

# Specific heat of alloys of the system $\text{Ni}_x\text{Mn}_{1-x}\text{Cl}_2$ at low temperatures

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We have investigated the specific heat of three alloys of the system  $\text{Ni}_x\text{Mn}_{1-x}\text{Cl}_2$ . In alloy I ( $x=0.093\pm 0.003$ ), a decrease was observed in the temperature of the transition from the paramagnetic to the antiferromagnetic state,  $\sim 9.6\%$  of  $T_N$  of  $\text{MnCl}_2$ . In alloy II ( $x=0.655$ ), a considerable disorder is observed, not accompanied by phase transitions. In alloy III ( $x=0.90$ ), a low-temperature anomaly of the specific heat was observed, apparently connected with a localized impurity level.

We have investigated the specific heat of alloys of two layered antiferromagnets,  $\text{MnCl}_2$  and  $\text{NiCl}_2$ , which have an isomorphic crystal structure of the  $\text{CdCl}_2$  type with nearly equal parameters.

The magnetic properties of the initial Mn and Ni chlorides are greatly different.

According to calorimetric measurement data, the temperature of the antiferromagnetic transition in  $\text{NiCl}_2$  is  $T_N = 52.3^\circ\text{K}$ .<sup>[1]</sup> The magnetic properties of  $\text{NiCl}_2$  offer evidence, as was first proposed by Landau,<sup>[2]</sup> that a strong ferromagnetic bond ( $A$ ) exists between the metal ions in the layer, and a weak antiferromagnetic interaction ( $B$ ) exists between the layers,  $\text{NiCl}_2$  has "easy plane" anisotropy and is practically isotropic above and below  $T_N$ .<sup>[3]</sup>

The energys spectrum of layered antiferromagnets with "easy plane" anisotropy, as shown by the theory,<sup>[4]</sup> contains two branches, of low and high frequency, with a gap. If  $A$  is much larger than  $B$  and the anisotropy is small, then a transition to a two-dimensional ferromagnetic system occurs already at low temperatures. The  $T^3$  law for the magnetic specific heat then goes over into a linear law.

The low-frequency branch of antiferromagnetic resonance was observed in  $\text{NiCl}_2$  experimentally.<sup>[5,6]</sup> It has a small energy gap  $\Delta_1 \sim 3.5$  kOe, i.e., the excitation spectrum in  $\text{NiCl}_2$  begins with small values of the energy ( $\Delta_1 \mu_B / k_B \sim 0.3^\circ\text{K}$ ).

The specific heat of  $\text{NiCl}_2$  was investigated at low temperatures from 1.8 to  $30^\circ\text{K}$ .<sup>[7,8]</sup> It was found that at helium temperatures the dependence of the magnetic specific heat of  $\text{NiCl}_2$  on the temperature is quadratic, and above  $14^\circ\text{K}$  it is close to linear. It was proposed that the  $T^2$  dependence reflects a singularity of the dispersion law of the spin waves in the region of the transition from the three-dimensional antiferromagnet to the two-dimensional ferromagnetic system. Taking into account the terms  $(\hbar\omega)^2 = (2A)^2 k_x^4 + (2B)^2 k_y^2$  in the dispersion law of [4], we get  $C_{\text{mag}} = R(9T^2 k_B^2 / 4\pi^2 AB)$ , where  $2A = (3/2)J_f B = J_{af} Z$ , and  $k^2 = \alpha^2(k_x^2 + k_y^2)$ . (The calculation of  $C$  for a similar phonon dispersion law was carried out in [16]). The low-temperature data below  $3^\circ\text{K}$ , where  $C_{\text{mag}} = 0.00218T^2$  cal/mole-deg, we estimated the constant of the ferromagnetic interaction in the layer,  $J_f/k_B = 20^\circ\text{K}$ ,<sup>[8]</sup> assuming  $B/k_B = 4.6^\circ\text{K}$ .

The exchange antiferromagnetic interaction between

layers  $B/k_B = \mu_B H_E / k_B = 4.6^\circ\text{K}$  was obtained from the values of the high-frequency gap  $\Delta_2 = \sqrt{2H_E H_A} = 27.7$  kOe<sup>[9,10]</sup> and the value of the critical field that destroys the antiferromagnetism,  $H_c = 2H_E + H_A = 129$  kOe<sup>[11]</sup> ( $H_A = 5.6$  kOe).

The temperature of the transition from the paramagnetic into the antiferromagnetic state for  $\text{MnCl}_2$  as obtained from calorimetric data is  $T_N = 1.96^\circ\text{K}$ .<sup>[12]</sup> A small additional maximum was observed in [13] on the specific-heat curve at  $T = 1.81^\circ\text{K}$ .

The neutron-diffraction data on  $\text{MnCl}_2$ <sup>[14]</sup> point to a complicated picture of antiferromagnetic ordering below  $1.96^\circ\text{K}$ . 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  $1.81^\circ\text{K}$ .

We have investigated the specific heat of three alloys of the system  $\text{Ni}_x\text{Mn}_{1-x}\text{Cl}_2$  with respective concentrations  $x_1 = 0.093$ ,  $x_2 = 0.655$ , and  $x_3 = 0.90$ .

The alloys were prepared by fusing a mixture of anhydrous chlorides of Mn and Ni at  $T \sim 1100^\circ\text{C}$  (the melt was kept at this temperature for several hours, and the temperature was then lowered slowly). According to the chemical analysis, the concentration spread  $\Delta x$  over the volume of the sample was  $\sim 0.005$ .

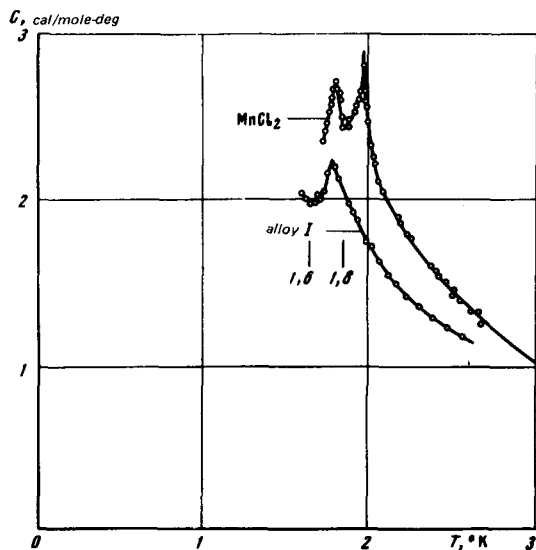


FIG. 1.

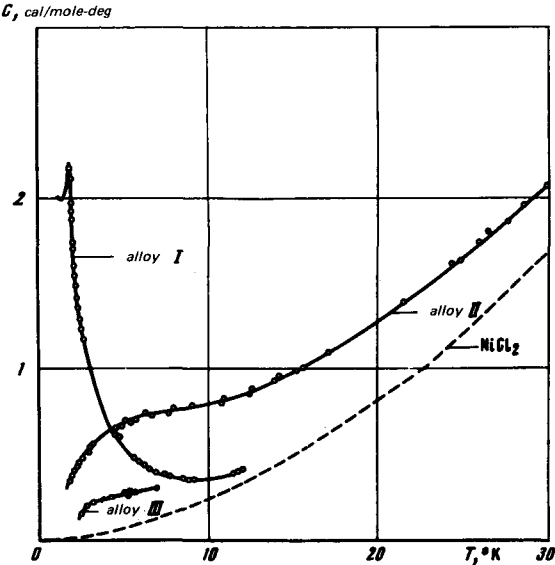


FIG. 2.

Figure 1 shows data on the specific heat of alloy I with concentration  $x_1 = 0.09_3$  and the specific heat of pure  $\text{MnCl}_2$ . The data on the specific heat of  $\text{MnCl}_2$ <sup>[12]</sup> were made more precise in our investigation in the region of existence of the second maximum of the specific heat at 1.81°K. It is seen that the principal specific-heat maximum, corresponding to the transition from the paramagnetic to the antiferromagnetic state, has shifted in alloy I towards lower temperatures,  $T_{\text{alloy}} = 1.77^\circ\text{K}$  as against  $T_N = 1.96^\circ\text{K}$  for  $\text{MnCl}_2$ . The transition of  $\text{NiCl}_2$  is high, 52.3°K. The second maximum of alloy I is evidently below 1.6°K.

Figure 2 shows data on the specific heats of alloys II and III with concentrations  $x_2 = 0.65_5$  and  $x_3 = 0.90$  and of alloy I ( $x_1 = 0.09_3$ ), plotted in coordinates  $C$  and  $T$ . The dashed curve in the figure shows the specific heat of pure  $\text{NiCl}_2$ .<sup>[7,8]</sup>

No sharp maximum is observed on the specific-heat curve of alloy II up to 30°K, whereas the specific curve of the alloy is appreciably higher than the curve of the pure  $\text{NiCl}_2$  in the entire temperature interval.

We have separated the magnetic part of the specific heat of alloy II and have estimated the magnetic entropy connected with the disorder process in alloy II between 1.5 and 30°K

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

The entropy of the completely disordered state of the spin system of alloy II is  $S_{\text{mag}} = 2.65 \text{ cal/mole-deg}$ , i. e., the degree of disorder of this alloy is high at 30°K and this disorder is not accompanied by a phase transition.

The specific heat of alloy III with its large Ni content (90 at. %) was investigated in the temperature range from 2 to 7°K. The specific heat of alloy III greatly exceeds that of  $\text{NiCl}_2$  at low temperatures (Fig. 2).

Figure 3 shows the temperature dependence of the difference  $\Delta C_{\text{mag}}$  between the specific heat of alloy II or III and that of pure  $\text{NiCl}_2$ . In the determination of  $\Delta C_{\text{mag}}$  it was assumed that the lattice specific heat of the alloy

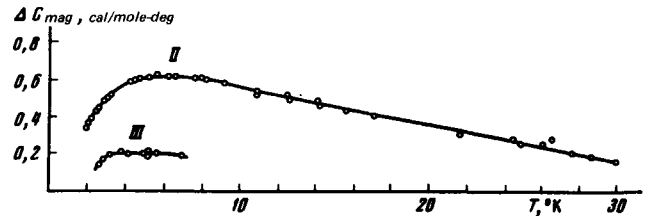


FIG. 3.

has a value intermediate between  $C_{\text{lat}}$  of  $\text{NiCl}_2$  and  $\text{MnCl}_2$ , proportional to their concentration in the alloy. Below 10°K, the difference between the lattice specific heats can be disregarded, since the contribution of the lattice is generally small at low temperatures (on the order of several per cent of  $C$  of the alloy).

We see that  $\Delta C_{\text{mag}}$  first increases sharply with increasing temperature, then stays practically constant, and begins to decrease at large  $T$ .

It can be assumed that the anomaly of the specific heat in alloys II and III is due to low-energy excitations of the spin system. These excitations can be attributed to the existence of impurities in the form of isolated small groups or in the form of individual atoms that are weakly bound to the matrix. The anomaly observed in alloy III recalls the anomaly of the specific heat of crystals with heavy impurity atoms, whose oscillation spectrum has a resonant character, as calculated by Kagan and Iosilevskii.<sup>[15]</sup> According to the calculations, the transition to the constant value of  $\Delta C$  occurs at  $T \gtrsim \hbar\omega_0/k_B$ , where  $\omega_0$  is the frequency of the localized level lying inside the energy band of the matrix. In our case, this is observed for alloy III at  $T \gtrsim 3^\circ\text{K}$ , with  $\Delta C_{\text{mag}} = (1-x)R = 0.2 \text{ cal/mole-deg}$ .

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