Magnetic Polytypes in Rb_2MnCl_4

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The compound Rb_2MnCl_4 was prepared by two different methods. Neutron diffraction did not reveal any difference in the crystallographic structure and the Néel temperature ($T_N \sim 57°K$) of the samples of the two preparations. The samples did, however, exhibit at $T < T_N$ two distinctly different magnetic structures. It is argued that the appearence of these magnetic polytypes is related to the two-dimensional magnetic behavior of this compound and could in general be expected to occur in compounds exhibiting this behavior.

In a previous work[1] we reported the magnetic structure of Rb_2MnCl_4 to be of the K_2NiF_4 type. We used at that time a sample which was prepared from molten salts (m.s.) at a temperature of 500°C.[1] Neutron diffraction of samples prepared from aqueous solutions (a.s.) at room temperature revealed a distinctly different magnetic structure. The latter method was carried out by dissolving 0.24 mole RbCl and 0.16 mole $MnCl_2 \cdot 4H_2O$ in water, and precipitating $Rb_2MnCl_4 \cdot 2H_2O$ by adding concentrated HCl to the solution. The precipitate was dried in a vaccum desiccator at 130°C until no changes in weight could be observed. This dried material was analyzed for the presence of water. It was found that the water content if any did not exceed 500 ppm (no more than 1 molecule of H_2O to 100 molecules of Rb_2MnCl_4). Neutron diffraction patterns of samples of the two kinds of preparations taken at room temperature (Fig. 1) exhibited no significant differences. It follows from these results that the unit cell dimensions and the atomic position for the two samples are equal within 3%. Neutron diffraction patterns of the two kinds of samples at liquid-helium temperature differ in their magnetic contributions (Fig. 2). In the first sample (prepared from m.s.) the magnetic reflections [Fig. 2(a)] are of the type $(\frac{1}{2}, \frac{1}{2}, l)$ with l integer, whereas the second sample (prepared from a.s.) has magnetic reflections [Fig. 2(b)] of the type $(\frac{1}{2}, \frac{1}{2}, l/2)$ with l odd integer. This shows that in the antiferromagnetic state the magnetic unit cell of sample (b) is doubled in the c direction. The magnetic unit cell translations in the xy plane are the same in both samples. Hence, below the magnetic transition temperature Rb_2MnCl_4 (b) is isostructural with antiferromagnetic Ca_2MnO_4.[2]

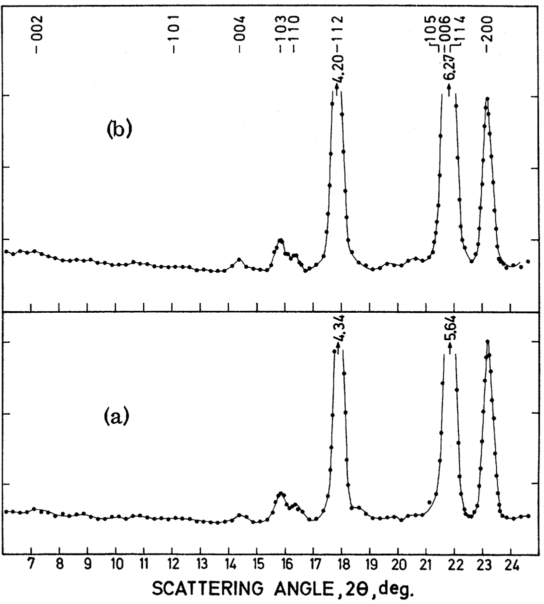

FIG. 1. Neutron diffraction patterns of the powder samples of Rb_2MnCl_4 at room temperature. (a) Prepared from molten salts, (b) prepared from aqueous solutions.

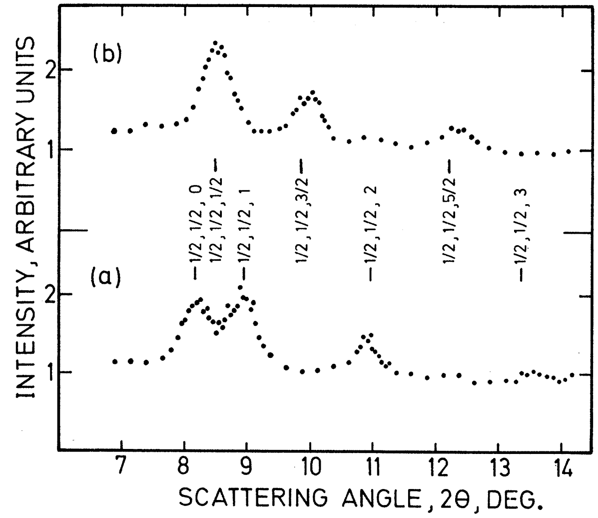

FIG. 2. Neutron diffraction patterns of the powder samples of Rb_2MnCl_4 at 4.2°K. (a) Prepared from molten salts, (b) prepared from aqueous solution.

In samples of the two preparations the transition temperature was found to be identical, about 57°K. The magnetic moment of the Mn^{2+} ion was found to be within 10% of $5\mu_B$ in all samples.

The direction of the spin axis in Rb_2MnCl_4 (a) and (b) is determined mainly by the anisotropy in the dipolar energy.[1] The dipolar energy in these magnetic structures comes from interactions in the xy planes (interaction between planes is negligible). The spin configuration in an xy plane is the same in the two types of magnetic structure. The two types are therefore expected to have identical dipolar fields and the same direction of the spin axis. Calculations[1] show that the minimum in dipolar energy is reached when the spin axis is parallel to c, in agreement with experiment.

The decrease in symmetry below the transition temperature is from $1'I4/mmm$ to $F_B mm'm'$ and $P_I\bar{4}'2m'$ in Rb_2MnCl_4 (a) and (b), respectively. The two space groups belong to different irreducible representations of $1'I4/mmm$ as required by Landau's theory of second-order phase transitions.[3]

Heat treatment was applied to sample (b), prepared by the a.s. "cold" method and having the Ca_2MnO_4-type magnetic structure. It was annealed in vacuum for 100 h at 430°C, and then quenched to room temperature. A neutron diffraction pattern of this heat-treated sample taken at 4.2°K showed a magnetic structure identical with that of sample (a), having the K_2NiF_4-type magnetic structure. This result implies that the K_2NiF_4 magnetic structure corresponds to the "true ground state" of this compound.

Temperature-dependent studies of the K_2NiF_4-type samples showed that it has two-dimensional magnetic behavior.[1] In such structures the magnetic interaction in the xy planes (J_{xy}) is about 10^4 times stronger than that between these planes (J_z).[4] Hence, a possible explanation of the appearence of the two magnetic structures is as follows: It may be that $J_z > 0$ in sample (a) favoring parallel alignment of spins along c and $J_z < 0$ in sample (b) favoring antiparallel alignment of spins along c. This will lead to a K_2NiF_4- and a Ca_2MnO_4-type magnetic structure in the two samples, respectively. Since J_z is small a slight difference in the crystallographic structure (smaller than 3%) may be responsible for the difference in J_z in the two samples. If this explanation is true, we should expect this kind of magnetic polytypism to be abundant among compounds with two-dimensional magnetic behavior.

Recently, Birgeneau, Guggenheim, and Shirane[5] noticed the existence of two such magnetic structures in Rb_2MnF_4. It should be mentioned that the two structures of Rb_2MnF_4 were found to exist simultaneously in the same sample, while in our case each structure of Rb_2MnCl_4 is separately prepared.

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