Investigation of the heat capacity of the compounds $Ni_xCo_{1-x}Cl_2$ at low temperatures

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The heat capacity of the compounds $Ni_xCo_{1-x}Cl_2$ was investigated in the range of concentrations x from 0 to 1 at temperatures 2–28 K. The results were compared with the conclusions of the theory of spin waves for layered antiferromagnets with easy-plane anisotropy. The singularities of the temperature dependence of the magnetic heat capacity of the $Ni_xCo_{1-x}Cl_2$ compounds are attributed to the change of the effective constants of their magnetic spectrum and of the value of the zone boundary with respect to k_z.

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The heat capacity of the mixed compounds $Ni_xCo_{1-x}Cl_2$ was investigated in a wide range of concentrations at temperatures 2–28 K. The initial layered antiferromagnets $NiCl_2$ and $CoCl_2$ have an isomorphous crystal structure of type D^5_{3d} with close values of the parameters; the hexagonal layers of the metal ions are separated in them by two layers of Cl ions, and the principal symmetry axis C_3 is directed perpendicular to the plane of the layer. A similar structure is possessed by the mixed compounds $Ni_xCo_{1-x}Cl_2$. X-ray diffraction investigations of several samples reveals the D^5_{3d} structure and do not indicate an appearance of additional lines.[1)]

The heat capacities of $NiCl_2$ and $CoCl_2$ were previously investigated in the high-temperature region[1–3]: the antiferromagnetic-transformation temperatures T_N are 52.3 K for $NiCl_2$ (Ref. 2) and 24.7 K for $CoCl_2$ (Ref. 3). The heat capacities of $CoCl_2$ and $NiCl_2$ in the low-temperature region were investigated in Refs. 4 and 5. The antiferromagnets $NiCl_2$ and $CoCl_2$, as first proposed by Landau,[6] are characterized by the presence of a strong ferromagnetic interaction between metal ions located in the layer, and a weak antiferromagnetic interaction between metal ions in neighboring layers.

The spins in $CoCl_2$ are oriented in a basal plane in which the anisotropy is small,[7] and a strong anisotropy of the magnetization is observed when the spins deviate from the basal plane.[8] The antiferromagnet $NiCl_2$, in contrast to $CoCl_2$, is practically isotropic[8] and the spins in it also lie in the basal plane. The singularities of the anisotropies of $CoCl_2$ and $NiCl_2$ were considered theoretically in Refs. 9 and 10. A feature of $CoCl_2$ is the presence of strong anisotropy of the exchange interaction.

The energy spectrum of layered antiferromagnets with easy-plane anisotropy was calculated theoretically, and in the discussion of the experimental data of the present paper use is made of Yoshimori's calculations[11] of the temperature dependence of the magnetic heat capacity. Yoshimori considers two types of Hamiltonian for $NiCl_2$ and $CoCl_2$, respectively. For $NiCl_2$ (spin $s = 1$ for Ni_{+2}) account is taken of the isotropic ferromagnetic interaction A, between the nearest metal ions in the layer, of the isotropic antiferromagnetic interaction B between the nearest metallic ions in the nearest layers, and of the small anisotropic term Ds_z^2 (z is the principal symmetry axis). The Hamiltonian of $CoCl_2$ (effective spin $s = \frac{1}{2}$ for Co^{+2} contains an isotropic and anisotropic part A and D_1 respectively of the ferromagnetic interaction between the metal ions in a layer, and an isotropic and anisotropic part B and D_2 respectively of the antiferromagnetic exchange interaction between the layers. It follows from the theory that the energy spectrum of easy-plane layered antiferromagnets contains two branches: low-frequency with small gap and high-frequency with gap $\Delta_1 = 2s(BD)^{1/2}$, where $D = D_1 + D_2$ in the case of $CoCl_2$. It is shown that if A is substantially larger than B and the anisotropy D is small, spin waves with wave vector directed along the z axis reach the zone boundary at lower energies than in other directions. The low-frequency spin waves are similar then to waves in a three-dimensional antiferromagnet and at low temperatures the magnetic heat capacity varies like T_3. High-frequency spin waves with energy exceeding the limiting energy in the k_z direction are similar to the waves of a two-dimensional ferromagnetic system; with increasing temperature, the T^3 law for the magnetic heat capacity changes than into a linear law.

The value of the critical field that destroys the antiferromagnetism of $NiCl_2$, $H_c = 4Bs/g\mu_B = 129$ kOe (Ref. 12) and from the value of the gap of the high-frequency branch $\Delta_1/k_B = (2s/k_B)(BD)^{1/2} = 3.73$ K (Refs. 13 and 14) yield the values $B/k_B = J_2z_2/k_B = 4.6$ K and $D/k_B = 0.8$ K for $NiCl_2$ ($z_2 = 6$ is the number of nearest neighbors in neighboring layers, J_2 is the exchange integral between the nearest ions of the metal in neighboring layers, $s = 1$ and $g = 2.23$). The estimated limiting energy in the k_z direction for $NiCl_2$ is[11] $h\omega/k_B = 2Bs/k_B + Ds/2k_B \approx 10$ K.

The heat capacity of $NiCl_2$ was investigated earlier at low temperatures from 2 to 30 K (Ref. 15); a linear temperature dependence of the magnetic heat capacity, which is typical of a two-dimensional ferromagnet, was observed above 13 K.

In $CoCl_2$, as shown by nuclear-resonance investigations,[15] the magnetization of the sublattices varies between 2 and 14 K in proportion to $T2$, i.e., $CoCl_2$ has below 14 K the properties of a three-dimensional antiferromagnet. The limiting energy in the k_z direction in $CoCl_2$ is high and coin-

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cides with the value of the gap of the high-frequency branch of the spectrum.[11] According to data on antiferromagnetic resonance, it is equal to $\Delta_1/k_B = (2s/k_B)(BD)^{1/2} = 27.3$ K, and the saturation field in the plane of the basis amounted in $CoCl_2$ is $H_c = 4Bs/g_\perp\mu_B = 32$ kOe (Ref. 16). These data yielded the values $B/k_B = J_2z_2/k_B = 6.5$ K and $D/k_B = 115$ K ($g_\perp = 6$ and $s = \frac{1}{2}$ for Co^{+2}).

We have investigated here the heat capacities of five $Ni_xCo_{1-x}Cl_2$ compounds with concentration x between 0 and 1:

Compound No.	I	II	III	IV	V
x:	0.095	0.18	0.31	0.80	0.905

The compounds were prepared by melting a mixture of the anhydrous halides of Ni or Co, placed in a sealed quartz ampoule, at a temperature ~1100 °C; the melt was kept at this temperature for several hours and was then cooled slowly.

The samples have a distinctly pronounced layered structure, just as the initial chlorides of Co and Ni, and are easily split along the cleavage planes. According to chemical analysis, the straggling of the concentration over the sample volume is $\Delta x \sim 0.005$.

The measurements of the heat capacity were carried out in the temperature range 2–28 K for compounds I, II, and IV, and between 4 and 28 K for compounds III and V. The heat-capacity measurement procedure was described earlier.[17]

In Fig. 1, the data on the heat capacities of the investigated compounds and of pure $NiCl_2$ (Ref. 5) and $CoCl_2$ are plotted in coordinates C and T at temperatures between 10 and 28 K, with the data of Chisholm and Stout used for $CoCl_2$ above 10 K. The $C(T)$ curves for compounds I ($x = 0.095$) and II ($x = 0.18$) reveal sharp heat-capacity peaks with a maximum at 24.85 K, i.e., near the maximum for $CoCl_2$ ($T_{IV} = 24.7$ K). For compounds III ($x = 0.31$), no sharp peak was observed on the heat-capacity curve, and the maximum became smoothed out. In compounds IV ($x = 0.80$) and V ($x = 0.905$) there is no hump at all near 25 K on the heat-capacity curve.

The weak shift of T_N in samples with small Ni content seems to indicate that the Co–Ni exchange bond is of the amd order as the Co–Co bond. The vanishing of the peaklike temperature dependence of the heat capacity with increasing Ni^{+2} concentration points to the existence of a critical concentration of the order of $x_c \sim 0.30$, at which the abrupt phase transition vanishes. At $x > x_c$ there exists apparently a concentration region in which a disordered state is established in the $Ni_xCo_{1-x}Cl_2$ compounds.

The heat capacity of the compounds $Ni_xCo_{1-x}Cl_2$ at helium temperature is shown in $C(T)$ coordinates in Fig. 2; the same figure shows data on the heat capacities of $NiCl_2$ and $CoCl_2$ (Ref. 4). It can be seen that the heat capacity of $NiCl_2$ is substantially larger than the heat capacity of $CoCl_2$

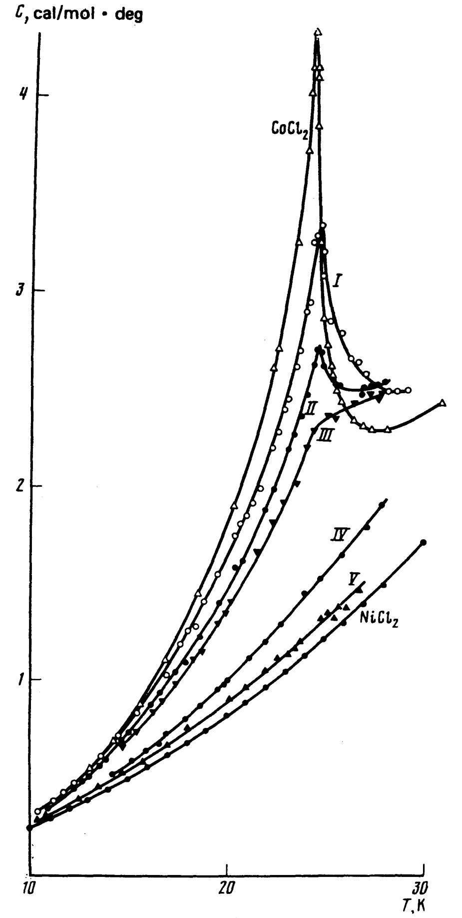

FIG. 1.

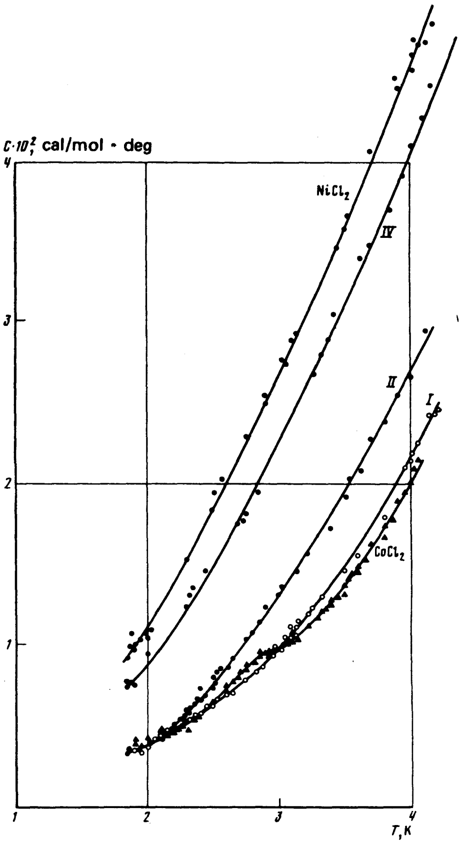

FIG. 2.

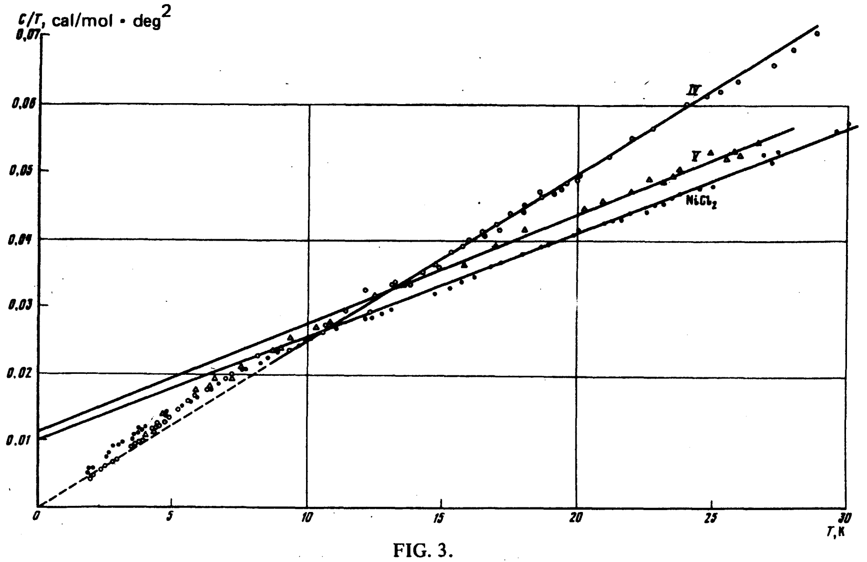

FIG. 3.

at helium temperatures, and the heat capacity of $Ni_xCo_{1-x}Cl_2$ compounds is intermediate between them. The small hump on the heat-capacity curve of $CoCl_2$ is apparently due to the presence of traces of water in the strongly hygroscopic cobalt chloride. The aqueous cobalt chloride has $T_N \sim 2.3$ K.

Figure 3 shows, in coordinates C/T and T, the heat capacities of compounds IV and V with small contents of Co^{+2}, and the data for $NiCl_2$ in the temperature range 2–30 K. Above 13 K the heat capacity of $NiCl_2$ is close to

$$C\,[\text{cal/mol} \cdot \text{deg}] = 1.55 \cdot 10^{-3}\, T^2 + 0.0098\, T.$$

The linear term in this relation is the magnetic contribution typical of a two-dimensional ferromagnet, while the quadratic term is the lattice heat capacitance.[5] The laws governing the variation of the heat capacities of the compound V and of $NiCl_2$ are analogous; above 14 K the heat capacity of the compound V can be described by the relation

$$C\,[\text{cal/mol} \cdot \text{deg}]\,] = 1.62 \cdot 10^{-3}\, T^2 + 0.0113\, T.$$

The lattice contribution to the compounds V is practically the same as that of $NiCl_2$.

The transition away from the T_3 law to a linear law with rising temperature was considered theoretically for layered lattices by I. M. Lifshitz[18]; a major role is played by the phonon-spectrum branch containing the term of the fourth order in the wave vector **k**. In the transition region $\omega^2 = ak^4 + bk_z^2$, $k^2 = k_x^2 + k_y^2$, the heat capacity of more the more lattice varies like T^2.

From the value of the linear term of the magnetic heat capacity, using the approximation of a two-dimensional ferromagnetic system[11] ($h\omega \approx 2Ask^2$, $k^2 = k_x^2 + k_y^2$ and $s = 1$ for Ni^{+2})

$$C_{\text{mag}} = R\frac{\pi}{12}\frac{k_BT}{2As} = 0.0098T,$$

an estimate was obtained for the ferromagnetic-interaction constant in a layer of $NiCl_2$ (Ref. 5):

$$\frac{2A}{k_B} = \frac{3}{2}\frac{J_l}{k_B} = 53\text{ K},$$

where J_l is the exchange integral in the layer.

The linear term of the magnetic heat capacity in compound V ($x = 0.905$) is $\sim 15\%$ larger than for $NiCl_2$. The increase of the linear term is apparently evidence of a decrease of the effective exchange interaction in the layer in the compound V for which $(2As/k_B)_{\text{eff}} = 45$ K.

In compound IV ($x = 0.80$) the linear temperature dependence of the magnetic heat capacity goes over into a quadratic one. The experimental points in Fig. 3 for the compound IV between 10 and 24 K lie on a straight line that passes through the origin, and the heat capacity of the compound IV in this temperature region is described by the expression

$$C\,[\text{cal/mol} \cdot \text{deg}] = 2.47 \cdot 10^{-3}\, T^2.$$

Assuming the lattice heat capacitance of compounds IV to be close to C_{lat} of $NiCl_2$ (as is the case in compound V), we can regard both the lattice heat capacity and the magnetic heat capacity of compound IV to be close to a T^2 law in the region of liquid-hydrogen temperatures, and that the magnetic contribution to the heat capacity of compound IV is of the order of

$$C_{\text{mag}} \approx 0.9 \cdot 10^{-3}\, T^2 \text{ cal/mol} \cdot \text{deg}.$$

Assuming that the significant terms in the spin-wave dispersion law in the region of the transition form a three-dimensional antiferromagnet into a two-dimensional ferromagnet are[11]

$$(h\omega)^2 = 2Ask^4 + 2Bs(2Bs + Ds/2)k_z^2, \qquad k^2 = k_x^2 + k_y^2,$$

we have for the heat capacity the T^2 law:

$$\frac{C_{\text{mag}}}{R} = 0.073\frac{T^2k_B^2}{As(B^2s^2 + DBs^2/4)^{1/2}}$$

(a calculation of C for a similar phonon dispersion law was carried out in Ref. 18).

In $NiCl_2$ the energy limit with respect to k_z is

$$h\omega/k_B = 2Bs/k_B + Ds/2k_B \sim 10\text{ K}.$$

It can be seen that with increasing concentration of Co^{+2} in the $Ni_xCo_{1-x}Cl_2$ compounds the limiting energy is

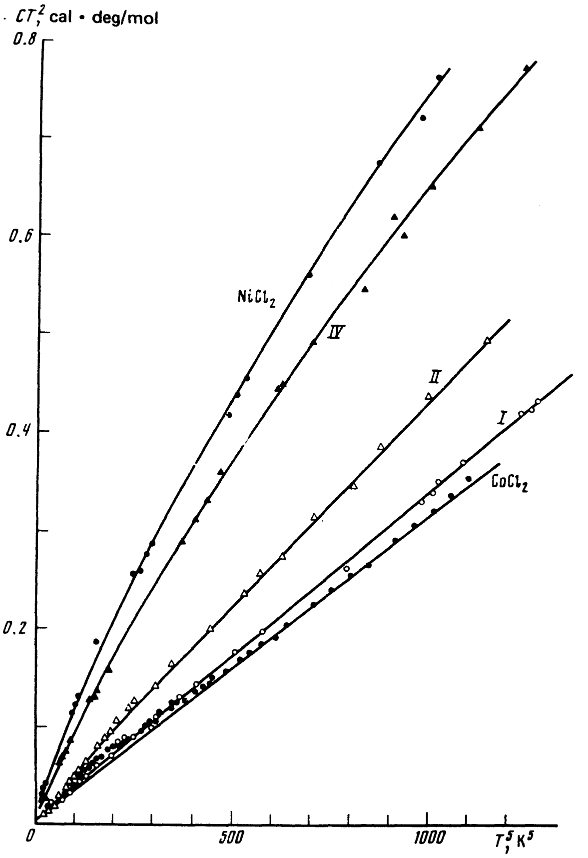

FIG. 4.

increased because of the increase of the effective value of the anisotropy $(Ds)_{\text{eff}}$ (the values of Bs in the initial chlorides of Ni and Co are of the same order, while those of Ds differ greatly) and the region of the quadratic magnetic heat capacity in compound IV lies above 10 K.

Figure 4 shows, in coordinates CT^2 and T^5, data on the heat capacities of compounds I, II, IV, $NiCl_2$, and $CoCl_2$ at helium temperatures. Just as for $CoCl_2$, the temperature dependence of the heat capacity of compound I ($x = 0.095$) is close to cubic (the experimental points lie on straight lines), it can therefore be assumed that both the heat capacity of the lattice and the magnetic heat capacity vary in proportion to T^3. The chosen coordinates make it possible to estimate the contribution of the nuclear heat capacity in compound I and in $CoCl_2$ at

$$C_{\text{nuc}} \approx 6\cdot 10^{-3}\, T^{-2} \text{ cal/mol} \cdot \text{deg}$$

(the coefficient 6×10^{-3} corresponds to the intercept of the straight lines on the ordinate exis). The cubic term of the heat capacity of $CoCl_2$ at helium temperatures is $3.1\times 10^{-4}\, T^3$ cal/mol·deg, and for compound I its value is $3.4\times 10^{-4}\, T^3$ cal/mol·deg. The heat capacity of compound II ($x = 0.18$) has a nearly cubic temperature dependence, while that of compound IV ($x = 0.80$) and of $NiCl_2$ evidently does not.

In the temperature range 1.8–2.2 K the heat capacities of compounds I, II, and $CoCl_2$ are close, as can be seen from the data in Figs. 2 and 4. At higher temperatures, when a low-frequency spin-wave branch is apparently excited, the heat capacities of compounds I and II become larger than those of $CoCl_2$, owing to the increased magnetic contribution to the heat capacity. It should be noted that the gaps Δ_2/k_B of the low-frequency branches in $CoCl_2$ and $NiCl_2$ are 2.8 K and ~0.5 K (Refs. 19 and 20, respectively).

Recognizing that the magnetic heat capacity of $CoCl_2$ is described by an expression of the form[11]

$$\frac{C_{\text{mag}}}{R} = 0.66\frac{k_B{}^3 T^3}{8s^3 A B^{1/2} (B+D/4)^{3/2}},$$

the increase of the magnetic heat capacity of compounds I and II can be attributed to a decrease of the effective anisot-

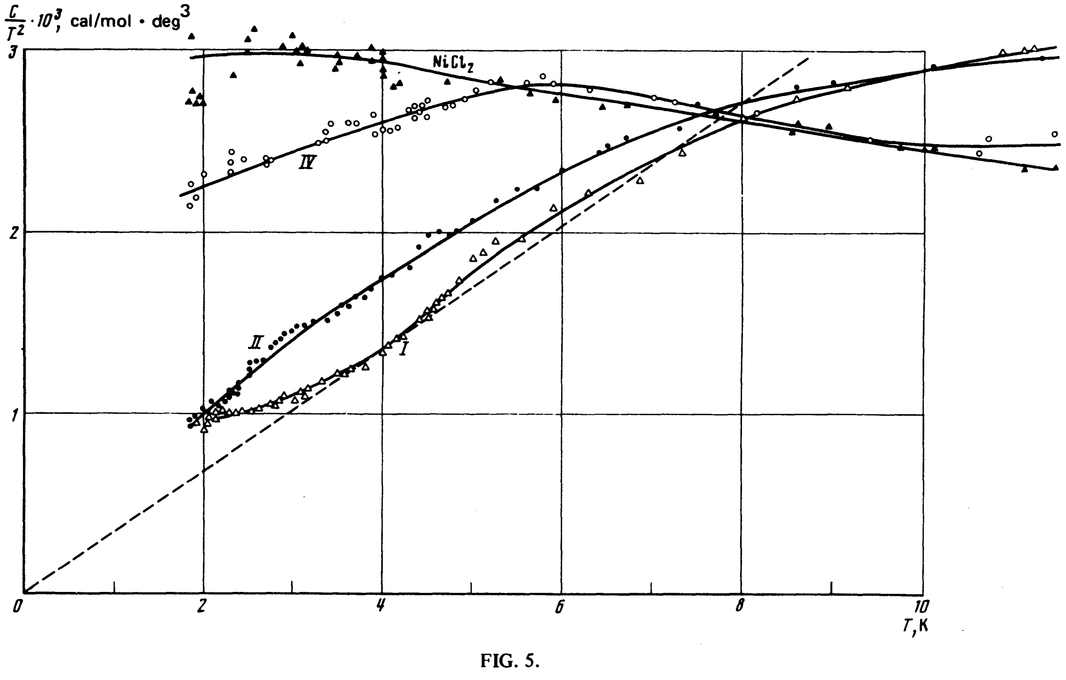

FIG. 5.

ropy $(Ds)_{\text{eff}}$ with increasing Ni^{+2} concentration, whereas the effective $(As)_{\text{eff}}$ apparently increases in this case, as follows from data for the compound V (the initial chlorides of Ni and Co have close values of Bs).

Figure 5 shows the data for NiCl_2 in the compounds I, II, and IV, plotted in coordinates C/T^2 and T, between 2 and 10 K. A rapid decrease of C/T^2 with decreasing temperature in compounds I and II sets in below 10 K. The temperature dependence of the heat capacity of compound I below 7 K is close to $3.4 \times 10^{-4}\ T^3$ cal/mol·deg (dashed straight line in Fig. 5) obtained in the region of helium temperatures; the deviation from this dependence below 3 K is due to the contribution of the nuclear heat capacity. In compound II, the temperature dependence of the heat capacity approaches cubic at helium temperature. In compound IV and in NiCl_2 the relation $C \propto T^3$ does not hold. The quantity C/T^2 in compound IV first increases between 10 and 5 K and begins to drop only below 5 K. For NiCl_2, the value of C/T^2 increases with decreasing temperature from 10 to 4 K, and is practically constant at helium temperatures.

The foregoing data indicate that the transition to the three-dimensional ferromagnetism (the $C_{\text{mag}} \propto T^3$ law) in the investigated $\text{Ni}_x\text{Co}_{1-x}\text{Cl}_2$ compounds compared with NiCl_2, sets in at higher temperatures that increase with increasing Co^{+2} in the compound; the energy limit with respect to k_z increases in this case. The singularities of the temperature dependence of the magnetic heat capacity of the $\text{Ni}_x\text{Co}_{1-x}\text{Cl}_2$ compounds can apparently be attributed to the change of the effective constants of their magnetic spectrum and of the value of the zone boundary relative to k_z.

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