Anomalies of the specific heat of $Ni_xMn_{1-x}Cl_2$ alloys at low temperatures

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The specific heat of six alloys of the system $Ni_xMn_{1-x}Cl_2$ were measured in a wide range of concentrations in a temperature range 2–28 K. The behavior of the alloys in the phase-transition region is investigated at Ni^{+2} concentrations lower than critical. At low Mn^{+2} concentrations, anomalies of the specific heat, due to the weakly-bound impurity have been observed in the alloys. The effective molecular field acting on the Mn^{+2} impurity is estimated.

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We have investigated the specific heat of alloys of the layered antiferromagnets $NiCl_2$ and MnC_2 in the temperature region 1.5–28 K. The initial antiferromagnets have isomorphic crystal structures of the $CdCl_2$ (D_{3d}^5) type with close values of the parameters. Hexagonal layers of metallic ions alternate in them with two layers of Cl ions, and the principal symmetry axis C_3 is perpendicular to the plane of the layer.

The magnetic properties of the chlorides of Mn and Ni differ greatly. The $NiCl_2$ crystal in the antiferromagnetic state has anisotropy of the easy plane type and is practically isotropic above and below T_N. The temperature of the antiferromagnetic transition in $NiCl_2$ has been found from calorimetric data to be $T_N = 52.3$ K.[1] Its magnetic properties, as first proposed by Landau,[2] indicate that a strong isotropic ferromagnetic interaction A acts in the layer between the metal ions, and a weak antiferromagnetic coupling B exists between the layers.

The energy spectrum of layered antiferromagnets with easy-plane anisotropy was investigated theoretically in the last few years.[3,4] The spectrum has two branches, low-frequency and high-frequency, each with a gap, and since A is larger than B in $NiCl_2$ and the anisotropy is small, a transition to a two-dimensional ferromagnetic system takes place already at low temperatures. The T^3 dependence of the magnetic specific heat gives way to a linear one in this case.

The low-frequency branch of the antiferromagnetic resonance in $NiCl_2$, with a small energy gap $\Delta_1 \sim 3.5$ kOe, was observed in experiment,[5,6] i.e., the excitation spectrum in $NiCl_2$ starts out from small values of the energy (~0.3 K). The antiferromagnetic interaction between the layers $B/k_B = \mu_B H_E/k_B = 4.6$ K was determined from the value of the critical field $H_c = 2H_E + H_A = 129$ kOe[7] that destroys the antiferromagnetism, and from the value of the high-frequency gap $\Delta_2 = (2H_E H_A)^{1/2} = 27.7$ kOe[8,9] ($H_A = 5.6$ kOe, $H_E = 68.2$ kOe).

The specific heat of $NiCl_2$ was investigated earlier at low temperatures from 2 to 30 K.[10,11] Above 14 K, the specific heat is given by the relation

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

where the linear term is the magnetic contribution typical of a two-dimensional ferromagnet, while the quadratic term is the lattice specific heat. At helium temperatures the temperature dependence of the specific heat is close to quadratic.

The transition from the T^3 law to the linear one for the specific heat of layered lattices was discussed theoretically by I. M. Lifshitz[12]; an important role is played by the phonon-spectrum branch that contains a term of fourth order in the wave vector. In the transition region, the dispersion law is $\omega^2 = ak'^4 + bk_z^2$ ($k'^2 = a_0^2(k_x^2 + k_y^2)$) and the specific heat of the lattice varies like T^2. A quadratic temperature dependence of the lattice specific heat was observed in experiment, for example, in the nonmagnetic $CdCl_2$.[13] From the value of the magnetic specific heat of $NiCl_2$ above 14 K, using the two-dimensional ferromagnetic system approximation ($\hbar\omega \approx 2ASk'^2$ and spin number $S = 1$ for Ni^{+2})

$$C_{\text{magn}} = R\frac{\pi}{12}\frac{k_B T}{2A} = 0.0098\,T\left[\frac{\text{cal}}{\text{mole-deg}}\right]$$

the ferromagnetic interaction in the layer was estimated at[11]

$$2A/k_B = 53 \text{ K}.$$

From data at low temperatures, where the temperature dependence of the magnetic specific heat is close to quadratic,

$$C_{\text{magn}} = 0.0022\,T^2\left[\frac{\text{cal}}{\text{mole-deg}}\right],$$

an estimate $2A/k_B = 30$ K [11] was obtained. In this case terms $(\hbar\omega)^2 = (2A)^2k'^4 + (2B)^2k_z'^2$ were taken into account in the dispersion law[3] and the expression used for the magnetic specific heat was of the form

$$C_{\text{magn}} = R\frac{9}{4\pi}\frac{k_B^2 T^2}{AB} = 2.2 \cdot 10^{-3} T^2\left[\frac{\text{cal}}{\text{mole-deg}}\right],$$

with $B/k_B = 4.6$ K (the value of C for a similar phonon dispersion law was calculated in[12]). The discrepancy between the estimates of $2A/k_B$ is of the order of 35% and is possibly due to the limitations of the employed approximations.

The temperature of the transition from the paramagnetic to the antiferromagnetic state in $MnCl_2$, as obtained from calorimetric data, is $T_N = 1.96$ K.[14] Murray[15] has observed on the specific-heat curve a small

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additional maximum at $T=1.81$ K. Neutron-diffraction data for $MnCl_2$ [16] point to a complicated picture of the antiferromagnetic ordering below 1.96 K. The spins are oriented in the basal plane. The additional maximum on the specific-heat curve is attributed to some change in the character of the ordering below 1.81 K.

It appears that antiferromagnetic interaction predominates in $MnCl_2$, and the paramagnetic Curie point is negative: $\Theta=-3.3$ K.[17] Douglass and Straudberg[18] have investigated antiferromagnetic resonance in $MnCl_2$ and estimated, with account taken of the magnetization data, the values of the exchange field ($H_E=17$ kOe) and of the anisotropy field ($H_A=5$ kOe).

The present paper reports the results of an investigation of the specific heat of six alloys of the system $Ni_xMn_{1-x}Cl_2$, in which the concentration x was varied in the wide range from 0 to 1[1]:

Alloy No:	I	II	III	IV	V	VI
x:	0.095	0.235	0.35	0.65	0.875	0.945

The alloys were prepared by fusing a mixture of anhydrous chlorides of Mn and Ni at $T\sim1100$ °C (the melt was kept at this temperature for several hours, after which the temperature was slowly lowered). Chemical analysis has shown the scatter of the concentrations over the sample volume to be $\Delta x\sim0.005$.

The specific heat was measured by a previously developed procedure.[14] The specific heats of alloys I, II, and III were measured in the temperature range 1.5–12 K, and those of alloys IV, V, and VI between 2 and 28 K.

Figure 1 shows data on the specific heat of alloys I, II, and III and of pure $MnCl_2$ at helium temperatures. These data enable us to evaluate the character of the behavior of the specific heat in the phase-transition region; the data for $MnCl_2$ [14] were refined in the present study in the region of the second specific-heat peak at $T=1.81$ K.

It is seen that in alloy I ($x=0.095$) the temperature of the principal peak of the specific heat, corresponding to a transition from the paramagnetic to the antiferromagnetic state, is decreased: $T_{N\,\mathrm{I}}=1.77$ K as against the Neel temperature $T_N=1.96$ K of MnCl. For $NiCl_2$, the transition temperature is high, 52.3 K. The second maximum for the alloy I is possibly located below 1.6 K. In alloy II ($x_2=0.235$), a small peak is observed at $T_{N\,\mathrm{II}}=1.65$ K against the background of a broader maximum, and the specific heat at the maximum is noticeably smaller than for $MnCl_2$. In alloys III ($x_3=0.35$), no abrupt peak is observed on the specific-heat curve, and the maximum broadens noticeably and becomes smoother; the specific heat at the maximum is half as large as for $MnCl_2$.

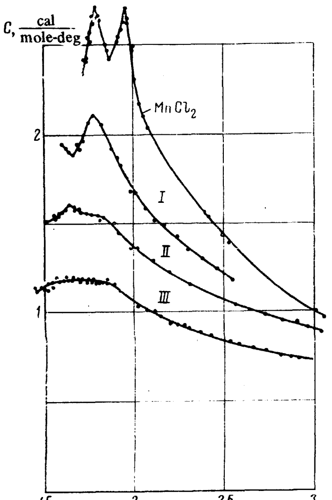

FIG. 1.

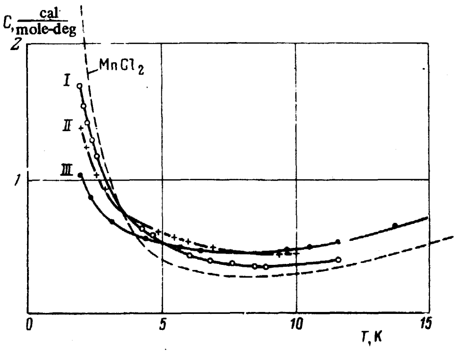

FIG. 2.

The data on the specific heats of the alloys I, II, III, and of $MnCl_2$ between 2 and 12 K are shown in Fig. 2. The specific heat of these alloys above 4 K is larger than that of $MnCl_2$.

The alloy IV ($x=0.65$), which has a large Ni^{+2} content, has a rather smeared-out anomaly of the specific heat, whose smooth hump is shifted towards higher temperatures. A plot of $C(T)$ for this alloy is shown in Fig. 3. The vanishing of the steep peak-like variation of the specific heat as a function of temperature when the Ni^{+2} concentration is increased in the alloys seems to point to an existence of a critical concentration on the order of $x_c\sim0.35$, at which the abrupt phase transition vanishes. A decrease of T_N is observed at concentrations $x\leq0.24$. These effects can be attributed to competition of the ferromagnetic and antiferromagnetic interactions between the ions in the alloys, inasmuch as the antiferromagnetic coupling of the ions seems to predominate in $MnCl_2$, whereas in $NiCl_2$ the ferromagnetic interaction in the layer is large.

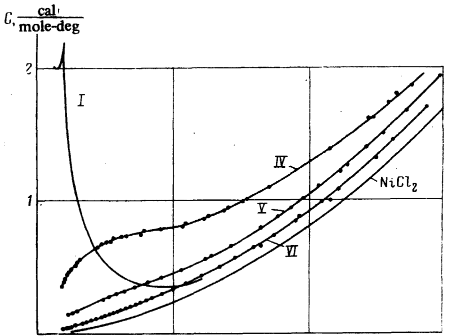

FIG. 3.

These questions were considered theoretically by Kasai *et al.*[20] for alloys of the ferromagnetic and antiferromagnetic components with different types of Ising lattice. Two critical concentrations were determined, for the ferromagnetic and antiferromagnetic transformations, respectively; a lowering of T_C and T_N was obtained, with a change of the concentrations of the component and with a vanishing of the specific heat peak as the critical concentration was approached.

The specific heats of the alloys IV, V, and VI, which have a large Ni^{2+} content, were investigated between 2 and 28 K. The data of these measurements, as well as the results for $NiCl_2$ and alloy I, are shown in Fig. 3 with C and T as the coordinates. It is seen that alloy IV ($x=0.65$) exhibits a rather smeared-out anomaly of the specific heat, and the plot of the specific heat lies much higher than that of pure $NiCl_2$. The maximum of the anomaly is located in the region of 6 K. The specific heats of alloys V ($x=0.875$) and VI ($x=0.945$) is also noticeably higher than the specific heat of $NiCl_2$ in the entire investigated temperature interval and is particularly large in comparison with the specific heat of $NiCl_2$ at low temperatures (below 10 K).

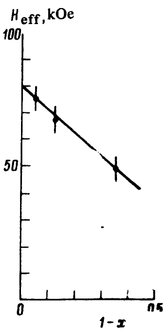

FIG. 5.

Figure 4 shows the temperature dependence of the difference ΔC_{magn} between the magnetic specific heats of the alloys IV, V, and VI, on one hand, and the magnetic specific heat of $NiCl_2$, on the other. The value of ΔC_{magn} was determined under the assumption that the lattice specific heat of the alloy has a value intermediate between the C_{lat} of $NiCl_2$ and $MnCl_2$ and proportional to their concentrations in the alloy. The specific heat of the $NiCl_2$ lattice was determined earlier[11] and its value at hydrogen temperatures is

$$C_{lat}=1.55\cdot 10^{-3}T^2\,[\text{cal/mole-deg}],$$

while Chisholm and Stout[21] cite for $MnCl_2$

$$C_{lat}=2.35\cdot 10^{-3}T^2\,[\text{cal/mole-deg}].$$

The difference between the lattice specific heats can be disregarded below 10 K, since it is of the order of 2–3% of the total specific heat of the alloys at 10 K and is negligibly small at low temperatures.

It is seen that ΔC_{magn} increases rapidly with rising temperature, reaches a maximum, and then falls off in the case of alloy IV, but changes little in the case of alloys V and VI. The maximum value of ΔC_{magn} is proportional to the concentration of the Mn^{+2} impurity in these alloys: $\Delta C_{magn}\propto(1-x)$ (the ratios of the maximal values of ΔC_{magn} and the ratios of the Mn^{+2} impurity concentrations in alloys IV, V and VI respectively are $0.61:0.21:0.09\approx 0.35:0.125:0.055$). These data suggest that the anomaly of the specific heat in the $Ni_xMn_{1-x}Cl_2$ alloys with small Mn^{+2} contents is due to low-energy excitations of the spin systems, which can occur if the coupling of the impurity with the matrix is weak, and lead to a noticeable increase of the spin specific heat at low temperatures.

Many authors have examined theoretically the character of the excitations due to magnetic impurities in a ferromagnet[22,23] and an antiferromagnet.[24] Experimental investigations of a weakly-coupled impurity in ferromagnets and antiferromagnets have also been reported. Thus, NMR was used to study the temperature dependence of the magnetization of Mn impurity in ferromagnetic iron[25]; electron impurity resonance was investigated in antiferromagnetic $FeCl_2$ with Mn^{+2} and Fe^{+3} impurities[26] and in antiferromagnetic $CoCO_3$ with Fe^{+2} impurity.[27] The impurity magnetic moment behaves in this system like a paramagnetic one in an effective field determined by the exchange coupling of the impurity and matrix spins (Dumesh *et al.*[27] took into account also the field of single-ion anisotropy of the Fe^{+2} impurity) and is proportional to the relative magnetization $M(T)/M(0)$ of the sublattices of the antiferromagnet[27] or the main ferromagnetic system.[25]

Figure 4 shows dashed the specific heats of alloys IV, V, and VI calculated in the approximation of a constant molecular field, when the specific heat per impurity atom is $C_{imp}=y^2B'(y)$ (where $B(y)$ is the Brillouin function, $y=g\mu_B SH_{eff}/k_BT$, and H_{eff} is the effective field in which the impurity spin is located; the spin of Mn^{+2} is

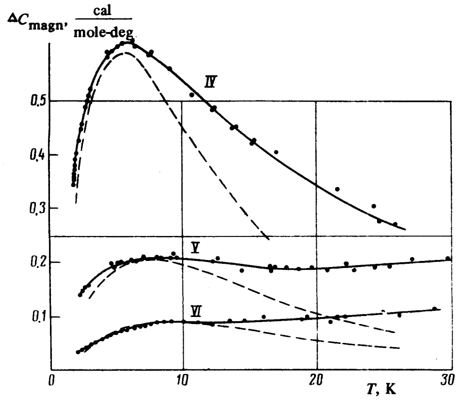

FIG. 4.

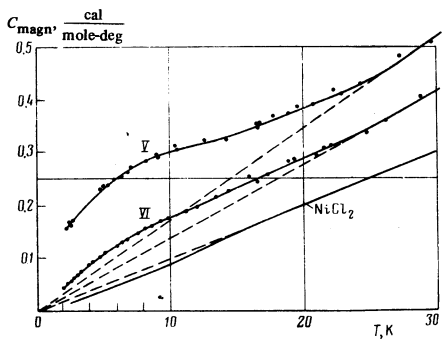

FIG. 6.

$S=5/2$). In the calculation of the impurity specific heat, the temperature of the maximum of the specific heat was assumed to be 5.5, 7.5, and 8.5 K for alloys IV, V, and VI, respectively. The estimated effective fields are (the uncertainty in the estimate of the maximum of the temperature is of the order of 1 K):

$H_{\text{eff}}=49\pm5$ kOe (alloy IV), $H_{\text{eff}}=67\pm5$ kOe (alloy V),

$H_{\text{eff}}=76\pm5$ kOe (alloy VI).

The dependence of H_{eff} on the Mn^{+2} concentration is shown in Fig. 5. No account is taken here of the temperature dependence of H_{eff}.

The $M(T)/M(0)$ dependence for pure NiCl_2 was investigated in[28]; the relative magnetization of the sublattices decreases by ~5% when the temperature is increased from 0 to 10 K, i.e., it is relatively weak at low temperatures. For alloys, this dependence is unknown.

The experimental data shown in Fig. 4 lie much higher than the calculated ones at high temperatures, apparently as a result of singularities in the disordering of the matrix spins. We have separated the magnetic part of the specific heat of alloy IV and estimated the magnetic entropy connected with the disordering process in this alloy between 1.5 and 30 K:

$$\Delta S_{\text{magn}}^{\text{alloy}} = \int_{1.5}^{30} \frac{C_{\text{magn}}}{T}\,dT \approx 1.7\,\frac{\text{cal}}{\text{mole-deg}}\ .$$

The same entropy in pure NiCl_2, in the interval 1.5–30 K, is $\Delta S_{\text{magn}}\approx 0.26$ cal/mole-deg. The entropy of completely disordered spins of the Mn^{+2} in the alloy is

$S=(1-x)R\ln 6=1.22$ cal/mole-deg

and the difference

$\Delta S_{\text{magn}}^{\text{alloy}}-S=1.7-1.22=0.48$ cal/mole-deg

is almost twice as large as ΔS_{magn} in pure NiCl_2, i.e., the disordering of the spins in the alloy is large at 30 K and the degree of the disordering of the Ni^{+2} is larger in the alloy than in pure NiCl_2.

Figure 6, with coordinates C and T, shows the magnetic specific heat of the alloys V and VI with small content of the Mn^{+2} impurity content, and the magnetic specific heat of pure NiCl_2, which varies linearly with temperature above 14 K. It is seen that the specific heats of alloys V and VI at high temperatures come close to having a linear temperature dependence, but with a coefficient larger than NiCl_2 (dashed lines). This behavior of the specific heat can be due to singularities in the disordering of the matrix spins. For a ferromagnetic system with impurity atoms whose excitation spectrum has a resonant character, a similar effect was discussed by Wolfram and Hall[22]; when the impurity–matrix coupling is small and the impurity states are excited, the matrix spins closest to the impurity are strongly perturbed when T_C is approached, and become noticeably disordered.

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