# Magnetically ordered state of two-dimensional ferromagnets with anisotropy of the "easy-plane" type

Yu. S. Karimov

*Chemical Physics Institute, USSR Academy of Sciences*

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The magnetic properties of layer compounds of $NiCl_2$ and $CoCl_2$ with graphite are studied. These compounds go over into the ferromagnetic state at 18.1°K ($NiCl_2$) and 8.2°K ($CoCl_2$). In the ordered state the plane of the layer is the easy-magnetization plane. After removal of the magnetizing field the samples possess a residual moment whose temperature dependence obeys the law $M(0)-M(T)\propto T^{1/2}$. The quantity $M(0)$ has the value $0.52M_0$ for the compound of $NiCl_2$ with graphite and the value $0.74M_0$ for the $CoCl_2$ compound ($M_0$ is the total ferromagnetic moment of the sample). On variation of the temperature the value of the coercive forces varies like $M^2(T)$. It is shown that the presence of exchange and dipole-dipole interactions in a plane lattice leads to the result that the formation of a ferromagnetic spiral is energetically favored. An anisotropic gap then arises in the spin-wave energy spectrum, and this qualitatively explains the observed properties.

Two-dimensional magnets describable by the isotropic Heisenberg model cannot be found in an ordered state at any finite temperature, since thermal fluctuations completely destroy the long-range order[1]. However, the magnets studied in practice differ fundamentally from the idealized Heisenberg model. First, such magnets, as a rule, have a layer structure. Despite the fact that the interaction between nearest magnetic ions within a layer is greater by several orders of magnitude than the interaction between ions from neighboring layers, in a number of cases it is precisely this weak interaction that is responsible for the establishment of long-range magnetic order. Second, real magnets always possess a definite anisotropy in their magnetic properties, which can arise from the most widely different types of interaction. The presence of even weak anisotropy leads to the result that easy-magnetization axes arise in the crystal. A gap appears in the energy spectrum of the spin waves, so that at sufficiently low temperatures a two-dimensional set of spin waves will be thermodynamically stable and the system will be in a magnetically ordered state.

Among the layer magnets a special place is occupied by the intercalation compounds, for which the interaction between neighboring layers can be made so weak that it will not affect the observable magnetic properties[2]. To describe the properties of the disordered state of such compounds it is sufficient to take into account only the exchange and dipole-dipole interactions between the magnetic ions[3], while the properties of the ordered state are determined to a considerable degree by the magnetic anisotropy.

It has been found earlier that layer compounds of graphite with nickel chloride and cobalt chloride are in an ordered ferromagnetic state at low temperatures[4]. This state is investigated in detail in the present paper.

## RESULTS

The Curie temperature for the compound of graphite with $NiCl_2$ is 18.1°K, and for the compound with $CoCl_2$ is 8.2°K. The magnetization curves for these compounds have been studied in the temperature range from 0.06°K up to the Curie temperature. For the preparation of the samples, oriented pyrolitic graphite was used and the quantity of intercalated chloride amounted to ~2% by weight. The samples studied were spherical in shape, with diameter 3 mm.

Polycrystalline samples with a large chloride content (up to 50% by weight), for which the arrangement of the alternating layers of graphite and chloride was determined by x-ray analysis, were studied first. $NiCl_2$ and graphite form only a stage-2 compound, in which the $NiCl_2$ layers are separated by two layers of graphite. It was also found that the magnetic properties of the stage-1 and stage-2 compounds of graphite with $CoCl_2$ are completely identical. In this case, separating the chloride layers by even a single layer of graphite makes the interaction between neighboring layers negligibly weak, so that further separation of the layers has no further effect on the magnetic properties of the compounds. An analogous phenomenon is also observed for the compound of $FeCl_2$ with graphite[2].

The pure chlorides of nickel and cobalt have a layer structure. The structure of the compounds of these chlorides with graphite is unknown, but by analogy with the compounds of $FeCl_3$ and $MoCl_5$ with graphite that have been studied[5,6], we can assume that the structure of a single layer in the pure chlorides is the same as in their compounds with graphite. The magnetic measurements confirm this. The ferromagnetic interaction between the magnetic ions within a layer is conserved, and, for the $NiCl_2$ investigated, the magnitude of this interaction is practically the same in the pure chloride and in its compound with graphite[3]. We shall therefore assume that the nickel and cobalt ions form a regular triangular lattice, the distances between them being 3.53 Å for $NiCl_2$ and 3.54 Å for $CoCl_2$.

It must be noted that for the samples investigated there was no crystalline order along the direction perpendicular to the layers, inasmuch as the layers of the initial pyrolitic graphite were also not ordered along this direction. The layers of magnetic ions, situated in parallel planes, could be displaced and rotated relative to each other. Thus, there was the possibility of studying the magnetization curves perpendicular and parallel to the layers; in the latter case, the experimentally observed magnetic moment was a quantity averaged over all directions in the plane of the layer.

The magnetic moment was measured by a ballistic method; fields of up to 500 Oe were created by a copper solenoid, and higher fields by a superconducting solenoid. Ultra-low temperatures were obtained by adiabatic demagnetization of iron ammonium alum; the apparatus

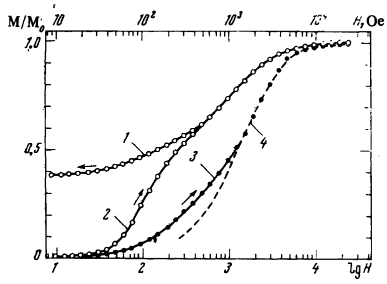

FIG. 1. Magnetization curves for the compound of NiCl$_2$ with graphite; T = 1.44°K. Curves 1 and 2—field parallel to the layers; curve 3—field perpendicular to the layers; the dashed curve 4 is calculated from formula (2).

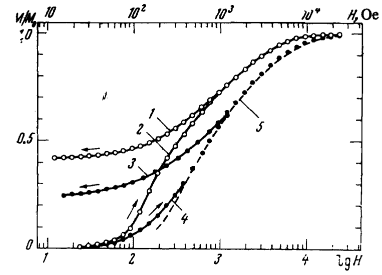

FIG. 2. Magnetization curves for the compound of CoCl$_2$ with graphite; T = 1.44°K. Curves 1 and 2—field parallel to the layers; curves 3 and 4—field perpendicular to the layers; the dashed curve 5 is calculated from formula (4).

for performing the magnetic measurements has been described briefly earlier[3,7].

The layer compounds studied possess a plane of easy magnetization, coinciding with the plane of the layer, and the direction perpendicular to this plane is the axis of difficult magnetization (Figs. 1, 2). In a study of the compound of NiCl$_2$ with graphite in the disordered state, it was found[3] that the magnetization curves along the "difficult" direction can be obtained from the magnetization curves along the "easy" direction by introducing a demagnetizing field. We shall show that this statement is also true for the ordered state.

Let the magnetic field be directed parallel to the plane of the layer. Then the internal field acting on the magnetic ions is equal in magnitude to the external field, since the demagnetizing factor for a ferromagnetic plane is equal to zero. But if the magnetic field is directed perpendicular to the plane of the layer, then, along with the external field, a demagnetizing field proportional to the magnetic moment of the sample also acts on the magnetic ions. Suppose that the magnetization curve of the completely demagnetized sample along the easy direction is a certain function of the external field:

$$M_\parallel/M_0=f(H), \tag{1}$$

where M$_0$ is the total ferromagnetic moment of the sample. It can be postulated that the magnetization curve along the difficult direction is described by the same dependence (1), but with a different value of the argument:

$$M_\perp/M_0=f(H-H_dM_\perp/M_0) \tag{2}$$

where $H_d$ is the demagnetizing field for $M_\perp/M_0 = 1$.

In Fig. 1, the dashed curve 4 is drawn to correspond to expression (2), the curve 2 gives the form of the function f(H), and the quantity $H_d$ is chosen to be equal to 1.96 kOe. The experimental results lie well on curve 4 for $M_\perp/M_0 \geq 0.5$, but for small values of the moment a considerable discrepancy is observed (curve 3). This discrepancy arises from the fact that, during the magnetization of the sample, the magnitude of the moment in weak fields is not a unique function of the external field (curves 1 and 2). Naturally, the expression (2) has no meaning in these conditions.

The value of $H_d$ differs from the value $H_d$ = 1.20 kOe found for the disordered state. If the field $H_d$ owed its origin entirely to the dipole-dipole interaction, its magnitude would be the same for the ordered and disordered states. It is necessary to postulate that, along with the dipole-dipole interaction, there are also other effects responsible for the anisotropy of the magnetic moment. Single-ion anisotropy and anisotropy of the exchange interaction can be such effects. The properties of the single ion are determined by the g-factor, which in real crystals is a tensor quantity. However, the compound of NiCl$_2$ with graphite has an isotropic g-factor within the experimental errors. Firstly, this follows from the magnetization curves. The total ferromagnetic moment of the sample is defined as

$$M_{0\parallel}=M_\parallel(T=0,\ H=\infty)=Ng_\parallel\beta S,\quad M_{0\perp}=M_\perp(T=0,\ H=\infty)=Ng_\perp\beta S, \tag{3}$$

where N is the number of magnetic ions with spin S, and the symbols ∥ and ⊥ denote parallel and perpendicular orientations of the external magnetic field **H** with respect to the plane of the layer. Since the experimentally determined quantities $M_{0\parallel}$ and $M_{0\perp}$ are the same, we have $|g_\parallel - g_\perp|/\bar{g} \leq 10^{-2}$. Secondly, this same result can be obtained from an analysis of the electron-resonance data of[4]. Single-ion anisotropy of such small magnitude can make no appreciable contribution to the magnitude of $H_d$.

Thus, the magnetic anisotropy of the compound of NiCl$_2$ with graphite is due to the dipole-dipole interactions and to the anisotropy of the exchange interaction. An important fact is that both contributions depend linearly on the magnitude of the magnetic moment, and it is extremely difficult to distinguish them experimentally. The field $H_dM_\perp/M_{0\perp}$ is more correctly regarded as an effective uniaxial-anisotropy field than as a demagnetizing field.

The magnetization curves for the compound of CoCl$_2$ with graphite differ in two respects from the curves studied for NiCl$_2$. Firstly, the saturation moment $M_{0\parallel}$ along a direction parallel to the plane of the layer is 1.71 times greater than the value of the saturation moment $M_{0\perp}$ in the perpendicular direction. It follows from (3) that $g_\parallel/g_\perp$ = 1.71, i.e., in the compound of CoCl$_2$ with graphite there is considerable single-ion anisotropy. This fact is not reflected in Fig. 2, inasmuch as the magnetization curves are given in normalized form. Secondly, hysteresis is observed in the magnetization of the sample in the perpendicular direction (curves 3 and 4 in Fig. 2) and the sample possesses a residual ferromagnetic moment after the external field has been switched off. At the lowest temperatures, the magnitude of this moment reaches 40% of the total moment of the sample. We remark that for the compound of NiCl$_2$ with graphite this quantity is considerably small and does not exceed 10%. However, for both compounds, a state with a spontaneous moment directed perpendicular to the plane of the layer is metastable. Light mechanical shaking of the sample leads to a severalfold decrease of the residual moment. The hysteresis phenomena in the perpendicular direction have not been studied in detail in the present work.

We shall show that in high fields, in which hysteresis is weakly manifested, the magnetization curves $M_\parallel(H)/M_{0\parallel}$ and $M_\perp(H)/M_{0\perp}$ can be described by the same function, but with a different value of the argument. Suppose that the dependence $M_\parallel(H)/M_{0\parallel}$ in the easy-

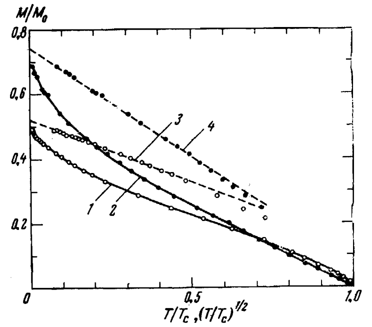

FIG. 3. Temperature dependence of the residual ferromagnetic moment: ○—compound of $NiCl_2$ with graphite, ●—the $CoCl_2$ compound. The curves 1 and 2 are plotted in direct coordinates and the straight lines 3 and 4 in the coordinates $M/M_0, (T/T_c)^{1/2}$.

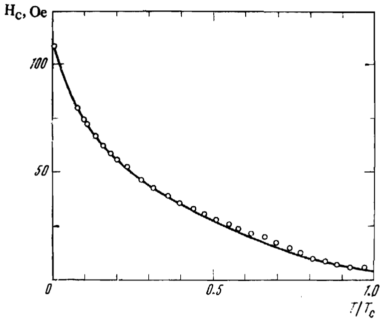

FIG. 4. Temperature dependence of the coercive force for the compound of $NiCl_2$ with graphite.

magnetization plane is again given by the expression (1). Then the magnetization curve in the perpendicular direction can be expressed as

$$M_\perp(H)/M_{0\perp}=f(g_\perp H/g_\parallel-M_\perp H_d/M_{0\perp}). \tag{4}$$

Formula (4) is the natural generalization of (2) in the presence of single-ion anisotropy, inasmuch as the magnetic field appears in the form of the product gH in the expression for the magnetic moment.

In Fig. 2, the curve 5 is drawn using formula (4), the function f(H) is given by the curve 2, and the magnitude of $H_d$ is 0.35 kOe. A comparison of the uniaxial-anisotropy fields for the compounds of $NiCl_2$ and $CoCl_2$ with graphite confirms the conclusion drawn earlier, that, along with the dipole-dipole interaction, anisotropy of the exchange interaction gives an important contribution to $H_d$. The nickel ion $Ni^{2+}$ has spin S = 1, and the ion $Co^{2+}$ has spin $S = 3/2$, the distances between the ions are the same for both compounds, and, with allowance for the anisotropy of the g-factor of the ion $Co^{2+}$, it can be postulated that the dipole-dipole interaction should be approximately the same in both cases. The fact that the magnitude of $H_d$ for the $NiCl_2$ compound is more than five times greater than the analogous quantity for $CoCl_2$ indicates directly the presence of a uniaxial-anisotropy mechanism differing from the dipole-dipole interaction and the single-ion anisotropy.

After removal of a magnetizing field applied parallel to the layers, the samples studied possess a residual ferromagnetic moment. As the temperature is lowered the magnitude of the residual moment increases, right down to the lowest temperatures (curves 1 and 2 in Fig. 3). The law of variation of the residual moment displays linear dependences (the straight lines 3 and 4 in Fig. 3), plotted in the coordinates M, $T^{1/2}$. Thus, for both the compounds investigated, the temperature dependence of the residual moment at low temperatures can be expressed by the relation

$$[M(0)-M(T)]\propto T^{1/2}. \tag{5}$$

If the law (5) is valid down to T = 0, then M(0) is the magnitude of the residual ferromagnetic moment of the samples at T = 0. As follows from Fig. 3, $M(0)/M_0 = 0.52 \pm 0.02$ for the compound of $NiCl_2$ with graphite, and $M(0)/M_0 = 0.74 \pm 0.03$ for $CoCl_2$.

The residual moment vanishes provided that a magnetic field of a certain magnitude (the coercive force of the ferromagnet) is applied to the sample in the opposite direction. The experimental results given in Fig. 4 were obtained as follows. First the sample was magnetized by a sufficiently strong magnetic field applied parallel to the layers. After removal of the magnetizing field, a weaker field of the opposite sign was applied, and then this field was removed and the residual ferromagnetic moment of the sample measured. The magnitude of the coercive force was taken to be that value of the demagnetizing field for which the ferromagnetic moment was equal to zero after its removal.

At all temperatures below the transition point, the coercive force and residual moment of the sample are connected by the relation

$$H_c=112[M(T)/M(0)]^2+5, \tag{6}$$

where $H_c$ is expressed in Oersteds (Fig. 4). The main contribution to the magnitude of the coercive force at low temperatures is given by the first term, proportional to the square of the residual moment, in (6). An analogous relation can also be written for the compound of $CoCl_2$ with graphite:

$$H_c=525[M(T)/M(0)]^2. \tag{6'}$$

In this case it was not possible to separate out a constant term, but its magnitude does not exceed 20 Oe.

Thus, the layer compounds of $NiCl_2$ and $CoCl_2$ with graphite are two-dimensional ferromagnets with anisotropy of the "easy-plane" type. The distinctive temperature dependence of the residual moment (5) and the relation ((6) and (6′)) between the coercive force and the residual moment are characteristic for these compounds.

## DISCUSSION

To explain the phenomena observed, we shall consider a two-dimensional lattice of magnetic ions, magnetized to saturation and of finite dimensions. With no external magnetic field, such a state of two-dimensional ferromagnet is thermodynamically unstable, since magnetic charges are formed at the edges of the plane. The field created by these charges is directed in opposition to the magnetic moment of the plane and tends to demagnetize the ferromagnetically ordered system of magnetic ions. On the other hand, demagnetization of the system leads to an increase of the exchange interaction energy. The equilibrium distribution of atomic magnetic moments corresponds to a minimum of the total magnetostatic and exchange energy of the system.

One of the possible distributions realized in two-dimensional ferromagnets is shown in Fig. 5. Such a configuration possesses a considerably lower magnetostatic energy, since the magnetic fluxes in this case are confined within the layer of magnetic ions. Thanks to the presence of hexagonal anisotropy in the plane of the layer, the orientation of the atomic magnetic moments is such that they retain a component along the initial direction of the magnetic field. The system as a whole possesses a ferromagnetic moment after the external field has been switched off. For the configuration shown, the magnitude of the residual moment $M(0)/M_0 = 0.5$. Such a pattern is possible when the hexagonal anisotropy in the plane of the layer is small and the angle between neighboring spins is determined by the competing effects of the exchange and dipole-dipole interactions.

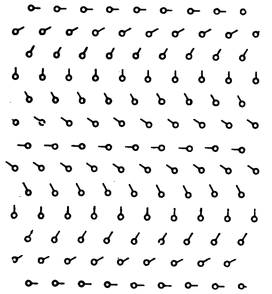

FIG. 5. Assumed magnetic order in the plane of the layer after the external field is switched off.

This is true, apparently, for the compound of $NiCl_2$ with graphite, in which $M(0)/M_0 = 0.52$.

But if the anisotropy field is of the same order as the fields arising because of the dipole-dipole interactions, the arrangement of the atomic moments will differ from that in Fig. 5. In accordance with the hexagonal anisotropy, the spins will be grouped about certain directions in the plane of the layer, and this leads to an increase in the residual ferromagnetic moment. This situation is realized, apparently, in the compound of $CoCl_2$ with graphite, in which $M(0)/M_0 = 0.74$.

It is highly probable that in real magnets the distribution of atomic moments in the plane differs appreciably from the configuration considered. In particular, an important role is played by all the possible defects in the structure and by the magnetostatic interaction between neighboring layers. In all cases, however, it may be stated, firstly, that the atomic moments in a two-dimensional ferromagnet are arranged in the form of a fan, and the angular density of the moment can vary in accordance with the anisotropy of the lattice. Secondly, the magnitude of the residual ferromagnetic moment is proportional to the magnetization of the sample. All the observable magnetic properties can be explained qualitatively on the basis of these statements.

The existence of an ordered state in two-dimensional ferromagnets is inevitably connected with the presence of an energy gap in the spin-wave spectrum. In the absence of such a gap an infinite number of spin waves arise in a two-dimensional system at any finite temperature, and this leads to the destruction of the long-range magnetic order. For the atomic-moment distribution under consideration, this gap will depend on the direction of the wave vector. Spin waves which propagate along a chain of magnetic ions all having the same direction in space (the horizontal rows in Fig. 5) have the minimum gap. Whereas for three-dimensional ferromagnets the number of spin waves is proportional to $T^{3/2}$, for two-dimensional and one-dimensional systems their number is proportional to $T$ and $T^{1/2}$ respectively. The experimentally observed dependence (5) corresponds exactly to the one-dimensional case.

It is obvious that the gap in the spin-wave spectrum arises because of the presence of hexagonal anisotropy in the plane of the layer. Using the primitive theory of spin waves, we can try to estimate the magnitude of this gap. Expressed as a magnetic field, it is equal to 3–10 Oe for the compound of $NiCl_2$ with graphite, and 10–30 Oe for $CoCl_2$. However, such estimates are at best true only within an order of magnitude. The point is that, in one- and two-dimensional systems, the spin waves at all values of the wave vector form bound states, which no longer have the properties of ordinary magnons[8]. Nevertheless, the dependence (5) will also be valid, apparently, for bound states. The energy of two bound magnons is equal to

$$E=\varepsilon(q_1)+\varepsilon(q_2)-\Delta, \tag{7}$$

where $\epsilon(q)$ is the energy of a noninteracting magnon and $\Delta$ is the binding energy; $q$ is the wave vector. Since the bound states also obey Bose statistics and, in the absence of an external magnetic field, the principal term in their energy is proportional to $q_1^2 + q_2^2$, it is obvious that the temperature dependence of the number of such excitations will be the same as the analogous dependence for linearized magnons.

Finally, we shall consider the nature of the coercive force of two-dimensional ferromagnets. As already pointed out, the energy gap in the spin-wave spectrum has an anisotropic character. The spin waves with wave vector corresponding to the greatest difference in orientation between neighboring atomic moments (Fig. 5) possess the maximum gap. If the magnitude of the external magnetic field does not exceed this gap, the previously magnetized sample displays anisotropic properties and maintains the direction of its spontaneous moment. But if the magnitude of this field is greater than the maximum gap in the spectrum, the anisotropy will not be manifested and the moment of the sample will be oriented along the external field. Thus, in the model considered, the magnitude of the coercive force is taken to be the value of the maximum gap in the spin-wave spectrum. The appearance of this gap is due to the decrease of the magnetostatic energy of the sample. To the extent that the total magnetostatic energy of a sample magnetized to saturation is proportional to $M^2$, any decrease in energy as a result of rearrangement of the atomic moments is also proportional to $M^2$, where $M$ is the spontaneous moment of the sample. If the arrangement of the atomic moments does not change with temperature, the value of the maximum gap will depend on the temperature like $M^2$, and this is observed experimentally (Fig. 4, and expressions (6) and (6′)). The small and temperature-independent term in (6) evidently appears as a result of the hexagonal anisotropy in the plane of the layer and corresponds to the minimum gap in the spin-wave spectrum. Thus, an arrangement of the spins in the form of a ferromagnetic spiral and a fan-like arrangement after the magnetizing field is switched off explain the observed magnetic properties of the compounds of $NiCl_2$ and $CoCl_2$ with graphite in the ordered state.

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