Specific heat of AMnX$_3$ crystals near the Neel temperature

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The critical parameters for $T < T_N$ and $T > T_N$ in the antiferromagnetic transition region are evaluated with a computer on the basis of calorimetric measurements for TlMnCl$_3$, RbMnCl$_3$, and KMnF$_3$ crystals. No appreciable effect of the anisotropy of the structural and magnetic properties of the crystals on the critical parameters is observed. For $10^{-3} < |T/T_N - 1| < 10^{-1}$ the temperature dependences of the specific heat can be described satisfactorily within the framework of the isotropic Heisenberg model.

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The theory of critical phenomena, established in recent years by means of the renormalization-group method, is extremely effective in describing physical properties near phase transitions in magnetic systems. For such systems there exists a relatively wide experimentally-accessible range of temperatures in the neighborhood of the transition temperature where well-deoped statistical fluctuations lead to an anomalous behavior of various physical quantities–in particular, the specific heat.[1-3] There have been a significant number of works in which the specific heat of various magnetic systems has been studied, as summarized in a number of reviews.[1,4-7]

Among crystals with a relatively simple structure and with a well-understood magnetic ordering, compounds with the general composition ABX$_3$ occupy a special place.[8,9] The thermal properties of these crystals in the neighborhood of magnetic phase transitions have not yet been extensively studied.

The selection of subjects in the present investigation was determined on the one hand by the fact that the magnetism of the halides AMnX$_3$ (with A either K, Rb, Cs, or Tl, and with X either Cl or F) is assumed, in a first approximation, to be determined only by spin. The Mn^{2+} ion has a small orbital component of the magnetic moment in the weakly-distorted octahedral environment of halogen ions. The physical properties of such compounds are usually described by the Heisenberg model.[4] Another reason for investigating crystals of the AMnX$_3$ series is that they can possess various structures, for example, cubic or distorted structures of the perovskite type (RbMnF$_3$, KMnF$_3$, and TlMnCl$_3$) and hexagonal six-layer structures (CsMnF$_3$ and RbMnCl$_3$).[9] This fact permits one to verify one of the predictions of critical-phenomena theory concerning the universality of the critical exponents in relation to type of structure a constant number n of components of the order parameter and at an effective lattice spacing d (in our case, $n=d=3$).[1-3] Thus, the specific heat of the crystals RbMnF$_3$ and CsMnF$_3$ with different structures is satisfactorily described within the framework of the theory of critical phenomena with the critical parameters ($\alpha=\alpha', A/A'$) that are characteristic of the Heisenberg model ($n=d=3$) in the temperature interval $10^{-3} < |\tau| < 10^{-1}$ ($\tau = T/T_N - 1$).[10,11]

It is also of interest to compare the specific heats of chloride and fluoride crystals near the Neel temperature.

The temperature dependence of the specific heat of the crystals TlMnCl$_3$ and RbMnCl$_3$ was measured with an adiabatic calorimeter utilized in earlier studies of KMnF$_3$ and TlMnCl$_3$[12,13] by the procedure described in Ref. 14. Single crystals of TlMnCl$_3$ and RbMnCl$_3$ grown from the melt by the Bridgman method were used in these experiments with respective masses of 15.763 and 6.030 g. The optical uniformity, together with the equality of the specific-heat maxima temperatures near T_N of two different specimens (preliminary specific heat measurements near T_N were conducted during a previous study of structural phase transitions[13]) provide evidence of the high quality of the thallium-magnesium chloride specimens. In comparison with TlMnCl$_3$, the optical quality of the RbMnCl$_3$ specimen was significantly lower.

The specific heats of the crystals TlMnCl$_3$, RbMnCl$_3$, and KMnF$_3$, whose measurements were reported in preliminary communications,[12,15] are shown as functions of T (Fig. 1) and $|\tau|$ (Fig. 2) in the vicinity of T_N.

The experimental behavior is approximated by functions of the type[10]

$$C_p = \frac{A}{\alpha}(|\tau|^{-\alpha}-1)+B+E\tau \tag{1}$$

for $T > T_N$ and with coefficients $\alpha', T_N', A', B', E'$ for

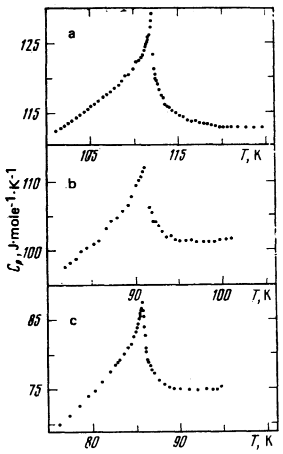

FIG. 1. Temperature dependence of the specific heat for the crystals: (a) TlMnCl$_3$ (b) RbMnCl$_3$ and (c) KMnF$_3$.

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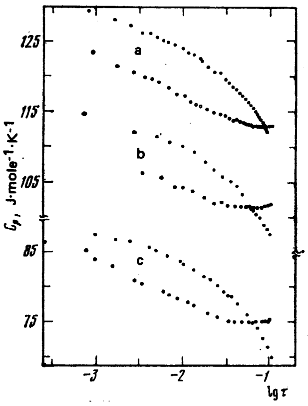

FIG. 2. Dependence of the specific heat on $\log|T/T_N - 1|$ for the crystals: (a) $TlMnCl_3$ (b) $RbMnCl_3$ and (c) $KMnF_3$ for $T < T_N$ (closed circles) and $T > T_N$ (open circles).

$T < T_N$. The inclusion in Eq. (1) of the term $E\tau$ eliminates the complicated process of calculating the separating by various methods the normal contribution to the specific heat of crystals. As shown in Ref. 10, near T_N an error in evaluating the normal contribution is equivalent to an error in the determination of E. Since the term $E\tau$ represents the normal contribution to C_p near T_N, it is appropriate to introduce in the analysis the condition $E = E'$.

The parameters of Eq. (1) were estimated simultaneously by direct computer scans for $T > T_N$ and $T < T_N$ using a least-squares technique. The magnitudes of α, α', T_N, T_N' and $E = E'$ varied within the intervals [-0.5 to 0.5], [$T_N - 0.5$ K to $T_N + 0.5$ K], and [$E - 10$ to $E + 10$ J/mole · K] with discrete steps of 0.02 K, 0.01 K, and 1 J/mole· K, respectively. A reduction in the spacing resulted in a change of less than 1% in the mean-square deviation s, which is the level of experimental error.

The intervals corresponding to a 95% confidence in the parameter values were calculated with a computer by a standard method.[16] The small change in the mean-square deviation from the fitted curve over the entire temperature interval in which the approximation was utilized allows one to assume that the measurement errors have a normal distribution.

In the analysis only experimental data in the interval $\tau_{\min} \le \tau \le \tau_{\max}$ were included. Because the minimum calorimetric step in the experiments[12,15] near T_N was ≈0.1 K for $TlMnCl_3$ and $KMnF_3$ and ≈0.2 K for $RbMnCl_3$, a $\tau_{\min}$ value of 10^{-3} was necessary to avoid the smeared region of the phase transition. With this $\tau_{\min}$ value only a few points near T_N were excluded from the calculation. The variation of $\tau_{\max}$ in the interval (6×10^{-2} to 10^{-1}) for $TlMnCl_3$ demonstrated that a reduction in $\tau_{\max}$ leads to an increase of s and, consequently, of the confidence intervals for the critical parameters of Eq. (1) while the values of the parameters themselves are essentially unchanged. For this reason, $\tau_{\max} \approx 10^{-1}$ was chosen for $RbMnCl_3$ and $KMnF_3$. For different types of crystals the values $\tau_{\min} \sim 10^{-3}$ and $\tau_{\max} \sim 10^{-1}$ turned out to be suitable for the determination of the critical exponents.[6,10,11]

TABLE I.

	$TlMnCl_3$	$RbMnCl_3$	$KMnF_3$	Heisenberg Model (n = d = 3)
$x = \lg|\tau|$	$-3.1 \le x \le 1.0$	$-2.8 \le x \le -1.0$	$-3.2 \le x \le 1.0$	
$T_N = T_N'$, K	112.13±0.02	91.34±0,07	85.78±0,01	
$\alpha = \alpha'$	−0.16±0.02	−0.20±0.06	−0.16±0.03	−0.09-−0,20 [17]
A, J/mole·K	6.848±0.458	7.21±1,96	7,15±0.90	
A', J/mole·K	5.066±0.540	5.19±1,13	4.12±0.64	
A/A'	1,35±0.23	1.39±0.68	1.73±0.49	1.24–1.52 [18]
B, J/mole·K	94.3±1.2	81.6±3.8	53.96±1.70	
B', J/mole·K	107.8±1.1	94.8±2,5	70,69±1.41	
$E = E'$, J/mole·K	54.0±4.6	67.0±10.6	76.0±5.9	
s, J/mole·K	0.1511	0.2350	0,2267	

An initial search for the parameters in Eq. (1) for $TlMnCl_3$ showed that imposing the physically-justified conditions $E = E'$ and $T_N = T_N'$, which lie within the confidence intervals, leads to an insignificant (less than 3%) increase in s. Moreover, if the region of smearing of the phase transition is excluded, then the condition $\alpha = \alpha'$, which follows from similarity theory, can be introduced. Analogous results were obtained in the works cited above.[6,11] Allowance for the above three equations decreases the number of parameters of the approximating function from 10 to 7. Accordingly, in the subsequent analysis we assume $E = E'$, $T_N = T_N'$, and $\alpha = \alpha'$.

The best estimates obtained for the parameters of the approximating function [Eq. (1)] for $TlMnCl_3$, $RbMnCl_3$ and $KMnF_3$ are listed in Table I, and the deviations of the experimental points from the theoretical smoothed curves are shown in Fig. 3.

The adequacy of the models (1) used for the approximation was estimated by the criteria of Pearson and Kolmogorov. In this evaluation a normal error distribution was assumed. For the results shown in Table I, the obtained probabilities of observing an error exceed 5% limit (30% for $TlMnCl_3$, and from 10 to 20% for $RbMnCl_3$ and $KMnF_3$), thus demonstrating the reliability of the approximation.

It should be noted that, due to the low quality of the $RbMnCl_3$ sample, it was impossible to investigate the neighborhood of T_N with a calorimetric step less than 0.2 K without a large increase in the scatter of experimental points. Consequently the values of the parameters of the approximating function [Eq. (1)] are less

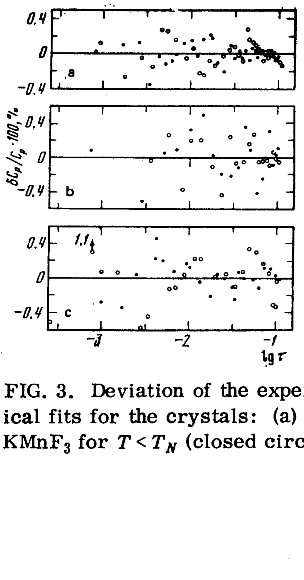

FIG. 3. Deviation of the experimental points from the theoretical fits for the crystals: (a) $TlMnCl_3$ (b) $RbMnCl_3$ and (3) $KMnF_3$ for $T < T_N$ (closed circles) and $T > T_N$ (open circles).

precise for $RbMnCl_3$ than for $TlMnCl_3$ and $KMnF_3$ as is evident from Table I.

From the results shown in Table I it follows that the values of the critical exponents $\alpha = \alpha'$ and of the amplitude ratios are, within their respective confidence intervals and for the constraints on α, T_N and E specified above, are in satisfactory agreement with the values calculated from various calculations for the Heisenberg model.[17,18]

The $AMnX_3$ crystals studied by us and by others[10,11] not only belong to different structure types but also posses a different symmetry within each structure type.[9,19] The fact that the critical parameters of these crystals, determined from specific-heat measurements, have identical values within experimental error, provides evidence for the universality principle that follows from symmetry theory.

As is known from Ref. 2, the effective anisotropy fields can alter the critical behavior in the immediate neighborhood of the phase-transition temperature. For example, on the basis of experiment it is assumed for the $CsMnF_3$ crystal that at $\tau \sim 10^{-3}$ the critical behavior of the specific heat changes from that typical of the isotropic Heisenberg model ($n = d = 3$) to that of the XY model ($n = 2, d = 3$).[11] The cause of this behavior, in the opinion of the authors of Ref. 11, is the presence in the $CsMnF_3$ crystal of a field of axial anisotropy $\approx 3 \times 10^{-3}$ relative to the exchange field. In this context it should be noted that, out of the considered $AMnX_3$ crystals, the most anisotropic with regard to symmetry[19] and values of the effective fields[20] is $RbMnCl_3$. It appears that in this crystal it may be possible to experimentally observe the effects of changes in the critical parameters in the immediate proximity of T_N. For this purpose, however, a higher quality sample is required.

The crystals considered in this work are of interest in another regard. In $KMnF_3$ and $TlMnCl_3$ the perovdkite structure which is cubic at room temperature becomes distorted as the Neel temperature is approached, undergoing two and three structural phase transitions, respectively. These distortions are characterized by mutual rotations of the BX_6 octahedra and lead to the following sequences of distorted phases: $O_h^1 \to D_{4h}^{18} \to D_{4h}^5$ for $KMnF_3$ and $O_h^1 \to D_{4h}^5 \to D_{2h}^{17} \to D_{2h}^{16}$ for $TlMnCl_3$.[21] Antiferromagnetic ordering appears in the last of these phases. A consequence of the structural distortions is the vanishing of the cancellation of sublattice magnetic moments, and transitions to the state of weak ferromagnetism below T_N.[22,23] This behavior takes place also in $RbMnCl_3$ as a consequence of the structural phase transition $D_{6h}^4 \to C_{2h}^2$ at 272 K.[19,20]

The results of the present work show that weak structural distortions, changing the final state of the magnetic system, do not produce a noticeable change of the critical exponent α of the ideal Heisenberg model.

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