Phase transitions of a layered ferromagnet with easy plane anisotropy

Yu. S. Karimov

Institute of Chemical Physics, USSR Academy of Sciences

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The magnetic properties and specific heat are studied in layered compounds of graphite with cobalt and nickel chlorides, in which two magnetic phase transitions are observed. At the higher temperature ($T_{c1} = 20.3$°K for the compound of graphite with $NiCl_2$ and $T_{c1} = 9.05$°K for the compound with $CoCl_2$), a transition occurs from the paramagnetic state to a disordered state with infinite initial susceptibility. This state persists over a certain temperature range, and then these compounds go over to a ferromagnetic state ($T_{c2} = 18.1$°K for $NiCl_2$ and $T_{c2} = 8.1$°K for $CoCl_2$). The magnetic specific heat goes through a maximum near the first phase-transition point, whereas the transition to the ordered states is not accompanied by any appreciable anomalies of the specific heat. The existence of an intermediate phase with infinite initial susceptibility is explained by the fact that the noninteracting layers of magnetic atoms possess anisotropy of the easy plane type.

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Two-dimensional magnetism shows up most clearly in layered compounds. The interaction between neighboring magnetic layers in such compounds may have a very small value, since between them there are usually located nonmagnetic layers. Chemically, neighboring layers are coupled very weakly; in some cases they are held together only by van der Waals forces. Mechanisms of any kind for transfer of spin density between layers are practically absent in such structures; therefore the exchange interaction between magnetic atoms of neighboring layers is many orders of magnitude smaller than the interaction of atoms within a layer.

A quite appreciable coupling between magnetic layers can be induced by dipole-dipole interaction. This interaction is long-range and falls off less rapidly than does the exchange interaction, so that at large distances it may exceed the latter. But the dipole-dipole interaction depends on the mutual arrangement of the magnetic dipoles and manifests itself differently in each concrete case. In particular, in layered ferromagnets with anisotropy of the "easy plane" type this interaction leads to a comparatively weak interaction between neighboring layers. In fact, if a ferromagnetic layer in which the moment lies in the plane of the layer has infinite dimensions, then it produces no magnetic field in its vicinity, and magnetostatic, or dipole-dipole, interaction of this layer with neighboring layers does not occur. Magnetostatic interaction is possible in layers of finite dimensions, when magnetic charges appear on the edges of the layer. The energy of this interaction depends linearly on the dimension L of the layer, whereas the energy of interaction of the layer of magnetic atoms with the external field and the energy of magnetic anisotropy are proportional to L^2. Therefore the interaction between layers of sufficiently large dimensions is usually far smaller than the energy of interaction of the magnetic atoms with the external fields and with the anisotropy fields. Thus layered ferromagnets possessing a plane of easy magnetization are quite close in their magnetic properties to two-dimensional ferromagnets.

Earlier, studies were made of the disordered paramagnetic state[1] and of the ordered state[2] of two-dimensional ferromagnets with "easy plane" anisotropy, in the example of layered compounds of graphite with nickel and cobalt chlorides. It was also discovered that in the compound of $NiCl_2$ with graphite there are two magnetic transitions, separated in temperature[3]. At the higher temperature, there occurs a transition from the paramagnetic state to a new intermediate state, which is characterized by absence of long-range order, while at the same time the initial susceptibility has an infinite value. The transition to an ordered state is observed at a lower temperature. The present paper is devoted to the further study of this phenomenon.

MAGNETIC PROPERTIES

The magnetic measurements were made on oriented specimens of layered compounds of graphite with nickel and cobalt chlorides. The method of obtaining such compounds and the crystal structure conjectured for them were described earlier[1,2]. The chloride content in the specimens studied was 1 to 2 weight %; the specimens had spherical shape; and the external magnetic field was applied parallel to the layers. This made it permissible to neglect the demagnetizing fields, because the demagnetizing factor of an individual layer in this case is zero, while the effect of surface magnetic charges is insignificantly small because of the smallness of the total ferromagnetic moment of the specimen.

In the paramagnetic state and in weak magnetic fields, the magnetic moment of the specimen is proportional to the value of the external magnetic field; the coefficient of proportionality is the magnetic susceptibility

$$\chi = M/H. \tag{1}$$

In many cases it is more convenient to use the reduced susceptibility[4], which is defined by the relation

$$\bar{\chi} = \chi/\chi_0, \tag{2}$$

where χ_0 is the susceptibility in the limiting case in which there is no interaction between the spins (according to Curie):

$$\chi_0 = N g_\parallel^2 \beta^2 S(S+1)/3kT. \tag{3}$$

Any deviation of $\bar{\chi}$ from unity will indicate the presence of interactions between the magnetic atoms.

Figure 1 shows the temperature dependence $\bar{\chi}(T)$ for the compound of $CoCl_2$ with graphite; the analogous dependence for the compound with $NiCl_2$ was given

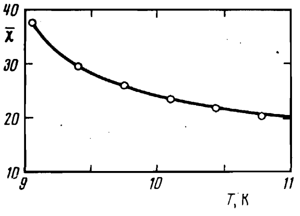

FIG. 1. Reduced susceptibility of the compound of $CoCl_2$ with graphite.

earlier[3]. The temperature $T_{c1} = 9.05$ K is critical; below this temperature the linear relation between the field and the moment is upset, so that the initial susceptibility becomes infinite; the definition of T_{c1} will be given below. The magnetic susceptibility has a singularity of the cusp type[4]: it remains finite everywhere for $T \geq 9.05$ K, and its dependence on temperature can be expressed in the form

$$\bar{\chi}=38-33\tau^{0,4}, \tag{4}$$

where $\tau = (T - T_{c1})/T_{c1}$. The susceptibility for the compound of $NiCl_2$ with graphite can be described by a similar expression, but the value of the susceptibility at the critical temperature T_{c1} in this case is about four times larger.

At the critical temperature T_{c1} the susceptibility undergoes a discontinuity, abruptly becoming infinite. This shows up in the fact that the linear relation between field and moment is upset; the dependence $M(H)$ becomes a power law:

$$M=cH^{1/\delta}, \tag{5}$$

where the index δ depends on temperature. In Fig. 2 the magnetization curves are shown on a log-log scale. On such a graph, the dependence of the magnetic moment on the field at each temperature is described by a straight line; the slope of the line is determined by the index δ.

In the paramagnetic state, $\delta = 1$; but beginning with $T = T_{c1}$, the index δ begins to increase. The initial susceptibility then becomes infinite, because

$$\chi=\lim_{H\to 0}(\partial M/\partial H)=\lim_{H\to 0} cH^{1/\delta-1}=\infty, \tag{6}$$

provided $\delta > 1$. The dependence of δ on temperature is shown in Fig. 3. For the compound of $NiCl_2$ with graphite, in the vicinity of T_{c1}, the dependence $1/\delta(T)$ was extrapolated with a straight line, and this made it possible to determine the critical temperature T_{c1}[3]. But in the case of $CoCl_2$ the accuracy of determination of the index δ is somewhat higher, and the linear extrapolation here appears to be a very rough approximation. The experimental results are described much better by the empirical expression

$$\frac{\delta-1}{\delta}=d\left(\frac{T_{c1}-T}{T_{c1}}\right)^{1/2}, \tag{7}$$

where the parameter $d = 1.30$. The curve in Fig. 3 was drawn in accordance with (7); the experimental points over the whole temperature interval fit this curve well—the scatter does not exceed the errors of measurement.

It must be noted that the relation (7) also describes well the temperature variation of the index δ for the compound of $NiCl_2$ with graphite[3]. In this case the parameter $d = 1.34$ and $T_{c1} = 20.3$ K; much better agreement with experiment is obtained than by linear extrapolation. The critical temperature T_{c1} found by this method is closer to the maximum of the specific heat (20.2 K) than is the temperature $T_{c1} = 20.5$ K determined by linear extrapolation.

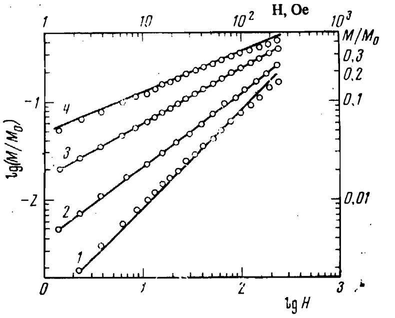

FIG. 2. Field dependence of the magnetic moment of the compound of $CoCl_2$ with graphite at various temperatures: 1, T = 9.41 K; 2, T = 8.65 K; 3, T = 7.97 K; 4, T = 7.25 K.

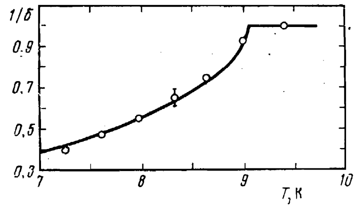

FIG. 3. Temperature dependence of the index $1/\delta$ for the compound of $CoCl_2$ with graphite: points, experiment; curve, theoretical.

At a certain temperature T_{c2} the layered compounds go over to an ordered state. This shows up in the fact that at $T < T_{c2}$ the magnetized specimens in the absence of an external field possess a remanent ferromagnetic moment. The remanent moment is proportional to the spontaneous magnetization of the specimen, and the effects of demagnetization can be neglected even near the critical point T_{c2}, where the magnetic anisotropy is most weakly expressed. The dependence of the remanent moment on temperature was given earlier[2]; but near the critical point T_{c2}, it is convenient to show this dependence on a log-log scale, as is done in Fig. 4. For both compounds studied, the remanent moment for $T \to T_{c2}$ decreases according to the power law

$$\frac{M(0)}{M_0}=b\left(\frac{T_{c2}-T}{T_{c2}}\right)^{\beta}, \tag{8}$$

where b is a certain constant, and where M_0 is the total ferromagnetic moment of the specimen. The index $\beta = 1.00 \pm 0.03$ for the compound of $CoCl_2$ with graphite, and $\beta = 0.75 \pm 0.03$ for the compound of $NiCl_2$ with graphite.

In the ordered state, when the temperature is close to the critical, the power-law relation between the moment of the specimen and the external field in a definite field interval continues to be observed (Fig. 2). The index δ changes smoothly in accordance with (7); the function $\delta(T)$ experiences no anomalies at $T = T_{c2}$. Only in very weak fields, less than 1 Oe, does the dependence (5) break down; the moment ceases to depend on the field, remaining finite clear down to $H = 0$. It is precisely this peculiarity of the magnetization curves that allows us to identify the temperature T_{c2} with the point of transition to the ordered state.

The anomalies considered in the magnetic properties of layered ferromagnets at the temperatures T_{c1} and T_{c2} are observed in comparatively weak fields, when the relative value of the magnetic moment $M/M_0 \leq 0.2$. In higher fields, the magnetic moment increases smoothly with lowering of the temperature; at fixed temperature, the value of the moment is proportional to the logarithm of the external field[1]. Such a dependence is in agreement with spin-wave theory, according

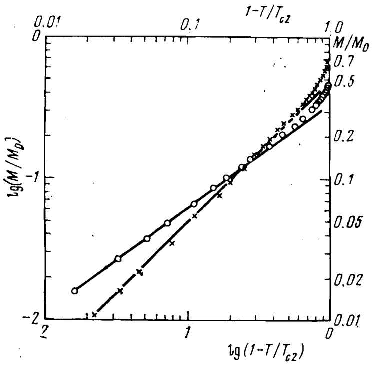

FIG. 4. Dependence of remanent moment on reduced temperature for compound of $NiCl_2$ (circles) and $CoCl_2$ (crosses) with graphite.

to which the magnetization curves are determined by a single parameter, the exchange integral between nearest spins, whereas the effect of magnetic anisotropy can be neglected in strong fields. At the same time, the presence of phase transitions is of necessity connected with anisotropy of the real magnets, and this finds expression in an anomaly of the magnetic properties of the specimens studied at weak fields.

SPECIFIC HEAT

Phase transitions in layered ferromagnets are observed also in study of their magnetic specific heat. The specific heat of the compound of $NiCl_2$ with graphite goes through a marked maximum at temperature 20.2 K[3]. This anomaly corresponds to transition of the compound from the paramagnetic state to the intermediate state with infinite initial susceptibility. The transition to the ordered state, which should occur in the vicinity of 18 K, cannot be detected. Apparently this transition is weakly manifested, and the increase of the specific heat does not exceed the experimental accuracy.

The phase transitions show up much more clearly in the compound of $CoCl_2$ with graphite. This is due primarily to the fact that here the phase transitions occur at lower temperatures. The relative contribution of the magnetic specific heat, as compared with the lattice specific heat, will be significantly higher in this case than for the compound of $NiCl_2$ with graphite. Figure 5 shows the specific heat of the compound of $CoCl_2$ with graphite in the temperature range from 3 to 14 K. The specific heat and the temperature are plotted in logarithmic coordinates; this makes it possible to show more graphically the law of variation of specific heat with temperature. At a temperature around 9 K the specific heat has a maximum, which indicates a phase transition. For a more detailed analysis, it is necessary to separate from the total specific heat its magnetic part.

For an absolute majority of solids, the lattice specific heat at low temperatures varies, in accordance with Debye's law, as T^3. This law corresponds to the model of a solid as a continuous elastic medium having three dimensions in space. But if the coupled atoms form a two-dimensional structure, then the law of variation of the specific heat should be quadratic:

$$C=aT^2. \tag{9}$$

For graphite, a quadratic dependence of the specific heat is observed from 50 K down to helium temperatures, where interaction between the graphite layers begins to show up, and also the conduction electrons begin to make an appreciable contribution.[5,6] In the same Fig. 5, the dotted line shows the specific heat of graphite. It is obvious that for the compound under study, the principal contribution to the lattice specific heat at low temperatures comes from the $CoCl_2$ layers, since the specific heat of graphite is orders of magnitude smaller than the specific heat of the compound of $CoCl_2$ with graphite.

We make two suppositions regarding the lattice specific heat. First, we assume that the temperature variation of the specific heat is subject to the law (9). This means that the coupling forces between neighboring layers in the present compound and in pure graphite are quantities of the same order of magnitude. Second, the lattice specific heats of the compounds of $CoCl_2$ and of $NiCl_2$ with graphite are completely identical, provided the chloride content of the specimens is the same. Both suppositions are entirely natural, and they allow us to determine the lattice specific heat of both layered compounds.

The specific heat of the compound of $NiCl_2$ with graphite is also shown in Fig. 5. We note that the magnetic specific heat for this compound is comparatively small[3] and does not exceed 10% of the total specific heat. We shall therefore consider that the solid line, drawn according to the low experimental points for $NiCl_2$, corresponds to the lattice specific heat. This specific heat can be written in the form

$$C=8.5\cdot10^{-5}T^2 \text{ J/g-}^\circ\text{K}. \tag{10}$$

when the chloride content of the specimen is 45 weight %. The accuracy of formula (10) can be estimated as within 10% under the condition that both suppositions are correct over the whole temperature range.

Knowing the lattice specific heat, we can separate from the total specific heat its magnetic part. Figure 6 shows this specific heat in conventional coordinates. The maximum of the specific heat is located at T_{c1} = 8.8 K; this temperature corresponds to the transition from the paramagnetic state to the intermediate state with infinite initial susceptibility. The specific-heat curve is strongly asymmetric with respect to the tem-

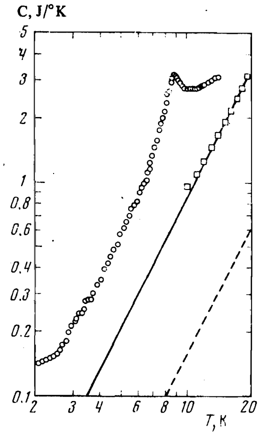

FIG. 5

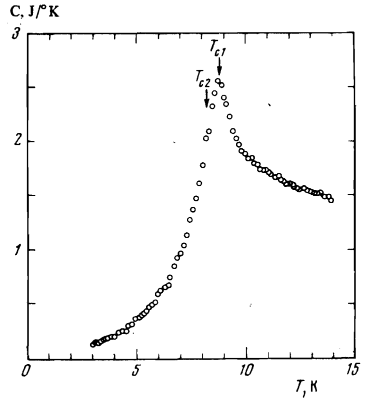

FIG. 6

FIG. 5. Temperature dependence of the specific heat (○) of the compound of $CoCl_2$ with graphite (CoCl₂ content 45.2 weight %). Dotted straight line, specific heat of graphite; solid straight line, lattice specific heat; □, specific heat of the compound of $NiCl_2$ with graphite.

FIG. 6. Magnetic specific heat of the compound of $CoCl_2$ with graphite.

perature T_{c1}: the right wing, corresponding to $T > T_{c1}$, is appreciably higher than the left, for which $T < T_{c1}$. This behavior of the specific heat is apparently a consequence of the bidimensionality of the compounds studied. The significant size of the magnetic specific heat for $T > T_{c1}$ is due to the anomalously large influence of short-range order, which is observed in two-dimensional magnets over a wide temperature interval from T_{c1} to $T \approx \Theta$.

For both the compounds investigated, the specific heat goes through no maximum at the temperature T_{c2} at which magnetic order originates. It is true, nevertheless, that for the compound of $CoCl_2$ with graphite a certain anomaly of the specific heat is observed in the vicinity of 8.2 K. With lowering of the temperature the specific heat falls sharply, but at 8.2 K there is noticeable on the smooth curve a definite irregularity, which may be regarded as a jump of the specific heat at the phase transition. It is obvious that the change of internal energy of the magnet connected with the transition to the ordered state is at least two orders of magnitude smaller than the analogous change of energy on transition from the paramagnetic to the intermediate state.

DISCUSSION

The properties of actual magnets are most completely and systematically reflected by the Heisenberg model. But the problem of phase transitions in the two-dimensional model has so far not been definitively elucidated. The possibility of such a transition was first pointed out by Rushbrooke and Wood[7], who noticed that in the two-dimensional case, the divergence of the high-temperature series expansion of the susceptibility is clearly traceable as far as the sixth term; this indicates a finite phase-transition temperature. Later Stanley and Kaplan used the values of the coefficients found by Rushbrooke and Wood and made a more careful analysis of the high-temperature susceptibility series[8]. They showed that the expansion coefficients vary completely regularly; therefore the existence of the phase transition in the two-dimensional Heisenberg model is as well substantiated as in the three-dimensional case.

Stanley and Kaplan considered also the problem of the nature of the low-temperature phase. Absence of spontaneous magnetization in a two-dimensional model[9] is not a proof of absence of phase transitions, since the spin correlations may be quite different above and below a certain critical temperature. Here arises a possibility in principle for the existence of a new magnetic phase in which spontaneous magnetization is absent, but the magnetic susceptibility is infinite.

After the work of Stanley and Kaplan, attempts were made to find higher terms of the expansion. In this the greatest success was attained by Yamaji and Kondo[10], who found eight terms in the expansion of the susceptibility and seven in the specific heat. Analysis of the newly found coefficients by the method of ratios, and also by Padé approximants, gave quite convincing evidence that the high-temperature series for the susceptibility and the specific heat do not diverge at finite temperatures. This means that there is no proof of the existence of phase transitions in the two-dimensional Heisenberg model.

On the other hand, a two-dimensional Bose liquid at low temperatures possesses the property of superfluidity, which has been quite well substantiated theoretically by many authors[11-14]. Here we have to do with an exceptional situation: long-range order is absent in a two-dimensional Bose system[15,16], but superfluidity none the less persists. The property of superfluidity in this case shows up in the presence of quantum vortices[13,14], which are due to a long-range potential, so that there are formed neutral groups with zero resultant circulation. Since a planar ferromagnet and a Bose liquid from the mathematical point of view are completely equivalent[17], a two-dimensional magnet should undergo a phase transition analogous to the transition of a Bose liquid to the superfluid state. The new property that emerges in a planar ferromagnet below the phase-transition point is a transverse stiffness, which corresponds to the density of the superfluid component ρ_s for a Bose system.

In the layered compounds that we have studied, the ferromagnetic exchange interaction that couples magnetic ions within each layer has a value of order 10^5 to 10^6 Oe. The uniaxial anisotropy that makes the plane of a layer a plane of easy magnetization is of order 10^3 Oe, while the hexagonal anisotropy within the plane of a layer is of order 10 Oe[1,2]. At sufficiently low temperatures $T < \Theta$, because of the uniaxial anisotropy, the compounds studied will be close in their properties to planar magnets.

The properties of a two-dimensional planar ferromagnet at temperatures below the phase-transition point were studied by Pokrovskiĭ and Uĭmin[18]. We shall compare certain deductions of this work with our experimental results. The dependence of the moment on the external field in the weak-field range has the form

$$M/M_0=(H/16J\rho_s)^{\Delta/(2-\Delta)}, \tag{11}$$

where

$$\Delta=T/4\pi J\rho_s. \tag{12}$$

and where J is the exchange integral. The index Δ increases monotonically with increase of temperature, and at the transition point it takes the value

$$\Delta(T_{c1})=1/\pi, \tag{13}$$

which corresponds to

$$M\sim H^{1/(2\pi-1)} \quad \text{at} \quad T=T_{c1}. \tag{14}$$

On comparison of theoretical results with experimental data, it is possible to state only qualitative agreement. The basic deductions of the theory regarding the absence of spontaneous ordering below the transition temperature and the power dependence of the moment on the external field $M \propto H^{1/\delta}$, where $\delta > 1$ and the initial susceptibility has an infinite value-all these deductions are confirmed experimentally. But in quantitative relationship, no agreement is perceptible. Thus, for both the compounds studied, the phase transition occurs at the temperature at which there is a breakdown of the linear relation between the field and the corresponding value of the magnetic moment. It may be considered that at the critical point the index $\delta = 1$, whereas theory gives the value $\delta \approx 5.28$.

We now consider the emergence of spontaneous ordering at temperature T_{c2}. It is obvious that this phase transition is due to the weak hexagonal anisotropy in the plane of the layer. As the analysis of Pokrovskiĭ and Uĭmin shows, turning on of an arbitrary weak uniaxial anisotropy in the plane of the layer leads to the appearance of a spontaneous moment; an intermediate phase with $\langle M \rangle = 0$ and $\rho_S \neq 0$ in this case does not appear. This phase is formed only when the lattice possesses axes of the third, fourth, and sixth orders. A spontaneous moment appears at temperature $T_{c2} < T_{c1}$ determined by the condition

$$\Delta(T_{c2}) = 2/p^2, \tag{15}$$

where p is the order of the axis of symmetry.

Precisely this situation is observed experimentally. Quantitative comparison of the critical temperatures found from formulas (13) and (15) with experimental data shows that the theory gives a much broader temperature range over which the intermediate phase should be observed. In this case also, despite the qualitative agreement of theory and experiment, a quantitative relation cannot be established.

The basic difference between the theory developed by Pokrovskiĭ and Uĭmin and the experimental data consists in the fact that actual systems are not planar magnets. The fact that the magnetic moment of the system is a three-component vector and that its behavior must be considered in three-dimensional space forbids us to identify a planar magnet and the actual system. It is obvious that the presence of a plane of easy magnetization makes the properties of the compounds under study similar to the properties of a two-dimensional planar model, but that for quantitative comparison a more rigorous theory is necessary.

In closing, I express my deep gratitude to Yu. N. Novikov for providing the specimens of layered graphite compounds.

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