JOURNAL OF SOLID STATE CHEMISTRY **11**, 245–253 (1974)

Crystal Structure of the Compounds $A_2MnX_{4-x}X'_x$ (A = NH_4, Rb, Cs; X = Cl; X′ = Br, I; x = 0, 1, 2) and Magnetic Susceptibility of A_2MnCl_4 (A = Rb, Cs)

H. T. WITTEVEEN

Gorlaeus Laboratories, Department of Solid State Chemistry, State University, P.O. Box 75, Leiden, The Netherlands.

Received December 8, 1973

Of the compounds A_2MnCl_4(A = Rb,Cs), it is known that they crystallize in the K_2NiF_4 structure. We have investigated a number of compounds $A_2MnX_{4-x}X'_x$ with A = NH_4,Rb,C_3, X = Cl, X′ = Br,I and x = 0, 1, 2. By means of X-ray powder diffraction it is determined, that these compounds also have the K_2NiF_4 structure. The X′ ions occupy special sites in the crystal lattice. The unit cell parameters of all compounds prepared are given.

Susceptibility data are obtained for Rb_2MnCl_4 and $CsMnCl_4$. The susceptibility is interpreted on the basis of the two dimensional antiferromagnetic Heisenberg model. The intralayer exchange constant is $J/k = -6.2$ K and -5.0 K for Rb_2MnCl_4 and Cs_2MnCl_4, respectively.

I. Introduction

As part of a research program on A_2BX_4 compounds in the chemical system AX–BX_2 (A = K, Rb, NH_4, Tl, Cs; B = Mn, Fe, Co, Ni, Cu; X = Cl, Br), we have investigated the case B = Mn. This case is particularly interesting, since it is known that the compounds Rb_2MnCl_4 (*1*) and Cs_2MnCl_4 (*2*, *3*) have the tetragonal K_2NiF_4 structure (Fig. 1) so that these compounds may exhibit two-dimensional (2D) magnetic behaviour.

As can be seen in Fig. 1 the metal layers are separated by 2 nonmagnetic layers. In the layers the superexchange interaction between nearest magnetic neighbours occurs via 1 intervening nonmagnetic ligand, whereas the interaction between metal ions in adjacent metal layers occurs via at least 2 nonmagnetic ligands. Using as a rule of thumb that each additional intervening nonmagnetic ligand reduces the magnetic interaction by about a factor 10^2, it is obvious that the interaction J' between the layers (interlayer interaction) is much smaller than the interaction J in the layers (intralayer interaction). In good approximation one can speak, therefore, of 2D magnetic systems in connection with compounds having the K_2NiF_4 structure.

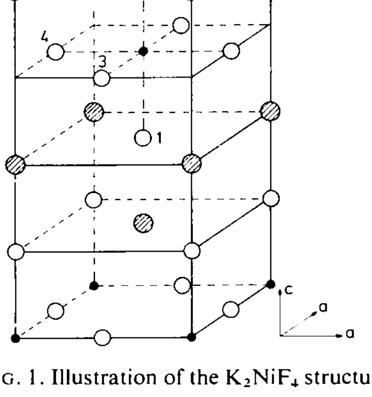

FIG. 1. Illustration of the K_2NiF_4 structure.

Printed in Great Britain

By means of neutron diffraction experiments, Epstein et al. (*4*, *5*) have determined the magnetic structure of Rb_2MnCl_4 and Cs_2MnCl_4 (below the antiferromagnetic transition temperature $T_N = 57°K$ and 52°K for Rb_2MnCl_4 and Cs_2MnCl_4, respectively, the spins are aligned along the *c*-axis) and have confirmed indeed the 2D magnetic behavior of these compounds. In this paper we describe the magnetic susceptibility in the temperature region 2–250°K of polycrystalline samples of Rb_2MnCl_4 and Cs_2MnCl_4 and we shall see that the susceptibility behavior agrees with the prediction of the 2D Heisenberg model.

Besides these two compounds we have also prepared several compounds of the type $A_2MnX_{4-x}X'_x (A = NH_4$, Rb, Cs; $X = Cl$; $X' = Br$, I; $x = 1, 2)$. On basis of theoretical considerations it is expected that they also possess the K_2NiF_4 structure and that they will show an ordering between Cl^- and Br^- ions on special sites in the structure.

The anions in the K_2NiF_4 structure are distributed over 2 crystallographic positions. If in A_2BX_4 halides with the K_2NiF_4 structure the anions are partly replaced by larger, and thus more polarizable, halogen ions, it is expected that these larger anions prefer the sites denoted by 1 and 2 in Fig. 1. The anions in these positions are coodinated by 5 A ions and 1 B ion, whereas the anions in sites 3 and 4 (Fig. 1) are coordinated by 4 A and 2 B ions. The linear configuration $A^+–X–B^{2+}$ of the former anion coordination is more favorable for more polarizable anions than the linear configuration $B^{2+}–X–B^{2+}$ of the latter anion coordination (sites denoted by 3 and 4).

In $A_2BX_2X'_2$ halides having the K_2NiF_4 structure, where the X′ halogen ion is larger and more polarizable than the X ion, one expects, therefore, that the equal abundance of X and X′ ions gives rise to a new kind of octahedra $(BX_4X'_2)$, in which the X ions lie within the equatorial plane of the octahedron (sites 3 and 4) and the X′ ions occupy the sites above and beneath this plane (1 and 2).

For the same reason one expects two possibilities for A_2BX_3X' halides: a structure containing (BX_6) octahedra along with an equal number of $(BX_4X'_2)$ octahedra, and another structure having exclusively (BX_5X') octahedra. ESR measurements on Mn^{2+}-doped Rb_2MgCl_4, Rb_2MgCl_3Br and $Rb_2MgCl_2Br_2$, which compounds also possess the K_2NiF_4 structure (*6*) have confirmed our expectations about the ordering of the X and X′ ions for the case $X = Cl, X' = Br$. From the ESR measurements it was also deduced that in Rb_2MgCl_3Br no $(MgCl_5Br)$ octahedra occur, but that only $(MgCl_6)$ and $(MgCl_4Br_2)$ species are present. It is reasonable to assume that in the other $A_2BX_{4-x}X'_x$ compounds with the K_2NiF_4 structure this will also be the case. For the compounds $Rb_2CuCl_{4-x}Br_x$ $(x = 0, 1, 2)$, that have a deformed K_2NiF_4 structure ($(NH_4)_2CuCl_4$ structure (*7*)), the occupation of sites 1 and 2 by Br^- ions is proved by structural (*8*) and magnetic investigations (*9*).

In Section II of this paper the preparation and characterization of the compounds $A_2MnX_{4-x}X'_x (A = NH_4$, Rb, Cs; $X' = Br$, I; $x = 0, 1, 2)$ is described. Although X-ray diffraction patterns of most of the compounds did not show reflections due to impurities, susceptibility measurements revealed the presence of paramagnetic impurities in all samples. Only for Rb_2MnCl_4 and Cs_2MnCl_4 was the amount of the impurities small enough to be able to correct for the influence of the impurities on the susceptibility behavior, so that only for these two compounds the susceptibility is described and interpreted.

II. Experimental Equipment and Preparation and Characterization of the Compounds $A_2MnX_{4-x}X'_x (A = NH_4$, Rb, Cs; $X = Cl$; $X' = Br, I; x = 0, 1, 2)$

Most of the compounds described below were prepared by melting stoichiometric amounts of the commercial products ACl, ABr and AI (A = alkali ion) and $MnCl_2$ for 1 or 2 days at 600°C in an evacuated and sealed silica tube and annealing afterwards at temperature of 300–400°C for about 2 weeks. $MnCl_2$ was obtained by dehydrating commercial $MnCl_2 \cdot 4H_2O$ at 350°C for 4 hr in a stream of dry HCl gas.

In this way we prepared in the first instance Rb_2MnCl_4 and Cs_2MnCl_4 which compounds are known to crystallize in the K_2NiF_4 structure (*1*, *3*). Due to the incongruent melting point of Rb_2MnCl_4 (at 460°C) the reaction product contained small amounts of $Rb_3Mn_2Cl_7$ and RbCl. Therefore, the reaction product was powdered again and annealed for a few weeks at about 350°C. After this treatment no impurities could be detected in the sample by means of X-ray diffraction.

However, susceptibility measurements on several samples of Rb_2MnCl_4 and Cs_2MnCl_4 revealed that paramagnetic impurities were still present, probably due to impurities in the starting compound $MnCl_2$. Especially in the low-temperature region (2–100°K), the susceptibility curve was influenced too much by these impurities. Therefore, we tried to obtain purer samples by means of another preparation method, using the hydrated compounds.

A precipitate of $Rb_2MnCl_4 \cdot 2H_2O$ was obtained by dissolving $MnCO_3$ and RbCl in the ratio 1:2 in an HCl solution. $Cs_2MnCl_4 \cdot 2H_2O$ could be prepared best by slow evaporation of an aqueous solution of $MnCl_2 \cdot 4H_2O$ and CsCl in the ratio 3:1. With differential thermal analysis of these compounds it was determined that dehydration started at about 80°C. By heating the hydrated compounds for several days at about 150°C in an Ar atmosphere, samples of Rb_2MnCl_4 and Cs_2MnCl_4 were obtained that were purer from a magnetic point of view than the samples prepared from the melt.

We tried to prepare the compound $(NH_4)_2MnCl_4$ in two ways. First, stoichiometric amounts of $MnCl_2$ and NH_4Cl were mixed and heated in a sealed gold tube for several days in the temperature region 300–400°C under a pressure of about 1 kbar. The X-ray diffraction patterns revealed the presence of a K_2NiF_4 phase in combination with relatively large amounts of other phases of the system NH_4Cl-$MnCl_2$.

Therefore $(NH_4)_2MnCl_4 \cdot 2H_2O$ was prepared in the same way as described above for $Rb_2MnCl_4 \cdot 2H_2O$. Thermal analysis shows that the dehydration process in $(NH_4)_2MnCl_4 \cdot 2H_2O$ starts at about 115°C and that at about 160°C the compound starts to decompose due to sublimation of NH_4Cl. The X-ray diffraction patterns of samples obtained by heating $(NH_4)_2MnCl_4 \cdot 2H_2O$ for several days at 120°C in an Ar atmosphere revealed a pure K_2NiF_4 phase for the compound $(NH_4)_2MnCl_4$. But susceptibility measurements in the low-temperature region indicated again the presence of impurities probably due to the sublimation of a small amount of NH_4Cl, during the preparation. Several attempts to improve the purity by varying time, temperature an Ar pressure were not successful.

In order to investigate the conjecture about the ordering of the X and X′ halogen ions in compounds $A_2MnX_{4-x}X'_x$ with the K_2NiF_4 structure, we have tried to prepare these compounds for the combinations (F, Cl), (Cl, Br) and (Cl, I). The attempts for the case (F, Cl) were not successful, but for the combination (Cl, Br) the expected behavior is, indeed, found. That for the combination (F, Cl) the expectations are not fulfilled is not so surprising, because the ratio of the Cl^- and F^- ions radii ($r(Cl^-)/r(F^-)$) is much larger than $r(Br^-)/r(Cl^-)$.

Using the Ahrens radii, these ratios are 1.36 and 1.08, respectively (*10*, *11*). For some compounds having the combination (Cl, I) for which $r(I^-)/r(Cl^-) = 1.21$, also indications for an ordering between Cl^- and I^- are found.

Several compounds of the type $A_2MnCl_{4-x}Br_x$ and $A_2MnCl_{4-x}I_x$ were prepared by means

TABLE I

CELL PARAMETERS OF COMPOUNDS $A_2MnX_{4-x}X'_x (x = 0, 1, 2)$

Compound	a-axis (Å)	c-axis (Å)
Rb_2MnCl_4	5.049(2)[a]	16.172(4)
Rb_2MnCl_3Br	5.060(3)	16.588(8)
$Rb_2MnCl_2Br_2$	5.073(2)	16.924(3)
$Rb_2MnCl_2I_2$	5.162(2)	17.84(1)
Cs_2MnCl_4	5.135(3)	16.88(1)
Cs_2MnCl_3Br	5.169(3)	17.25(1)
$(NH_4)_2MnCl_4$	5.049(2)	16.148(7)
$(NH_4)_2MnCl_2Br_2$	5.055(5)	16.83(1)
$(NH_4)_2MnCl_2I_2$	5.102(4)	17.71(1)

[a] The values between parentheses indicate the uncertainty in the last decimal place.

of the melting method for A = Rb, Cs and for A = NH_4 by means of the method described above, in which sealed gold tubes are used. In some of the samples prepared, small amounts of AX, other phases of the AX–MnX_2 system (X = Cl, Br, I) and unknown impurities were detected. The unit cell parameters of all compounds prepared are listed in Table I. The occupation of sites 1 and 2 (Fig. 1) by the X′ ions is clearly reflected in the values of the *a*- and *c*-axes. The value of the *c*-axis increases strongly when Br^- of I^- is substituted in the compounds, caused by the larger radius of Br^- and I^- compared to the Cl^- ion (Ahrens radii (*10*, *11*): $r(Cl^-) = 1.81$ Å, $r(Br^-) = 1.96$ Å). The differences in the values of the *a*-axes are much smaller.

The cell parameters of Rb_2MnCl_4 and Cs_2MnCl_4 agree with those reported in the literature (*1*, *3*, *4*).

A last remark about the preparation of the compounds concerns Cs_2MnCl_3Br and $Cs_2MnCl_2Br_2$. The compound $Cs_2MnCl_2Br_2$ could not be prepared. For most of our Cs_2MnCl_3Br samples the X-ray reflexions were rather broad, indicating that these samples were not well crystallized. Possibly $Cs_2MnCl_2Br_2$ is not stable, whereas Cs_2MnCl_3Br is a borderline case. Thermal analysis of Cs_2MnCl_3Br revealed a phase transition (possibly to the β-K_2SO_4 structure) at 295°C, just as in the case for Cs_2MnCl_4 (see above).

In Table II the results are given of the chemical analysis of a number of the samples prepared of the various compounds.

Because of the hygroscopic character of $MnCl_2$ and the compounds prepared, all manipulations were carried out in a glove box filled with dry nitrogen.

X-ray powder diffraction patterns of the compounds were obtained by means of a Philips PW1050 diffractometer, suited for the investigation of hygroscopic samples and using Cu*Kα* radiation.

The differential thermal analysis experiments have been carried out by means of a Mettler Vacuum Thermal Analyzer TA1.

Susceptibility measurements in the temperature region 2–250°K were carried out with a commercial PAR vibrating sample magnetometer model 150.

Spin-flop measurements on the compounds Rb_2MnCl_4 and Cs_2MnCl_4 (described in Section III) were carried out with a high field pulse magnet of which details are described elsewhere (*12*).

Many calculations were carried out on the IBM 360/65 computer at the University Computer Centre of Leiden.

III. Results and Discussion

The results of the susceptibility measurements on polycrystalline samples of Rb_2MnCl_4 and Cs_2MnCl_4, corrected for diamagnetism according to the table of Selwood (*13*), are plotted in Figs. 2 and 3. The broad maxima in the χ-curves are characteristic for an antiferromagnetic system with a low dimension. In view of the crystal structure it is expected that the compounds behave as 2D systems. At low temperature a minimum is noticed in the χ-curve of each compound. This deviation from the expected behaviour can be explained

TABLE II

CHEMICAL ANALYSIS OF COMPOUNDS $A_2MnX_{4-x}X'_x$

Compound	Mn(theor.)%	Mn(exp.)%	X + X′(theor.)%	X + X′(exp.)%
Rb_2MnCl_4	14.94	14.98	38.6	38.5
Rb_2MnCl_3Br	13.33	13.44	45.2	45.1
$Rb_2MnCl_2Br_2$	12.03	12.32	50.5	50.0
$Rb_2MnCl_2I_2$	9.98	10.15	59.0	58.4
Cs_2MnCl_4	11.88	11.93	30.7	30.8
Cs_2MnCl_3Br	10.84	10.81	36.7	36.7
$(NH_4)_2MnCl_4$	23.60	23.48	60.9	61.2

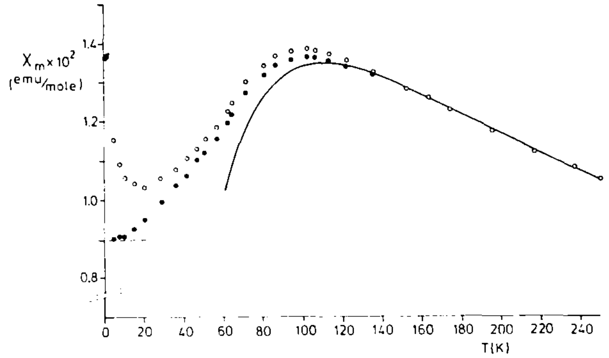

FIG. 2. Molar susceptibility χ_m as a function of temperature of Rb_2MnCl_4 ○ = experimental data; ● = experimental data corrected for the presence of paramagnetic impurities; ——: best fit according to the series expansion curve for $J/k = -6.2K$ and $g = 2.00$; -----: indicates the corrected value for $\chi_p(T = O)$.

by the presence of a paramagnetic impurity in the samples. The data in Figs. 2 and 3 were collected on samples prepared by dehydration of the compounds $A_2MnCl_4 \cdot 2H_2O (A = Rb, Cs)$, as described in Section II, Samples that were prepared from the melt showed minima in their χ-curves at higher temperatures (40°K) so that in these samples probably a larger amount of impurities was present. For these samples the influence of the impurities on the susceptibility behavior was too large to correct for so that no reliable values of the intralayer interaction J/k could be obtained (see below). The same holds for the other Mn compounds discussed in Section II. Therefore, no susceptibility data of these compounds are given in this paper. It may be remarked, however, that all these compounds show the characteristic broad maximum in their χ-curves and can be described as 2D antiferromagnetics.

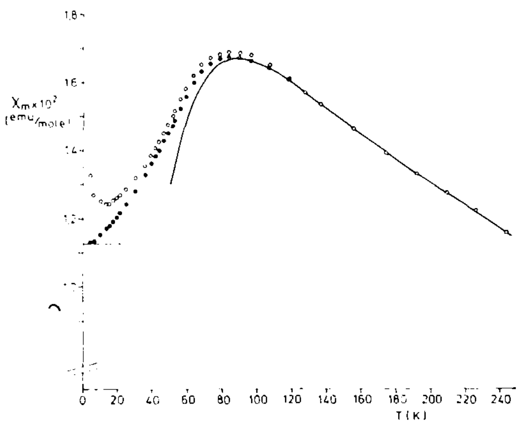

FIG. 3. Molar susceptibility χ_m as a function of temperature of Cs_2MnCl_4 ○ = experimental data; ● = experimental data corrected for the presence of paramagnetic impurities; ——: best fit according to the series expansion curve $J/k = -5.0$ K and $g = 2.00$ -----: indicates the corrected value for $\chi_p(T = O)$.

The chemical analysis results (Table II) shows that the impurities cannot amount to more than a few percent.

Similar deviations, due to impurities, were observed by Van Amstel and De Jongh (*14*) for the 2D Mn compound $(CH_3NH_3)_2MnCl_4$. They conclude from their single crystal measurements that the deviations are probably caused by small amounts of $MnCl_2(T_N = 1.9°K$(*15*)) or $MnCl_2 \cdot 4H_2O(T_N = 1.6°K$ (*16*)). In some of our samples of Rb_2MnCl_4 and Cs_2MnCl_4 a sharp maximum was observed in the χ-curve at about 2°K, so that probably also in our compounds, $MnCl_2$ or $MnCl_2 \cdot 4H_2O$ is present as impurity.

Van Amstel and De Jongh (*14*) have developed in their paper a scheme to correct for the presence of the paramagnetic impurities. This scheme will also be used by us.

The magnetic system in Mn^{2+} compounds is usually described well by the Heisenberg model, since the most important sources of anisotropy, such as dipolar anisotropy, crystal field effects and anisotropy in the superexchange mechanism are usually very small in these compounds. Therefore, it should be expected that the susceptibility in the high-temperature region is well described by the series expansion results for the antiferromagnetic quadratic Heisenberg lattice with spin $S = 5/2$ (the Hamiltonian $\mathscr{H} = -2J \sum_{ij} \vec{S}_i \cdot \vec{S}_j$ is used, where J is th enearest neighbor intralayer interaction parameter) Lines has shown (*17*), that, although in this series expansion in powers of J/kT only a finite number of terms is known, the susceptibility is well described down to the temperature region, where the maximum in the susceptibility ($\chi_{\max}$) is located. Van Amstel and De Jongh (*14*) report that the series expansion can be used in the region $kT/|J| > 12$.

Using J/k as the variable parameter and $g = 2.00$ (as is usual for Mn^{2+} compounds), a preliminary value of J/k is obtained by fitting the experimental χ data in the high-temperature region to the series expansion χ-curve. J/k is also determined from $\chi_{\max}$ and the temperature $T_{\max}$, where $\chi_{\max}$ occurs, by means of the relations:

$$kT_{\max}/|J|S(S+1) = 2.04 \pm 0.01 \qquad (1)$$

and

$$\chi_{\max}|J|/Ng^2\beta^2 = (5.516 \pm 0.006) \times 10^{-2} \qquad (2)$$

which are obtained from the series expansion results for the antiferromagnetic, quadratic Heisenberg lattice with $S = 5/2$ (*17*, *18*). The value in the right-hand-side Eq. (1) is somewhat lower than the value given by Lines (*17*) and seems more reliable. The difference is probably due to the extrapolation procedure used by Lines (*18*).

The J/k-values calculated from Eqs. (1) and (2) and from the experimental values:

$$\chi_{\max} = (1.385 \pm 0.015) \times 10^{-2}\,\text{emu/mole},$$
$$T_{\max} = 100 \pm 3°\text{K}$$

and

$$\chi_{\max} = (1.690 \pm 0.015) \times 10^{-2}\,\text{emu/mole},$$
$$T_{\max} = 86 \pm 3°\text{K}$$

for Rb_2MnCl_4 and Cs_2MnCl_4, respectively, are given in Table III.

It has been found by De Jongh and Colpa (*19*) that $\chi_{\max}$ is more suitable than $T_{\max}$ for estimating J/k, since $\chi_{\max}$ is established theoretically and usually also experimentally more accurate.

Another determination of J/k can be obtained from the prediction for the perpendicular susceptibility at zero temperature $\chi_\perp(T = 0)$. For this quantity Keffer has given the following expression (*20*):

$$\chi_\perp(T = 0) = \frac{\chi_\perp^0}{1 + \frac{1}{2}\alpha}\left[1 - \frac{\Delta S(\alpha)}{S} - \frac{e(\alpha)}{(2 + \alpha)zS}\right], \qquad (3)$$

that, according to De Jongh (*21*), shows good agreement with experimental results obtained on 2D antiferromagnets.

In Eq. (3) $\chi_\perp{}^o = Ng^2\beta^2/4z|J|$ denotes the molecular field prediction for $\chi_\perp(T = 0)$. Further, α is the anisotropy parameter H_A/H_E, in which H_A denotes the anisotropy field and H_E is the exchange field that is related to the intralayer coupling J/k by means of the molecular field expression:

$$H_E = 2z|J|S/g\beta. \qquad (4)$$

The number of nearest magnetic neighbors is given by z (for the quadratic lattice $z = 4$), $\Delta S(\alpha)$ and $e(\alpha)$ are corrections to $\chi_\perp{}^o$, due to zero-point spin reduction.

Values for $\Delta S(\alpha)$ have been given by Lines (*17*) and Colpa et al. (*22*). Breed (*23*) has shown that $e(\alpha)$ is nearly independent of α. Therefore, we use the value $e(0) = 0.632$ (20). It is clear that in Eq. (3) also α has to be known to obtain the value of J/k from the experimental $\chi_\perp(T = 0)$-value.

TABLE III

PHYSICAL QUANTITIES OF Rb_2MnCl_4 AND Cs_2MnCl_4

	Rb_2MnCl_4	Cs_2MnCl_4
J/k from $T_{\max}$ uncorrected (K)	−5.6(2)	−4.8(2)
J/k from $\chi_{\max}$ uncorrected (K)	−6.0(1)	−4.9(1)
J/k corrected (K)	−6.2(2)	−5.0(2)
$H_{s.f.}$ (kOe)	60(5)	50(5)
$\chi_p(T = 0) \times 10^2$ corrected (emu/mole)	0.895	1.130
H_A(kOe)	1.9(4)	1.6(3)
H_A/H_E	2.2×10^{-3}	2.1×10^{-3}
T_N(K)	55(5)	55(5)

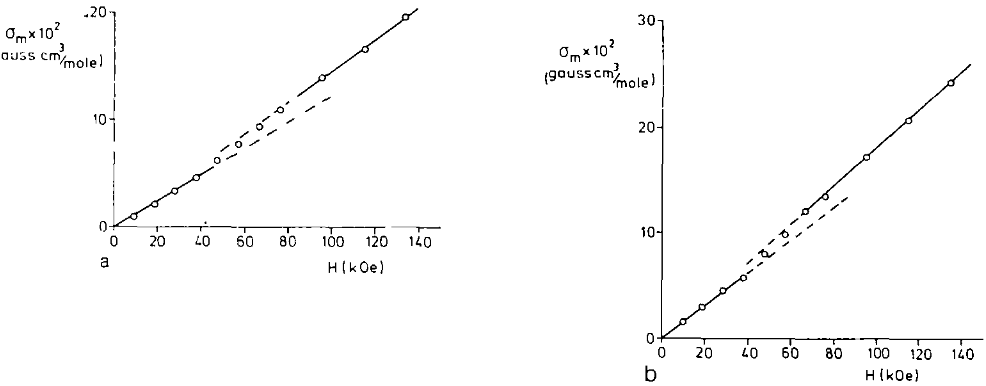

FIG. 4. Magnetization curve of polycrystalline samples of Rb_2MnCl_4 (Fig. 4a) and Cs_2MnCl_4 (FIG. 4b), showing the spin-flop transition ○ = experimental data.

The quantity $\alpha = H_A/H_E$ is determined by means of spin-flop (s.f.) measurements of which the results for Rb_2MnCl_4 and Cs_2MnCl_4 (obtained at 4.2°K) are shown in Fig. 4a, b[1]). Since the measurements were carried out on polycrystalline samples, the s.f. transition is not as sharp as usual for s.f. measurements on single crystals. Assuming that the s.f. occurs at the field value for which $\partial\sigma/\partial H$ reaches its maximum, the s.f. fields given in Table III, were obtained.

Using the formula (*20*)

$$H^0_{\text{s.f.}} = 2H_E H_A/(1 - \chi_\parallel/\chi_\perp), \qquad (5)$$

H_A is obtained if $H_{\text{s.f.}}$, H_E, and $\chi_\parallel/\chi_\perp$ are known ($\chi_\parallel$ denotes the susceptibility in the direction of the *c*-axis along which the spins are aligned below the transition temperature T_N(4); $\chi_\perp$ is the susceptibility perpendicular to the *c*-axis). From the powder susceptibility data, the ratio $\chi_\parallel/\chi_\perp$ cannot be determined. For other 2D Mn compounds it is known that at $T \ll T_{\max}$ $\chi_\parallel$ is already very small compared to $\chi_\perp$, so that in good approximation it may be assumed that $\chi_\parallel/\chi_\perp \approx 0$ at 4.2°K.

The preliminary value of J/k, and thus of H_E (Eq. (4)), is obtained from the best fit of the susceptibility data to the series expansion curve. In this way, an estimate of α is acquired and a value for $\Delta S/(\alpha)$ is derived (*22*).

If the polycrystallites in the sample are distributed at random, and if $\chi_\parallel(T=0) = 0$, the powder susceptibility at $T = 0$ is given by $\chi_{\text{powder}}(T=0) = 2/3\ \chi_\perp(T=0)$. Hence, from this relation, $\chi_\perp(T=0)$ is obtained from the experimental χ_{powder}-value. This value has not yet been corrected for the presence of the paramagnetic impurity. The susceptibility of the most probable impurities $MnCl_2$ and $MnCl_2 \cdot 4H_2O$ is described by the Curie–Weiss law down to low temperature (*15*, *16*), with an asymptotic Curie temperature $\theta \approx -2$°K. Adding the Curie–Weiss law $\chi_{\text{impurity}} = C_{\text{impurity}}/(T = \theta)$, with $\theta = -2$°K, to the series expansion result, we are now able to determine the combination of J/k and C, for which best agreement between the experimental values for $\chi_\perp(T=0)$ and $T_{\max}$, and the theoretical results is obtained. In this way the values for $\chi_p(T=0)$ corrected for the paramagnetic impurity, the final value of J/k, and the H_A and H_A/H_E-values are determined (Table III).

In Figs. 2 and 3 are also depicted the χ-data, corrected for the paramagnetic impurity. It is noticed that for Cs_2MnCl_4 a good fit is found down to $T_{\max}$ between the corrected experimental data and the series expansion curve for $J/k = -5.0$°K. For Rb_2MnCl_4 the fit for $J/k = -6.2$°K is also good, except for the region around $\chi_{\max}$, where the deviations are somewhat larger than in the case of Cs_2MnCl_4.

Apparently, the intralayer coupling J/k is smaller for Cs_2MnCl_4 than for Rb_2MnCl_4, which is in accordance with the larger distance

---

[1] These measurements were carried out by Dr. C. J. Schinkel at the Natuurkundig Laboratorium of the University of Amsterdam.

between nearest Mn ions in the layers in the former compound (Table I).

Since the $H_{s.f.}$-values could not be determined very accurately, the uncertainty in the H_A-values is rather large. But their magnitude does not differ very much from the theoretical values of the anisotropy field caused by the dipole anisotropy: $H_A^{\text{dip}} = 1325$ and 1270 Oe for Rb_2MnCl_4 and Cs_2MnCl_4, respectively, as calculated according to Breed (*23*) and Colpa (*24*). Probably a large part of the anisotropy originates from the dipolar anisotropy.

It is possible to obtain an estimate of the antiferromagnetic transition temperature T_N, where long-range ordering sets in. Although Mermin and Wagner (*25*) have proved rigorously that an isotropic 2D magnetic system cannot exhibit long-range order at $T > 0$, in practice a transition to long-range order is always detected in experimental 2D systems. This is due to deviations from the isotropic model, caused by i.e., dipolar anisotropy, anisotropy in the superexchange mechanism, crystal field effects and interlayer coupling. The value T_N is often nearly equal to or higher than the so-called "Stanley–Kaplan transition temperature." Stanley and Kaplan (*26*) have pointed out that in an isotropic 2D system a transition probably occurs, where, in accordance with the result of Mermin and Wagner, no spontaneous magnetization occurs, but where the susceptibility diverges. This transition temperature is given by the relation:

$$kT_N/|J| \simeq \tfrac{1}{5}(z-1)\{2S(S+1)-1\} \qquad (6)$$
$$\text{for } S > 1/2.$$

Taking into account the fact that in all known 2D Mn compounds below T_N $\chi_{\parallel}$ decays to zero and $\chi_{\perp}$ rises only slowly at decreasing temperature, it seems an acceptable procedure to locate T_N in the χ-curves of polycrystalline samples in the temperature region where $\partial\chi/\partial T$ reaches its maximum. For Rb_2MnCl_4 and Cs_2MnCl_4, these maxima are found at 55 ± 5°K (Table III) These values agree within experimental uncertainty with those reported by Epstein et al. (*4*) from neutron diffraction experiments.

The "Stanley–Kaplan transition temperature" as calculated from Eq. (6) by substituting the calculated J/k-values, are 61°K and 50°K for Rb_2MnCl_4 and Cs_2MnCl_4, respectively. They show reasonable agreement with the experimental T_N-values.

Acknowledgments

The present investigations have been carried out under the auspices of the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure research (Z.W.O.).

The author is indebted to Prof. Dr. W. J. Huiskamp and Dr. W. J. A. Maaskant for many valuable discussions. The aid with the spin-flop measurements by Dr. C. J. Schinkel (Natuurkundig Laboratorium of the University of Amsterdam) and the chemical analysis by Mr. J. A. Smit (Department of Coordination Chemistry, Leiden) is gratefully acknowledged.

References

1. H. J. Seifert and F. W. Koknat, *Z. Anorg. Allgem. Chem.* **341**, 269 (1965).

2. D. J. W. Ijdo, Thesis, University of Leiden (1960).

3. J. J. Foster and N. S. Gill, *J. Chem. Soc.* 1968, A2625 (1968).

4. A. Epstein, E. Gurewitz, J. Makovsky, and H. Shaked, *Phys. Rev.* **B2**, 3703 (1970).

5. E. Gurewitz, A. Epstein, J. Makovsky, and H. Shaked, *Phys. Rev. Letters* **25**, 1713 (1970).

6. H. T. Witteveen and J. Reedijk, *Solid State Commun.* **12**, 397 (1973).

7. R. D. Willett, *J. Chem. Phys.* **41**, 2243 (1964).

8. V. Brandwijk, H. T. Witteveen, and D. L. Jongejan, *Mater. Res. Bull.* **9**, 345 (1974).

9. H. T. Witteveen, *Physica* **71**, 204 (1974).

10. R. D. Shannon and C. T. Prewitt, *Acta. Cryst.* **B25**, 925 (1969).

11. R. D. Shannon and C. T. Prewitt, *Acta. Cryst.* **B26**, 1046 (1970).

12. L. W. Roeland, F. A. Muller, and R. Gersdorf, *Proc. Int. Conf. on High Magnetic Fields*, p. 153, Nottingham (1969).

13. P. W. Selwood, "Magnetochemistry," Interscience, New York (1956).

14. W. D. van Amstel and L. J. de Jongh, *Solid State Commun.* **11**, 1423 (1972).

15. D. Douglass and M. Strandberg, *Physica* **27**, 1 (1961).

16. M. A. Lasheen, J. van der Broek, and C. J. Gorter, *Physica* **24**, 1061 (1958).

17. M. E. LINES, *J. Phys. Chem. Solids* **31**, 101 (1970).
18. L. J. DE JONGH, private communication.
19. L. J. DE JONGH AND J. H. P. COLPA, to be published.
20. F. KEFFER, "Spiwaves, Handbuch der Physik," Band 18, Teil II, Springer Verlag (1966).
21. L. J. DE JONGH, *Phys. Rev. Letters* **40A**, 33 (1972).
22. J. H. P. COLPA, E. G. SIEVERTS, AND R. H. VAN DER LINDE, *Physica* **51**, 573 (1971).
23. D. J. BREED, *Physica* **37**, 35 (1967).
24. J. H. P. COLPA, *Physica* **56**, 205 (1971).
25. N. D. MERMIN AND H. WAGNER, *Phys. Rev. Letters* **17**, 1133 (1966).
26. H. E. STANLEY AND T. A. KAPLAN, *Phys. Rev. Letters* **17**, 913 (1966).