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Structural changes of $KMnF_3$ at low temperatures.* By OLOF BECKMAN,† *Department of Physics, University of California, Berkeley 4, California,* IVAR OLOVSSON,‡ *Department of Chemistry, University of California, Berkeley 4, California,* KERRO KNOX, *Bell Telephone Laboratories, Murray Hill, New Jersey, U.S.A.*

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Fluorides of the type $KMeF_3$ crystallize with perovskite-like structures. The manganese compound $KMnF_3$, which is cubic at room temperature ($a = 4\cdot186$ Å), becomes antiferromagnetic with a Neel temperature $T_N = 88$ °K. (Martin *et al.*, 1956, Shulman *et al.*, 1959). In order to determine whether any change in the crystal symmetry takes place when the Neel temperature is passed, an X-ray analysis of a single crystal of $KMnF_3$ was performed. The crystal was grown by zone-refining material that had been precipitated from aqueous solution and sintered in anhydrous hydrogen fluoride. In order to reduce oxygen contamination the material to be zone-refined was placed in a graphite boat in a dry nitrogen atmosphere.

The crystal analysis was done using Cu *K*-radiation in a Weissenberg camera modified for use at temperatures down to 77 °K. (Olovsson & Templeton, 1959). The crystal was cooled by a stream of nitrogen gas obtained from a liquid nitrogen dewar. By means of a heater in the gas stream the sample temperature could be adjusted to the desired value. The temperature was held constant to within ± 5 °K. and measured with a thermocouple close to the sample.

Photographs taken at room temperature showed the pattern of the cubic perovskite structure. However, a series of photographs taken at lower temperatures gave the unexpected result that the spots split somewhat below 200 °K., nearly 100° above the Neel temperature. The splitting may be explained as a lowering of the symmetry to tetragonal. (The symmetry can be still lower, e.g. orthorhombic with two axes nearly equal. This cannot be determined from the present data, however). Different crystallites may be expected to have their fourfold axes oriented along one of the three former cube axes. Reflections ($h00$) at large Bragg angles give two spots with the intensity ratio 2:1, while (hhh) spots does not show any splitting in the diffracting angle. They can only split in the azimuthal angle because of different layer line separations. This splitting is too small to detect in the actual case because of the small difference between the a- and c-axial lengths.

The change of the a- and c-axes with temperature is plotted in Fig. 1 as calculated from the splitting of the (510), (420) and (400) cubic reflections. Below 200 °K. c/a increases linearly with decreasing temperature. The c/a ratio reaches its maximum value $c/a = 1\cdot007$, at the Neel temperature. At the antiferromagnetic transition the a-axis elongates and the c-axis contracts, reducing the axial ratio to a value very close to unity. The change in lattice symmetry below 200 °K. is not accompanied by any noticeable discontinuity in the volume contraction. In Fig. 1 the volume contraction is represented by a dotted line, calculated as the weighted mean of the changes in a- and c-axes.

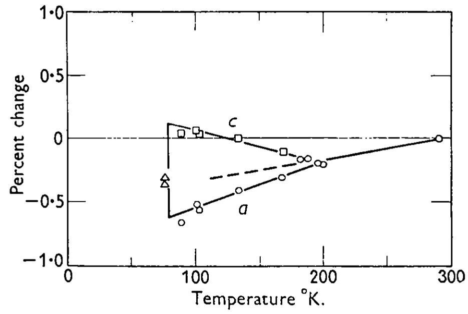

Fig. 1. $KMnF_3$. Change in c- and a-axes with temperature.

When mounted in the Weissenberg camera with the temperature control device, the crystal was also investigated for optical anisotropy using two crossed polaroids. The crystal appeared dark at room temperature, indicating optical isotropy in the cubic state. The crystal showed optical anisotropy at lower temperatures, however. The transition to this state occurred at 184 ± 5 °K. in agreement with the change from cubic to lower symmetry as obtained from the X-ray data. The crystal appeared to divide into crystallites with optical axes parallel to the former cube edges. No further change in the optical properties could be observed at the Neel point.

Recently, Scatturin (1959) has observed by neutron diffraction a distortion from cubic symmetry in $KMnF_3$ at 4·2 °K., which, however, he describes as an orthorhombic modification.

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