Low-temperature heat capacity of the pseudo-one-dimensional magnetic systems CsMnCl$_3$·2H$_2$O, α-RbMnCl$_3$·2H$_2$O, and CsMnBr$_3$·2H$_2$O

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The heat capacity of the isomorphic pseudo-one-dimensional magnetic systems CsMnCl$_3$·2H$_2$O, α-RbMnCl$_3$·2H$_2$O, and CsMnBr$_3$·2H$_2$O has been analyzed using recently developed estimates for the lattice heat capacity of anisotropic media. The magnetic contribution in the paramagnetic region could be described very well by the $S = 5/2$ linear-chain Heisenberg model. The intrachain interaction is found as $J/k = -3.0$ K for the former two compounds and $J/k = -2.6$ K for the latter compound. The interchain interactions are smaller by two orders of magnitude. The results are compared with other experimental evidence. A study of the critical behavior of the magnetic entropy increase yields $\alpha' = \alpha = +0.10 \pm 0.01$ for all three substances.

I. INTRODUCTION

CsMnCl$_3$ · 2H$_2$O (CMC), α-RbMnCl$_3$ · 2H$_2$O (α-RMC) and CsMnBr$_3$ · 2H$_2$O (CMB) belong to a series of isomorphic compounds AMB_3 · 2H$_2$O with $A =$ Cs, Rb; $M =$ Fe, Co, Mn; $B =$ Cl, Br. Their crystallographic structure is orthorhombic with space group $Pcca$ and four formula units in a chemical unit cell.[1,2] Especially CMC has been the subject of a very large number of experimental investigations. The intrachain exchange interaction has been determined from susceptibility,[3] neutron diffraction,[4] and EPR studies.[5,6] The magnetic space group in the ordered state has been determined from NMR experiments as $P_{2b}c'ca'$.[7] The interchain interactions were estimated by a Green's-function method[7] and have been found experimentally from neutron diffraction,[4] EPR line shape,[6] and NMR studies.[8] Recently, a fairly consistent set of interactions has been determined from a spin-wave analysis of the susceptibility,[9] the magnetic heat capacity,[10,11] and sublattice magnetization[9,10] in the ordered state. The available evidence indicates that the ratio of the interchain interactions to the intrachain interaction is on the order of 10^{-2}–10^{-3}.

In a previous paper[12] we reported the experimental heat capacity of CMC in the temperature region 1.1–52 K. The data in the paramagnetic region were interpreted by assuming that the magnetic contribution to the heat capacity above 9 K could be represented by a Heisenberg $S = \frac{5}{2}$ antiferromagnetic linear-chain model. It was shown that the lattice contribution could not be described properly by the usual three-dimensional Debye model. Given the *chemically* layered structure of this compound, the lattice heat capacity was represented by a model proposed by Tarasov,[13] which was slightly modified to account for the different modes of vibration. The intrachain exchange interaction J/k was found from a simultaneous fit of both the lattice and the magnetic contribution to the data above 12 K as $J/k = -3.3 \pm 0.3$ K.

One should note that the model of Tarasov only offers a drastically simplified description of the lattice-dynamical problem—even in the acoustic limit—which may readily affect the determination of the magnetic heat capacity C_M, since in the paramagnetic region $C_L > C_M$. Recently, a more-refined model has been proposed,[14] which is particularly suitable for the description of the low-temperature lattice heat capacity of very anisotropic compounds, and involves only a small number of adjustable parameters. Because, moreover, reliable estimates for the heat capacity of Heisenberg magnetic linear-chain systems have been reported,[15,16] we thought it worthwhile to consider the experimental data on CMC in more detail. Secondly, specific-heat measurements were performed on the isomorphic α-RMC and CMB. The results on the latter two compounds may yield additional information about the applicability of the theoretical model for the lattice heat capacity, since the various isomorphs involve rather different atomic masses. On the other hand, by comparison of the magnetic behavior of CMC, α-RMC, and CMB the influence of both the intermediate alkali ion and the halide ions on the various magnetic interactions may be studied.

In the following analysis of the experimental data on CMC, α-RMC, as well as CMB, the lattice heat capacity will be described by the simplified form of the expression for the heat capacity of a layered structure given by[14]

$$C_L(T) = F_1(2\Theta_t, \Theta_c, T) + F_1(\Theta_t, \Theta_c, T)$$
$$+ F_2(\Theta_0, 2\Theta_c, T). \tag{1}$$

It was assumed that in the temperature region of interest the H$_2$O molecules vibrate as a whole and
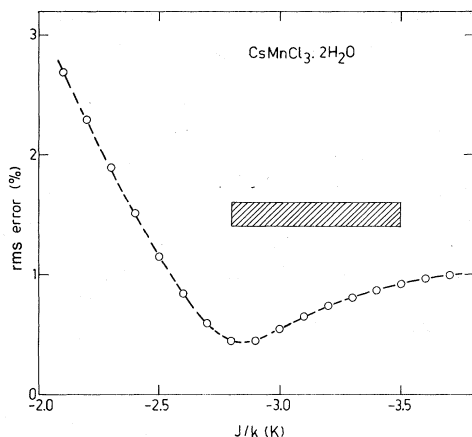
FIG. 1. rms error of fits to the experimental data on CsMnCl$_3\cdot$2H$_2$O between 9 and 52 K. The shaded bar denotes the region in which the total magnetic entropy increase amounts to R ln6 within the experimental uncertainty.

that rotational states are of no importance. This yields a total of seven vibrating units in a formula unit.

II. CsMnCl$_3\cdot$2H$_2$O

The data on CMC above 9 K were fitted simultaneously varying the three parameters $\Theta_t, \Theta_0, \Theta_c$ in the expression for the lattice-specific heat as well as the parameter J/k in the expression for the magnetic-specific heat, which was represented by the Heisenberg $S = \frac{5}{2}$ antiferromagnetic linear-chain model.[15] This yielded

$$J/k = -2.85 \pm 0.02 \text{ K}, \quad \Theta_t = 287 \pm 1.0 \text{ K},$$

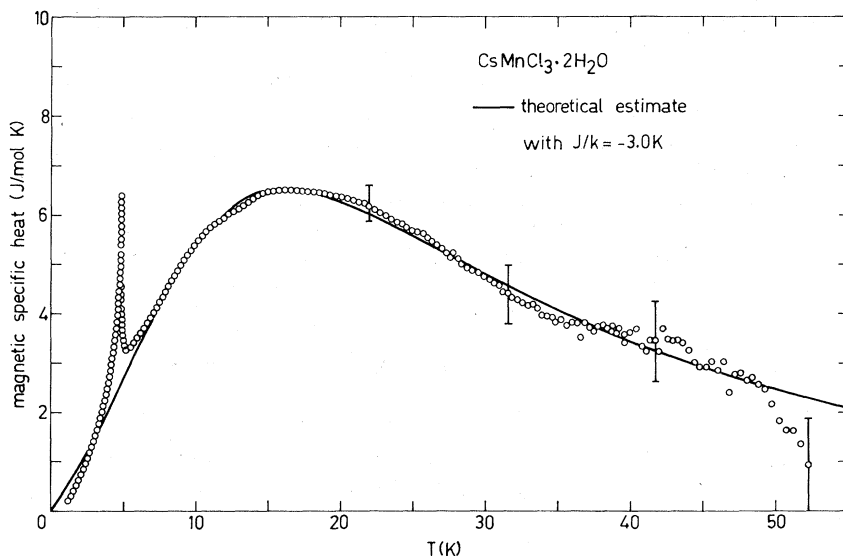$$\Theta_0 = 204 \pm 1.5 \text{ K}, \quad \Theta_c = 56.0 \pm 0.5 \text{ K}.$$

The quoted error bounds correspond to the uncertainty of the parameter values assuming that the deviations are purely statistical in nature. The actual uncertainty, however, may be larger. Since we are primarily interested in the value of the exchange interaction J/k, we performed several fits in which this parameter was fixed at a certain value. In Fig. 1 the rms error of these fits is plotted as a function of J/k. Since in the neighborhood of the minimum the error varies rather slowly with the parameter J/k, the uncertainty was estimated independently by considering the total magnetic entropy associated with these fits. The magnetic entropy increase ΔS was determined in a similar way as described in Ref. 12. It appeared that ΔS did agree with the theoretical value R ln6 within the experimental error for $-2.8 > J/k > -3.5$ K, which is indicated by the shaded bar in Fig. 1. The intrachain interaction was estimated as a weighed average of both procedures outlined in this figure as $J/k = -3.0^{+0.2}_{-0.4}$ K. The experimental magnetic heat capacity $C_{\text{expt}} - C_{L,\text{calc}}$ is represented by open circles in Fig. 2. The drawn curve denotes the theoretical estimate for a $S = \frac{5}{2}$ Heisenberg linear-chain system with $J/k = -3.0$ K. The error bars reflect the uncertainty in the determination of the *total* heat capacity (~1%). Inspection of this figure shows a good agreement between experiment and theory above 9 K.

The magnitude of the intrachain exchange interaction in CMC inferred from the present analysis is somewhat smaller than the magnitude given in Ref. 12. Both results, however, are well within the range of values reported in the literature. On the other hand, the present estimate for the magnetic contribution in the ordered state, which is

FIG. 2. Magnetic heat capacity of CsMnCl$_3\cdot$2H$_2$O. The open circles correspond to $C_{\text{expt}} - C_{L,\text{calc}}$, the error bars reflect the uncertainty in C_{expt}. The drawn curve denotes the theoretical estimate for a $S = \frac{5}{2}$ Heisenberg linear-chain system with $J/k = -3.0$ K.

based upon extrapolation of $C_{L,\text{calc}}$ down to $T = 0$, agrees within 2% with earlier estimates,[12] and hence the spin-wave analysis given in a previous paper[10] is still correct. In view of these results we feel confident to state that the behavior of the magnetic heat capacity of CMC is rather well established, both above and below the ordering temperature.

III. α-RbMnCl$_3$ · 2H$_2$O AND CsMnBr$_3$ · 2H$_2$O

The magnetic properties of α-RMC and CMB have been studied less extensively than those of the isomorphic CMC. α-RMC has been found to order antiferromagnetically at $T_N = 4.56$ K,[17] with the same magnetic space group as CMC, i.e., $P_{2b}c'ca'$,[18] while CMB orders antiferromagnetically at $T_N = 5.75$ K,[17] with magnetic space group $Pc'c'a'$.[19] From the corresponding magnetic arrays it is obvious that in CMB the interchain interaction along the crystallographic b direction is positive, in contrast to both CMC and α-RMC.

Single crystals of α-RMC were grown by cooling a saturated solution of MnCl$_2$ · 4H$_2$O and RbCl in molar ratio 5 : 1 in 8M HCl from 50 to 5 °C. The crystallized mixture of α and β modification gradually transforms into the α modification after a few weeks at 5 °C. The crystals were more or less needle-shaped with average dimensions of $10 \times 1 \times 1$ mm. Single crystals of CMB were grown by slow evaporation of a saturated solution of MnBr$_2$ · 4H$_2$O and CsBr in molar ratio of 6 : 1 at room temperature. The crystals were rather large (typical dimensions $3 \times 8 \times 15$ mm) and showed roughly the same morphology as CMC.

Specimens consisting of ~0.1 mol of small crystals were measured with a vacuum calorimeter

of conventional design, which was fitted with a temperature-controlled heat screen to enable very accurate measurements at temperatures up to about 50 K. Temperature readings were obtained from a calibrated germanium thermometer that was measured with an ac resistance bridge operating at ~170 cycles/sec. For both compounds, the total heat capacity showed the same behavior as the data on CMC. The heat capacity of CMB, however, appeared to be considerably larger than that of the two chlorine isomorphs.

The separation of the magnetic and the lattice contribution to the heat capacity has been achieved by analyzing the data between 9 and 52 K according to the procedure described above. The intrachain exchange interaction in α-RMC is found as $J/k = -3.0^{+0.2}_{-0.4}$ K, the corresponding interaction in CMB is found as $J/k = -2.6^{+0.2}_{-0.6}$ K. Due to the relatively high lattice heat capacity, the uncertainty in the value of J/k in CMB is somewhat larger than that in both chlorine isomorphs. The lattice contribution in α-RMC is represented by $\Theta_t = 254$ K, $\Theta_0 = 232$ K, $\Theta_c = 63$ K; for CMB the parameters $\Theta_t = 204$ K, $\Theta_0 = 165$ K, $\Theta_c = 52$ K are obtained. If these values are compared with the values $\Theta_t = 277$ K, $\Theta_0 = 219$ K, $\Theta_c = 53$ K obtained for CMC from the fit with $J/k = -3.0$ K, it is obvious that the lattice-specific heats of these compounds cannot be related to each other by a simple temperature-independent scaling factor.

The experimental magnetic heat capacity $C_{\text{expt}} - C_{L,\text{calc}}$ is shown by open circles in Figs. 3 and 4 for α-RMC and CMB, respectively. The drawn curve denotes the corresponding theoretical estimate. The magnetic heat capacity of α-RMC appears to be basically identical to that of CMC,

FIG. 3. Magnetic heat capacity of α-RbMnCl$_3$ · 2H$_2$O. The open circles correspond to $C_{\text{expt}} - C_{L,\text{calc}}$, the error bars reflect the uncertainty in C_{expt}. The drawn curve denotes the theoretical estimate for a $S = \frac{5}{2}$ Heisenberg linear-chain system with $J/k = -3.0$ K. The anomaly at 2.19 K is due to a small fraction of β-RbMnCl$_3$ · 2H$_2$O.
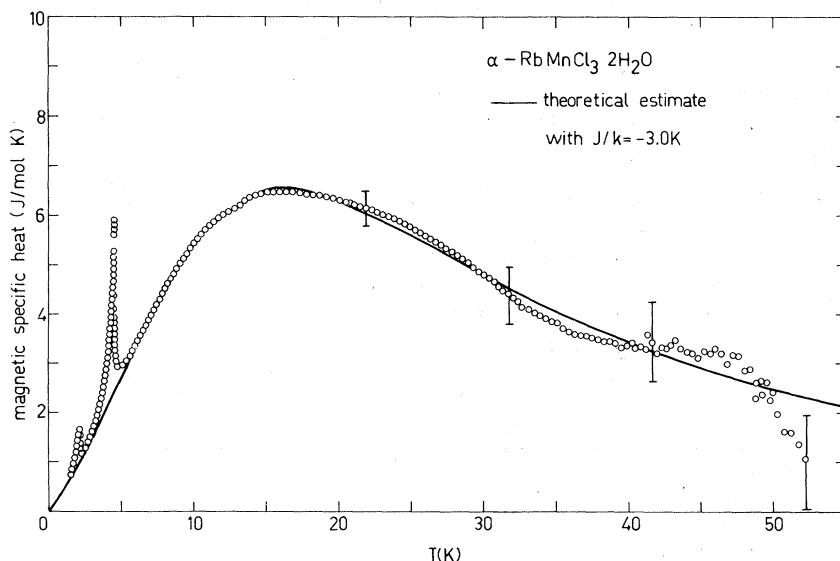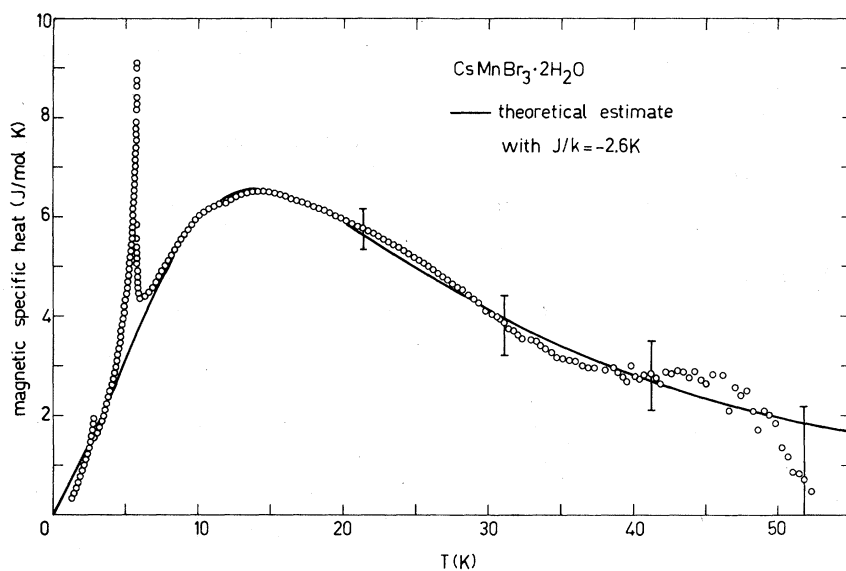
FIG. 4. Magnetic heat capacity of $CsMnBr_3 \cdot 2H_2O$. The open circles correspond to $C_{expt} - C_{L, calc}$, the error bars reflect the uncertainty in C_{expt}. The drawn curve denotes the theoretical estimate for a $S = \frac{5}{2}$ Heisenberg linear-chain system with $J/k = -2.6$ K. The anomaly at 2.8 K is due to a small fraction of $Cs_2MnBr_4 \cdot 2H_2O$.

TABLE I. Values for the intrachain exchange interaction J_1 and the interchain interactions J_2 and J_3 for $CsMnCl_3 \cdot 2H_2O$, α-$RbMnCl_3 \cdot 2H_2O$, and $CsMnBr_3 \cdot 2H_2O$. The last column gives the fraction of the total magnetic entropy increase removed below the ordering temperature.

	$CsMnCl_3 \cdot 2H_2O$	
Neutron diffraction[a]	$J_1/k = -3.53$ K, $\|J_2 + J_3\| = 7 \times 10^{-3}\|J_1\|$	
ESR line shape[b]	between $\|J_2\| = \|J_3\| = 2 \times 10^{-2}\|J_1\|$	
	and $\|J_2\| = 100\|J_3\| = 2.6 \times 10^{-2}\|J_1\|$	
Paramagnetic NMR[c]	$\|J_2\| = 3.5 \times 10^{-2}\|J_1\| \gg \|J_3\|$	
Proton spin-lattice ralaxation[d]	$\|J_2\| = 5 \times 10^{-2}\|J_1\|, J_3 \approx 0$	
Oguchi's formula[e]	$\|J_2\| = \|J_3\| = 8 \times 10^{-3}\|J_1\|$	
Susceptibility below T_N[f]	$J_1/k = -3.2$ K, $\|J_2\| = 6 \times 10^{-3}\|J_1\| = 5\|J_3\|$	
Specific heat[g]	$J_1/k = -3.0$ K, $\|J_2 + J_3\| = 8 \times 10^{-3}\|J_1\|$	$S_{crit} = 13.9\%$
	α-$RbMnCl_3 \cdot 2H_2O$	
Susceptibility[h] above T_N	$J_1/k = -2.9$ K	
below T_N	$J_1/k = -3.8$ K	
Specific heat plus Oguchi's formula	$J_1/k = -3.0$ K, $\|J_2\| = \|J_3\| = 7 \times 10^{-3}\|J_1\|$	$S_{crit} = 13.6\%$
	$CsMnBr_3 \cdot 2H_2O$	
Susceptibility[h] above T_N	$J_1/k = -3.0/-3.2$ K	
below T_N	$J_1/k = -3.7$ K	
Specific heat plus Oguchi's formula	$J_1/k = -2.6$ K, $\|J_2\| = \|J_3\|$	$S_{crit} = 20.9\%$
	$= 1.4 \times 10^{-2}\|J_1\|$	

[a]Reference 4.　　　[e]Reference 20.
[b]Reference 6.　　　[f]Reference 9.
[c]Reference 8.　　　[g]Reference 10.
[d]Reference 23.　　　[h]Reference 22.

except for the three-dimensional ordering, which occurs at slightly lower temperatures. The small peak at $T = 2.19$ K is due to a small fraction (1%–2%) of β-RbMnCl$_3 \cdot$2H$_2$O. Unfortunately, this peak precludes a determination of the interchain interactions from the magnetic heat capacity at low temperatures by linear spin-wave theory.[10] Therefore, these interactions were estimated from Green's function theory[20] using the values J/k $= -3.0$ K and $T_N = 4.56$ K as $|J'/J| = 7 \times 10^{-3}$. A similar procedure for CMC yields $|J'/J| = 8 \times 10^{-3}$. In CMB, an analysis of the low-temperature magnetic heat capacity with linear spin-wave theory is hampered by the small peak at $T = 2.8$ K, which is due to a small fraction of Cs$_2$MnBr$_4 \cdot$2H$_2$O.[21] Substitution of the values $J/k = -2.6$ K and $T_N = 5.75$ K in Oguchi's expression[20] yields $|J'/J| = 1.4 \times 10^{-2}$.

In view of the results given above, one might be tempted to conclude that the magnitude of the interchain interactions increases going from α-RMC via CMC to CMB. We wish to emphasize, however, that the observed change of the ordering temperature may also be explained by a variation of the (relatively small) magnetic anisotropy, which has been found to increase going from α-RMC via CMC to CMB.[22] Since the influence of anisotropy is not included in Oguchi's theory, the estimated values of $|J'/J|$ should be considered with some reservations. A survey of some representative results obtained from various experimental techniques is presented in Table I.

IV. CRITICAL BEHAVIOR

Next, we shall give some attention to the critical behavior of the magnetic heat capacity. In the neighborhood of the three-dimensional ordering temperature, very accurate measurements were performed with typical temperature increments $\Delta T \leqslant 0.5$ mK, in order to avoid experimental "rounding" of the specific heat anomaly. For $\Delta T < 2$ mK, the experimental rounding appeared to be negligible. The magnetic specific heat C_M was obtained by subtracting the lattice contribution presented above from the experimental data.

As a first attempt to obtain the critical exponents α' and α, we plotted $\log_{10} C_M$ vs $\log_{10} |\epsilon|$ for several values of T_N. For all three compounds these plots showed a rather pronounced curvature of the data, both for $|\epsilon| < 5 \times 10^{-3}$ and for $|\epsilon| > 5 \times 10^{-2}$, which could not be removed by a physically acceptable readjustment of the value of T_N. Since the data on α-RMC showed the smallest rounding, we performed least-squares fits of the magnetic heat capacity of this substance to the more general expression

$$C_M = A |\epsilon|^{-\alpha} + E\epsilon , \qquad (2)$$

with the additional conditions $\alpha' = \alpha$, $T_N = T_N'$, and $E = E'$. This equation did satisfactorily describe the data for $7 \times 10^{-3} < -\epsilon < 10^{-1}$ and $7 \times 10^{-3} < \epsilon < 5 \times 10^{-2}$, with the parameter values $\alpha = +0.11 \pm 0.01$, $A = 2.01 \pm 0.05$ J/mol K and $A' = 3.05 \pm 0.05$ J/mol K. Unfortunately, attempts to refine the fit by including a constant term B in Eq. (2) or by removing the condition $\alpha' = \alpha$ were unsuccessful, since they all resulted in rather strong correlations between the parameters.

The systematic deviations for larger values of $|\epsilon|$ may partly be caused by the fact that the heat-capacity anomaly has a rather weak divergence, and hence correction terms to the limiting behavior $C_M = A |\epsilon|^{-\alpha}$ may be important already close to the ordering temperature. As there seems to be some evidence that the relative importance of these correction terms is smaller for quantities having a larger value of the critical exponent, we shall next consider the critical behavior of the magnetic entropy increase S, given by

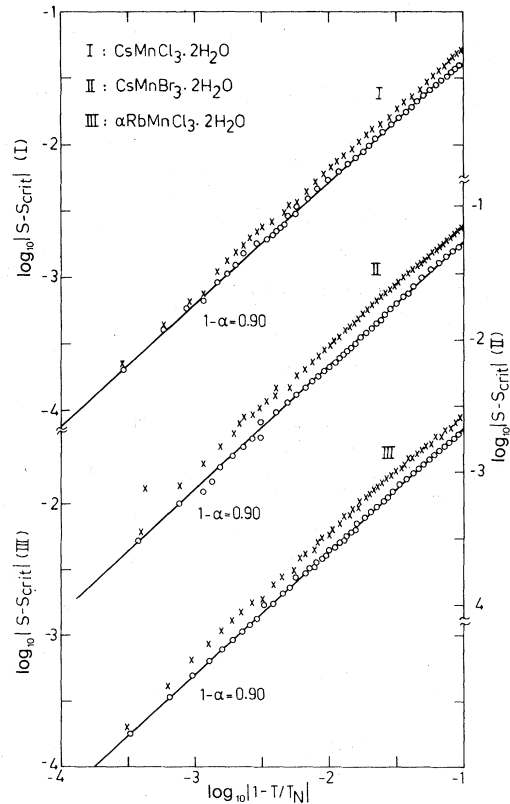$$\lim_{\epsilon \to 0} \left\{ \ln[S(\epsilon) - S_{crit}]/\ln\epsilon \right\} = 1 - \alpha . \qquad (3)$$

FIG. 5. Double logarithmic plot of $S - S_{crit}$ vs $|1 - T/T_N|$ for CsMnCl$_3 \cdot$2H$_2$O, α-RbMnCl$_3 \cdot$2H$_2$O, and CsMnBr$_3 \cdot$2H$_2$O. The open circles represent the data for $T > T_N$, the crosses are the data for $T < T_N$.

We evaluated both S and S_{crit} from the experimental data by numerical integration of C_M/T. The results were plotted doublelogarithmically for several values of T_N. For all three compounds the data for $T > T_N$ could be represented surprisingly well by straight lines over more than two decades of ϵ if T_N was chosen a few mK above the heat capacity maximum. The fact that the actual value of T_N is found at somewhat higher temperatures than C_{max} seems to be a rather common feature, caused by the rounding of the asymmetric heat capacity anomaly.[24-26] The results are shown in Fig. 5 for CMC, α-RMC, and CMB. The data for $T < T_N$ reveal some curvature, but the results suggest that $\alpha' = \alpha$. *For all three compounds* the critical exponent is found to be equal, and amounts to $\alpha = +0.10 \pm 0.01$. Although a study of the critical behavior using the magnetic entropy increase is somewhat unconventional, the value of α is consistent with the results from renormalization group theory[27] for a three-dimensional ordering of a system with spin dimensionality close to 1, and agrees very well with the value found from a direct fit to the data on α-RMC.

ACKNOWLEDGMENTS

[1] S. J. Jensen, P. Andersen, and S. E. Rasmussen, Acta Chem. Scand. 16, 1890 (1962).

[2] S. J. Jensen, Acta Chem. Scand. 21, 889 (1967).

[3] T. Smith and S. A. Friedberg, Phys. Rev. 176, 660 (1968).

[4] J. Skalyo, G. Shirane, S. A. Friedberg, and H. Kobayashi, Phys. Rev. B 2, 1310, 4632 (1970).

[5] N. Nagata and Y. Tazuke, J. Phys. Soc. Jpn. 32, 337 (1972).

[6] M. J. Hennessy, C. D. McElwee, and P. M. Richards, Phys. Rev. B 7, 930 (1973).

[7] R. D. Spence, W. J. M. de Jonge, and K. V. S. Rama Rao, J. Chem. Phys. 51, 4694 (1969).

[8] F. Ferrieu, Phys. Lett. A 49, 253 (1974).

[9] T. Iwashita and N. Uryû, J. Phys. Soc. Jpn. 39, 1226 (1975).

[10] W. J. M. de Jonge, K. Kopinga, and C. H. W. Swüste, Phys. Rev. B 14, 2137 (1976).

[11] T. Iwashita and N. Uryû, J. Chem. Phys. 65, 2794 (1976).

[12] K. Kopinga, T. de Neef, and W. J. M. de Jonge, Phys. Rev. B 11, 2364 (1975).

[13] V. V. Tarasov, New Problems in the Physics of Glass (Oldbourne, London, 1963).

[14] K. Kopinga, P. van der Leeden, and W. J. M. de Jonge, Phys. Rev. B 14, 1519 (1976).

[15] T. de Neef, Phys. Rev. B 13, 4141 (1976).

[16] H. W. J. Blöte, Physica B 79, 427 (1975).

[17] C. H. W. Swüste, K. Kopinga, W. J. M. de Jonge, J. P. A. M. Hijmans, and A. C. Botterman, in Proceedings of the International Conference on Magnetism, Moscow, 1973 (unpublished).

[18] W. J. M. de Jonge and C. H. W. Swüste, J. Chem. Phys. 61, 4981 (1974).

[19] C. H.W. Swüste, Ph.D. thesis (Eindhoven, 1973) (unpublished).

[20] T. Oguchi, Phys. Rev. 133, A1098 (1964).

[21] H. Forstat, J. N. McElearny, and P. T. Bailey, in Proceedings of the International Conference of Low-Temperature Physics, St. Andrews, 1968 (unpublished).

[22] A.C. Botterman, Ph.D. thesis (Eindhoven, 1976) (unpublished).

[23] H. Nishihara, W. J. M. de Jonge, and T. de Neef, Phys. Rev. B 12, 5325 (1975).

[24] J. Skalyo and S. A. Friedberg, Phys. Rev. Lett. 13, 133 (1964).

[25] R. F. Wielinga, Ph. D. thesis (Leiden, 1968) (unpublished).

[26] L. W. Kreps and S. A. Friedberg, J. Low. Temp. Phys. 26, 317 (1977).

[27] For an excellent review see, for instance, M. E. Fisher, Rev. Mod. Phys. 46, 597 (1974).