates the presence of weak ferromagnetism in this dielectrics. Nevertheless a quantitative estimate of the value of ferromagnetic moment is difficult because of smallness of the observed effect.

Among the anhydrous carbonates of the iron family (Mn, Fe, Co and Ni) that possess antiferromagnetic properties at low temperatures, $NiCO_3$ is distinguished by a number of specific qualities which are of great interest in the study of the magnetism of carbonates.

Anhydrous $NiCO_3$ is not found in minerals and was first synthesized by Senarmon[1] in the form of a whitish green microcrystalline powder. Much later, $NiCO_3$ was obtained successfully by Saint Leon Langles[2], who isolated two modifications of the carbonate (green and yellow) under different thermal conditions. The isomorphic modifications obtained, the lattice constants of which differ by 0.5%, are extremely stable and practically do not dissolve in boiling aqua regia.

An investigation of the magnetic properties of the specimens of $NiCO_3$ synthesized by Langles was carried out by Bizette and Tsai[3]. It showed the complex character of the magnetic properties observed in $NiCO_3$. The susceptibility was measured over a broad temperature range from 290° to 4°K. Down to 60°K, the susceptibility of both modifications follows the Curie-Weiss law. Below 40°K, it experiences a break and deviates from the linear law. Here, the magnetization is not proportional to the field and the carbonate exhibits typical ferromagnetic properties. At 20° and 4°K, hysteresis loops are observed, and saturation was not attained for the yellow modification in a 24,500 oersted field.

On the whole, the results of magnetic measurements give a picture of antiferromagnetism similar to that observed in $MnCO_3$, $CoCO_3$, $NiF_2$ and other antiferromagnetics with weak ferromagnetism, but with a significantly more developed ferromagnetic accompaniment. The magnitude of the ferromagnetic moment estimated by extrapolation to $H=0$ of the magnetization curve is equal to 1550 CGSM/mole and 2100 CGSM/mole for the green and yellow modifications, respectively. This is 14% and 19% of the saturation moment of the ion $Ni^{++}$—11,100 CGSM/mole (on the condition that the $q$-factor=2). This magnitude of ferromagnetic moment is a record for the carbonates of the iron family.

In connection with the diversity of anomalous properties exhibited by $NiCO_3$, it is of interest to make a neutron diffraction study of it with the purpose of establishing the character of antiferromagnetism in this carbonate, inasmuch as earlier studies of $CoCO_3$[4] had revealed a new type of arrangement of the moments sublattice, and also in order to observe the weak ferromagnetism by an independent method that would permit investigating spontaneous ferromagnetism in the absence of an external field.

In the present case, a study was made of light-green microcrystalline powder $NiCO_3$ prepared by the Langles method by the Department of the Technology of Materials, IPP.

The experimental conditions practically did not differ from those earlier described in investigations of other carbonates[5].

Two series of measurements were carried out on samples of 2.6 gm and 40 gm at various temperatures. The neutron-diffraction pattern on a large specimen at the temperature of liquid helium is shown in Fig. 1. Just as in the case of $MnCO_3$ and $CoCO_3$, at

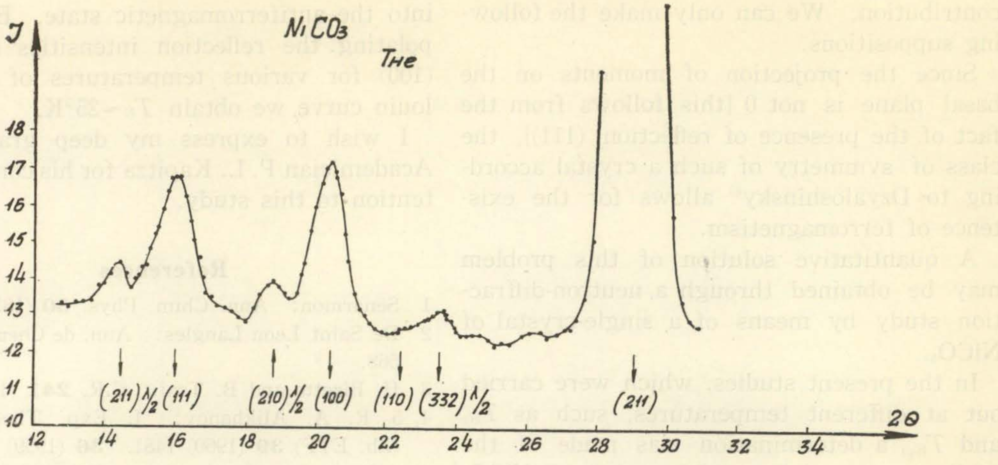


Fig. 1.

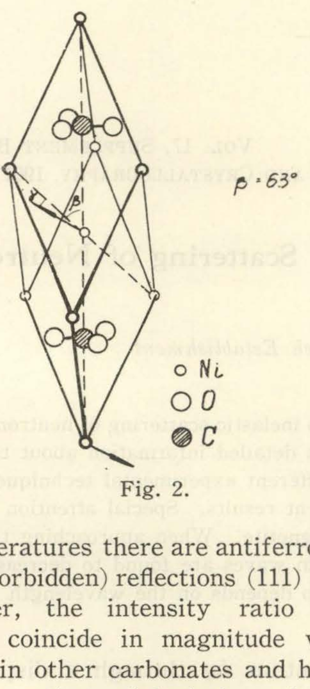


Fig. 2.

low temperatures there are antiferromagnetic (nuclear-forbidden) reflections (111) and (100).

However, the intensity ratio $I_{(100)}/I_{(111)}$ does not coincide in magnitude with that observed in other carbonates and has an intermediate value. Calculation of the angle between the moments of the sublattices and the rhombohedral axis, carried out on the basis of the ratio obtained, yields a value of $\beta=63°$ (Fig. 2), which is closest to that observed in $CoCO_3$.

Thus, in the series of antiferromagnetics with a $CoCO_3$ type structure, for which the direction of moments of the sublattices between the rhombohedral axis and the basal plane is characteristic, there is also the green modification of $NiCO_3$.

On the whole, the distribution of angles $\beta\pm10\%$ in isomorphic carbonates is at present as follows:

| Ion | $Fe^{++}$ | $Co^{++}$ | $Ni^{++}$ (green) | $Mn^{++}$ |
|---|---|---|---|---|
| $\beta$ | 0° | 46° | 63° | 90° |

Clarification of the nature of such diversity of antiferromagnetic structures of the carbonates, apparently, requires a study of the ground state of each given ion and the degree of participation of the orbital momentum in the formation of the total momentum of the ion.

Another "anomaly" exhibited by $NiCO_3$, as compared with the other carbonates, is that the nuclear structural factor of reflection (110) is extremely small (it is approximately 0.001 of the reflection (211)). This makes a favourable situation for observing the ferromagnetic contribution when the temperature decreases.

According to the expression for the magnetic structural factor, the ferromagnetic contribution in rhombohedral crystals is introduced into the reflection with an even sum of indices. In the given instance such a reflection at the smallest Bragg angle (the smallness of the angle is significant due to the decline in the magnetic form-factor) is precisely (110).

Slight reflections are seen on the neutron-diffraction pattern of $NiCO_3$. The presence of reflection (110) is possibly manifested in an increase in the left-hand wing of the adjacent reflection $(332)_{\lambda/2}$.

The smallness of the observed effect and the statistical spread does not permit an exact determination of the ferromagnetic contribution. We can only make the following suppositions.

Since the projection of moments on the basal plane is not 0 [this follows from the fact of the presence of reflection (111)], the class of symmetry of such a crystal according to Dzyaloshinsky[6] allows for the existence of ferromagnetism.

A quantitative solution of this problem may be obtained through a neutron-diffraction study by means of a single-crystal of $NiCO_3$.

In the present studies, which were carried out at different temperatures, such as $T_{He}$ and $T_{H_2}$, a determination was made of the earlier unknown transition point of $NiCO_3$ into the antiferromagnetic state. By extrapolating the reflection intensities (111) and (100) for various temperatures of the Brillouin curve we obtain $T_N \sim 25°K$.

I wish to express my deep gratitude to Academician P. L. Kapitza for his constant attention to this study.

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# Some Experiments on Magnetic Inelastic Scattering of Neutrons

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Thermal excitations in magnetic substances give rise to inelastic scattering of neutrons. The characteristic scattering surface which results gives detailed information about the nature of the excitations and may be studied by two different experimental techniques. The techniques are described and shown to give consistent results. Special attention is paid to the temperature behaviour of spin waves in magnetite. When approaching the Curie temperature, the lifetime and the energy of the spin waves are found to decrease. The temperature region in which the decrease shows up depends on the wavelength of the spin waves.

The angular and energy distribution of neutrons scattered inelastically by magnetic spin waves are determined by the conservation laws of momentum and energy:

$$\boldsymbol{k}_f - \boldsymbol{k}_i + 2\pi\boldsymbol{\tau} + \boldsymbol{q} = 0 \tag{1}$$

$$\frac{\hbar^2}{2m}(k_f^2 - k_i^2) - \hbar\omega = 0 \tag{2}$$

$m$ is the neutron mass, $\boldsymbol{k}_i$ and $\boldsymbol{k}_f$ are the wavevectors of the incoming and outgoing neutrons respectively and $\boldsymbol{\tau}$ is a reciprocal lattice vector of the crystal. The spin wave energy $\hbar\omega$ is connected with the corresponding momentum $\hbar q$ through a dispersion relation

$$\omega = Dq^n \tag{3}$$

where $n=1$ for an antiferromagnet and 2 for ferri- and ferromagnets. $D$ is the effective exchange coupling.

From the equations above it is readily shown that the locus of $\boldsymbol{k}_f$, the scattering surface, is a sphere (This is only an approximation in the case of an antiferromagnet). The scattering surface has its centre displaced from the reciprocal lattice point through a small distance, but is otherwise a conformal mapping of a constant energy surface for

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