THE CRYSTAL STRUCTURES OF RbMnP₂O₇

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The crystal and magnetic structures of RbMnP₂O₇ have been determined. The crystal structure (a=7.3672(2), b=9.6782(2), c=8.6467(2) Å, β=105.488(1)° space group P2₁/c, was determined from X-ray and neutron powder diffraction, and was found to be isostructural with RbFeP₂O₇. Magnetic susceptibility measurements showed that RbMnP₂O₇ behaves as a Curie-Weiss paramagnet at high temperatures and orders antiferromagnetically below a Neel temperature of 20K. From low temperature neutron diffraction, the magnetic structure was found to be commensurate with the nuclear cell, with a magnetic symmetry group P2₁/c.

Introduction. Diphosphates of the trivalent transition metals of the stoichiometry A⁺M⁺³P₂O₇ (A=alkali metal, M=V,Fe,Mo) exhibit several structure types [1–3]. The frameworks of these phases are built up from corner-sharing MO₆ octaedra and P₂O₇ groups. The size of the alkali metal cation plays an important role in the crystal structures of A⁺M⁺³P₂O₇. The diphosphate group is very adaptive to the bonding

Figure 1. 2(°) diagram
requirements of other groups in the structure by adjusting the P–O–P bond angle and configuration of two phosphates tetraedra. In our continuing study of magnetic exchange interactions in these systems, we have investigated the nuclear and magnetic structure of RbMnP$_2$O$_7$ using neutron powder diffraction data recorded on HRPT at a wavelength of 1.886 Å at 2K and 100K. Analysis was performed using the GSAS suite of programs and the Rietveld plot from the 2K data is displayed in figure 1.

**Results and discussion.** The resulting nuclear structure was found to consist of a framework of corner-sharing Mn$_0$$_6$ octaedral and P$_2$O$_7$ groups, creating intersecting tunnels, with the Rb$^+$ cation located at the intersection of these tunnels. The Mn$_0$$_6$ octaedral were found to display an untypical (2+2+2) distorted arrangement (2 long, 2 medium and 2 short bonds) instead of the traditional (4+2) Jahn-Teller distortion expected for Mn$^{3+}$. The diphosphate group contained two distorted PO$_4$ tetraedra, with long P-O bonds to the bringing O atom and shorter bonds to terminal O atoms.

After the nuclear contribution was fitted for the 2K neutron diffraction pattern, extra peaks and intensity were evident and were assigned as magnetic diffraction. Subsequently, the nuclear and magnetic cells were found to be commensurate and consistent with the magnetic space group P2$_1$/c, with the magnetic moments lying in the ac plane resulting in a moment of 3.65 $\mu_B$. The relative direction of the four Mn spins in the unit cell were found to be (0.23, 0.90, 0.26)$^+$, (0.23, 0.60, 0.76)$^-$, (0.77, 0.40, 0.25)$^+$ (0.77, 0.10, 0.75)$^-$, orientated closely to the two long axial Mn–O bonds (fig. 2).

**Conclusion**

Interestingly, this magnetic structure was found to consist of both antiferromagnetic and ferromagnetic exchange interactions mediated through Mn–O–Mn–O pathways.

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**Figure 2. Orientated closely Mn–O bonds**

Досліджено кристалічну і магнітну структуру RbMnP_2O_7. Параметри кристалічної решітки (a=7.3672(2), b=9.6782(2), c=8.6467(2) Å, β=105.488(1)° просторової групи P2_1/c, було визначено рентгеновською та нейтронною силовою дифракцією, яка підтвердила ізоструктурність отриманого фосфату з RbFeP_2O_7.

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АНАТОЦІЯ


Исследована кристаллическая и магнитная структура RbMnP_2O_7. Параметры кристаллической решетки (a=7.3672(2), b=9.6782(2), c=8.6467(2) Å, β=105.488(1)° пространственной группы P2_1/c, были определены рентгеновской и нейтронной силовой дифракцией, которая подтвердила изоструктурность полученного фосфата с RbFeP_2O_7.

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