WEAK FERROMAGNETISM IN $NiCO_3$

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The static magnetic properties of an $NiCO_3$ single crystal are investigated in the 4.2–40°K temperature range. The transition point of the weak ferromagnetic state, $T_N = 25.2$°K, is found. Induction of antiferromagnetic ordering in the vicinity of the transition point is studied. The temperature dependence of the $NiCO_3$ spontaneous ferromagnetic moment is measured. The main parameters characterizing the properties of the three carbonates, $MnCO_3$, $CoCO_3$ and $NiCO_3$ are compared.

$NiCO_3$ has the largest spontaneous moment of all the carbonates of transition elements that have weak ferromagnetism. However, owing to the difficulties in the synthesis of $NiCO_3$, this substance has not been thoroughly investigated to this day. All the published investigations have been carried out on polycrystalline samples.

The existence of a spontaneous ferromagnetic moment in $NiCO_3$ was observed by Bizette and Tsai[1] in 1955. They measured the magnetic moment of the sample at three temperatures: 4.2, 14, and 20.4°K. Later, Alikhanov[2] established by means of neutron diffraction that an antiferromagnetic structure is produced in $NiCO_3$ below 25°K. According to Dzyaloshinskiĭ's theory,[3] this structure admits of weak ferromagnetism. Kalinkina[4] observed a maximum at $T_N = 22.2$°K on the plot of the temperature dependence of the specific heat.

$NiCO_3$ is the most interesting object for the study of the effect of induction of antiferromagnetic region by a magnetic field in the region of the transition point.[5] The purpose of the present work was to investigate the strong susceptibility anisotropy near T_N, due to this effect, and also to study the temperature dependence of the spontaneous moment and of the magnetic susceptibility of $NiCO_3$ in the antiferromagnetic state. We used for this purpose $NiCO_3$ samples recently obtained by A. A. Shternberg at the Crystallography Institute of the U.S.S.R. Academy of Sciences.[1)] He succeeded in obtaining by a hydrothermal method small single crystals with linear dimensions on the order of 0.1–0.2 mm.

The static magnetic properties of $NiCO_3$ were investigated by the Faraday method with a magnetic balance[6] in the temperature interval 1.3–40°K and in magnetic fields 0–15 kOe.

SAMPLES AND MEASUREMENT RESULTS

Nickel carbonate is isomorphic with $MnCO_3$ and $CoCO_3$, and has a rhombohedral structure with two molecules per unit cell; the symmetry space group is D_{3d}^6 It crystallizes in the form of rhombohedra with good external faceting. The crystals have a light green color. The three-fold axis coincides with the spatial bisector of the obtuse angle of the rhombohedron.

We used for the measurements a complex sample made up of eight identically oriented single crystals glued on a quartz plate. The total weight of all crystals was 1.07 mg. The accuracy of the mutual orientation of the crystallites was not worse than 10°. All the investigations were carried out on the same sample and at the same position of the sample on the balance.

The suspension axis was perpendicular to the trigonal (z) and binary (x) axes of the crystal. The magnetic moment was measured at two directions of the magnetic field **H**, namely $\mathbf{H} \parallel z$ and $\mathbf{H} \parallel x$.

A study of the magnetic properties below 25°K has shown that along the binary axis (the basal plane) the dependence of the total magnetic moment on the magnetic field, in fields exceeding 5 kOe, is described sufficiently well by the formula

$$m_\perp(H, T) = \sigma(T) + \chi_\perp(T)H, \tag{1}$$

where $m_\perp(H, T)$ and $\chi_\perp(T)$ are the total magnetic moment and the magnetic susceptibility in the basal plane, and $\sigma(T)$ is the spontaneous ferromagnetic moment.

Measurements along the trigonal axis could be made only above 25°K, since a strong twisting of the suspension of the sample took place in a field parallel to the trigonal axis below 25°K, as a result of the strong anisotropy of the magnetic moment. Above 27°K, the magnetic moment along both axes is proportional to the magnetic field:

$$m = \chi H. \tag{2}$$

A graphic reduction of the experimental plots of m(H) for different temperatures has made it possible to determine the values of σ and χ. Their temperature dependences are shown in Figs. 1 and 2. As seen from Fig. 1, in the region of 25°K there is a strong anisotropy of the susceptibility: $\chi_\perp$ passes through a high maximum, $\chi_\parallel$ (the susceptibility along the trigonal axis) changes very little in the temperature region from 40 to 25°K, and the value of $\chi_\parallel$ at 25°K is only 20% smaller than the value of $\chi_\perp$ as $T \to 0$°K. One can therefore assume that the change of $\chi_\parallel$ below 25°K will be small. The maximum of $\chi_\perp$ and the presence of anisotropy offer evidence of the transition of the substance into the antiferromagnetic state at approximately 25°K. At the transition point itself, the perpendicular susceptibility is larger than the parallel one by a factor 2.5.

[1)] The authors are sincerely grateful to A. A. Shternberg for kindly supplying the $NiCO_3$ samples.

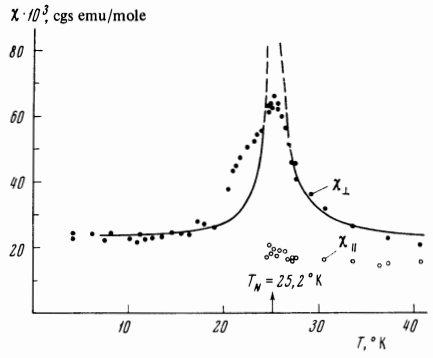

FIG. 1. Temperature dependence of the magnetic susceptibility of $NiCO_3$. Points – experimental values, solid curve – calculated by means of formulas (5) and (6).

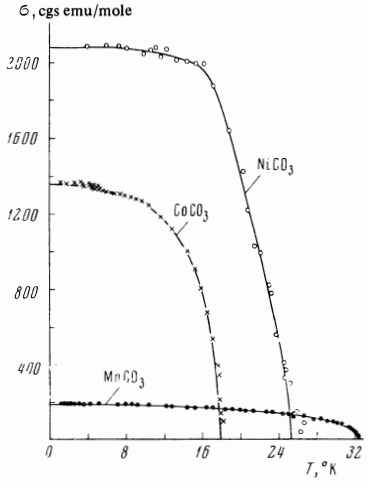

FIG. 2. Temperature dependences of the spontaneous ferromagnetic moment σ for the carbonates of Mn^{++}, Co^{++}, and Ni^{++}.

Below 16°K, $\chi_\perp$ is practically independent of the temperature.

The spontaneous ferromagnetic moment σ (see Fig. 2) exists up to 27°K. Above 25°K, however, its value is very small.

DISCUSSION OF RESULTS

1. The presence of a large anisotropy of the susceptibility and the occurrence of a spontaneous moment at 25°K show that $NiCO_3$ goes over into the antiferromagnetic state with weak ferromagnetism. The spontaneous ferromagnetic moment σ, as follows from the Dzyaloshinskiĭ theory,[3] for a given symmetry of the crystal, lies in the basal plane.

2. The spontaneous ferromagnetic moment in $NiCO_3$ reaches 2080 cgs emu/mole at T = 4.2°K. This amounts to ~20% of the nominal ferromagnetic moment $2M_0$ for the given substance. M_0, the total moment of sublattice, was calculated under the assumption that the orbital moments are fully quenched ($M_0 = N\mu_\beta S$, S is the spin of the magnetic ion).

From the values of σ and $\chi_\perp$ at T = 0°K we calculated the following effective fields: the Dzyaloshinskiĭ field $H_D = \sigma_0/\chi_\perp = 90 \pm 10$ kOe, and the exchange field $H_E = M_0/\chi_\perp = 240 \pm 12$ kOe. Thus, the weak ferromagnetism in $NiCO_3$ is sufficiently strong and the Dzyaloshinskiĭ interaction is comparable in magnitude with the exchange interaction.

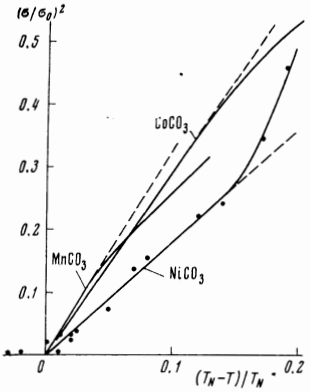

FIG. 3. Temperature dependence of the square of the relative spontaneous moment near the temperature transition for $MnCO_3$, $CoCO_3$, and $NiCO_3$. The solid curves correspond to the experimental curves for $MnCO_3$ and $CoCO_3$.

Figure 2 shows for comparison the temperature dependences of the spontaneous moment for $MnCO_3$ and $CoCO_3$. The data were taken from [7,5]. We see that in the case of $NiCO_3$ the spontaneous moment has the largest absolute magnitude.

3. The thermodynamic theory of weak ferromagnetism, developed for rhombohedral crystals in [3], in the case when the antiferromagnetic vector l lies in the basal plane, gives the following temperature dependence for the spontaneous ferromagnetic moment near T_N:

$$\sigma = [\beta^2\lambda(T_N - T)/B^2C]^{1/2}, \qquad (3)$$

where β, B, and C are the coefficients in the expansion of the thermodynamic potential.

In the present experiments, the accuracy of measurement and the temperature resolution are insufficient to permit a comparison with the theories pertaining to the narrow temperature interval near T_N.

A comparison of the experimentally obtained temperature dependence of the spontaneous moment near T_N with formula (3) has shown good agreement for $T_N - T \lesssim 4°$ (see Fig. 3), under the condition that $T_N = 25.2°$K. The transition temperature determined in this manner does not contradict the data of [2], and is somewhat higher than the value obtained by measurement of the specific heat.[4] The discrepancy between the Néel points (on the order of 10%) determined from the magnetic and specific-heat measurements is characteristic of most antiferromagnets. The presence of several experimental points indicating the existence of a small moment at a temperature 2° higher than 25.2°K is apparently due to the poor quality of the sample.

Figure 3 shows the dependence of $(\sigma/\sigma_0)^2$ on the relative temperature difference $(T_N - T)/T_N$ near T_N for the three carbonates $McCO_3$,[7] $CoCO_3$,[5] and $NiCO_3$. We see that all three substances satisfy the law

$$(\sigma/\sigma_0)^2 = \xi(1 - T/T_N), \qquad (4)$$

with ξ equal to 3.6, 3, and 1.8 for $MnCO_3$, $CoCO_3$, and $NiCO_3$, respectively. It is known that the theory of the molecular field leads to the law (4) with $\xi = 3$.[8] Thus, the molecular-field model describes sufficiently well the behavior of the spontaneous magnetization of $MnCO_3$ and $CoCO_3$, and somewhat worse $NiCO_3$.

4. Borovik-Romanov and Ozhogin[5] have shown that in antiferromagnets with weak ferromagnetism, near the transition point (both above and below), the magnetic field applied along the direction of the spontaneous moment induces additional ferromagnetic ordering. This is manifest in an increase of the susceptibility $\chi_\perp$ near T_N and leads to a sharp increase of the susceptibility when the transition point is approached:

$$T > T_N, \quad \chi_\perp = \frac{1}{B} + \frac{\beta^2}{B^2\lambda(T - T_N)} \tag{5}$$

$$T < T_N, \quad \chi_\perp = \frac{1}{B} + \frac{\beta^2}{2B^2\lambda(T_N - T)}. \tag{6}$$

As seen from (5) and (6), the increment of the susceptibility is proportional to the coefficient β, i.e., to the spontaneous ferromagnetic moment σ_0, since

$$\sigma_0 = \beta l_0 / B. \tag{7}$$

Inasmuch as the spontaneous moment of $NiCO_3$ is large compared with the other carbonates, it reveals a relatively large growth of $\chi_\perp$ near T_N (see Fig. 1). A quantitative comparison with formulas (5) and (6) has shown that the experimental data at $T > T_N$ fit well the curve (5). Below T_N, the experiment does not agree with theory, namely, in the temperature region 20–24° K the experimental points lie considerably higher than the theoretical curve. It should be noted that in the same temperature region there is observed a strong excess of the experimental values of m(T) for $NiCO_3$ compared with the Brillouin function for S = 1 (see Fig. 4). One of the causes of the presence of these anomalies in $NiCO_3$ may be the existence of a more complicated m(H) dependence than described by formula (1). However, the experimental data available to us do not permit a final clarification of this question.

5. The experimental results presented above have enabled us to determine the values of the coefficients in the expansion of the thermodynamic potential: B = 42, β = 7.8, λ = 0.78, C = 7.85×10^{-8}. With the aid of the obtained values of the expansion coefficients it is possible to estimate the temperature interval $\Delta T = |T - T_N| \approx (\beta^2 CH^2/B^2\lambda^3)^{1/3}$, in which the formulas (3), (5), and (6) employed by us no longer hold (see [5]). It turned out that in our case $\Delta T \sim 0.8°$. It follows therefore that the observed disparity between experiment and theory lies in the temperature region where the employed theoretical formulas are valid.

6. Since $NiCO_3$ is isomorphic with $MnCO_3$ and $CoCO_3$, it is natural to compare its properties with the well investigated properties of these compounds. To this end, we present a table of the main parameters, characterizing the properties of all three compounds, obtained from magnetic measurements. The data for $MnCO_3$ and $CoCO_3$ were taken from [7, 5].

Compound	T_N, °K	$\chi_\perp \cdot 10^3$, cgs emu/mole	σ_0, cgs emu/mole	$2M_0 \cdot 10^3$, cgs emu/mole	H_D, kOe	H_E, kOe	$\frac{\sigma_0}{2M_0}$, %	β	B	C	λ
$MnCO_3$	32.4	43	188	27.7	4.4	320	0.7	0.16	—	—	—
$CoCO_3$	18.1	52	1400	16.7	27	160	8.5	1.5	18	$4.5 \cdot 10^{-9}$	0.25
$NiCO_3$	25.2	23.8	2030	11.1	90	240	18.7	7.8	42	$7.8 \cdot 10^{-8}$	0.78

As seen from the table, $NiCO_3$ is the strongest ferromagnet of the entire carbonate group. It is interesting to note in this connection that in the group of anhydrous fluorides only the compound with Ni^{++} is a weak ferromagnet; the remaining compounds are purely antiferromagnetic.

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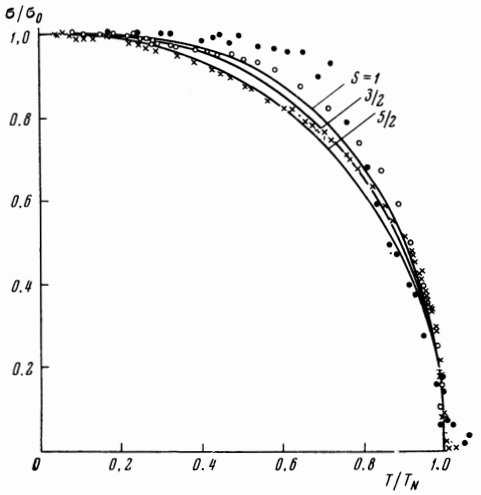

FIG. 4. Dependence of the relative spontaneous moment on the relative temperature for: × – $MnCO_3$, ○ – $CoCO_3$, and ● – $NiCO_3$. The solid curves correspond to the Brillouin functions for different values of S.

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61