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Magnetic Properties of Layer Compounds $RbVF_4$ and $Cs_{0.5}Rb_{0.5}VF_4$

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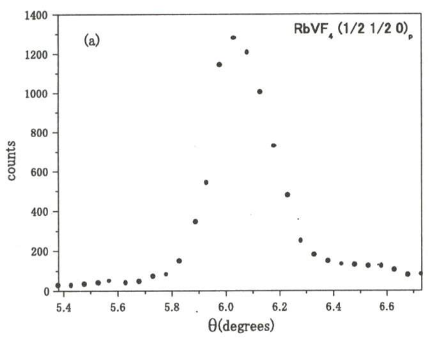
Magnetic properties of $RbVF_4$ and $Cs_{0.5}Rb_{0.5}VF_4$ are studied by neutron diffraction and magnetic susceptibility. Although the compounds show successive structural phase transitions related to the tilting around the primitive axes of the VF_6 octahedron and the distortion from its rigid shape, the anti-ferromagnetic transitions are found to occur at about 45 K and 36 K on $RbVF_4$ and $Cs_{0.5}Rb_{0.5}VF_4$, respectively. The unit cell of the anti-ferromagnetic structure is $2a_p$ x $2b_p$ x c_p for $RbVF_4$ and $2a_p$ x $2b_p$ x $2c_p$ for $Cs_{0.5}Rb_{0.5}VF_4$, where the suffix 'p' means a pseudo unit cell, a_p x b_p x c_p of an ideal $TlAlF_4$-type structure. Such the magnetic properties are interpreted by the difference magnetic interaction among V^{+3} magnetic moments in the two-dimensional networks of VF_6 octahedra.

KEYWORDS: layer compound, magnetic structure, phase transition, $RbVF_4$, $Cs_{0.5}Rb_{0.5}VF_4$

§1. Introduction

The structure of the layer compounds $RbVF_4$ and $Cs_{0.5}Rb_{0.5}VF_4$ is mainly characterized by two-dimensional networks of VF_6 octahedra, and Rb^{+1} and Cs^{+1} ions intercalated among these networks. $RbVF_4$ shows the structural phase transitions at about 184 K, 413 K and 482 K,[1)] while $Cs_{0.5}Rb_{0.5}VF_4$ at about 123 K and 368 K.[2)] The similar compound $CsVF_4$ has the structural phase transitions at about 142 K, 425 K, 510 K and 535 K.[3)] These successive phase transitions give a cooperative tilting in the two-dimensional networks of the rigid-like VF_6 octahedra stacked along the c axis. The structure in a lowest-temperature phase of these compounds has an orthorhombic symmetry of space group $P2_12_12$. It is therefore expected that the localized structure property is slightly different among $RbVF_4$,$Cs_{0.5}Rb_{0.5}VF_4$ and $CsVF_4$ from their characteristic tilting-scheme and tilting-angles around primitive axes of the VF_6 octahedra in addition to an ionic radius and a spatial distribution of Rb and Cs ions intercalated among the two-dimensional networks of VF_6 octahedra. Hidaka *et al.*[4,5)] and Ikeda *et al.*[6)] reported that $CsVF_4$ showed the magnetic phase transition at about 43 K, and the magnetic structure depends on the outer magnetic field applied to its single crystal. It was also found that, at 5 K, the magnetic unit cell was $2a_p$ x $2b_p$ x $2c_p$ in zero field-cooling and $2a_p$ x $2b_p$ x c_p in 2T field-cooling. Thus, it is considered that the structural modulations induced by the successive structural phase transition affect the characterized magnetic interactions among magnetic moments of V^{+3} ions in the layer compound having the $TlAlF_4$-type structure. The ordering of the magnetic moments is considerably related to the inner and interplane magnetic interaction in the VF_6 networks. In the present investigation, we will report the experimental results of the neutron diffraction and the magnetic susceptibility for $RbVF_4$ and $Cs_{0.5}Rb_{0.5}VF_4$.



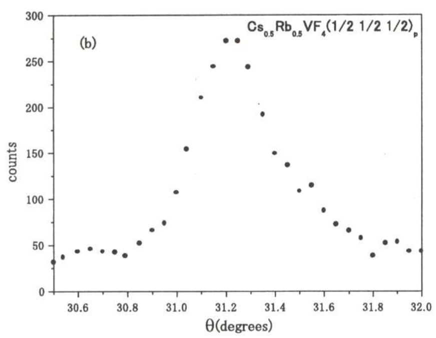


Fig. 1. Peak profile of the magnetic reflection; (a) $(1/2\ 1/2\ 0)_p$ in $RbVF_4$, and (b) $(1/2\ 1/2\ 1/2)_p$ in $Cs_{0.5}Rb_{0.5}VF_4$.

§2. Experiments

2.1 Neutron diffraction

In order to study the magnetic transition of $RbVF_4$ and $Cs_{0.5}Rb_{0.5}VF_4$, we carried out measurements of the

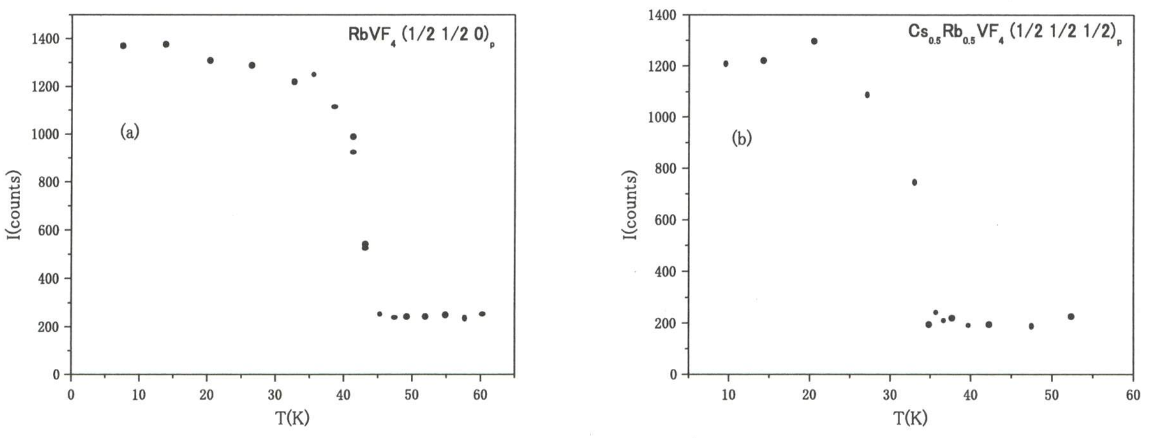


Fig.2. Temperature dependence of the integrated intensity of magnetic reflection;(a) $(1/2\ 1/2\ 0)_p$ in $RbVF_4$, and (b) $(1/2\ 1/2\ 1/2)_p$ in $Cs_{0.5}Rb_{0.5}VF_4$.

intensity of some magnetic reflections as a function of the specimen temperature by using a reactor JRR-3M. The size of the used single crystal was about 8 x 8 x 2 mm^3 and 5 x 5 x 3 mm^3 for $RbVF_4$ and $Cs_{0.5}Rb_{0.5}VF_4$, respectively. The large surface was a nice cleavage $(0\ 0\ 1)_p$ plane. Figs.1 (a) and (b) show a peak profile of the magnetic reflection having a index $(1/2\ 1/2\ 0)_p$ and $(1/2\ 1/2\ 1/2)_p$ obtained at 8.4 K in $RbVF_4$ and at 9.6 K in $Cs_{0.5}Rb_{0.5}VF_4$, respectively. The data were taken under the zero field-cooling and no applied magnetic field. Therefore, it becomes clear that the magnetic structure should be the anti-ferromagnetic super-lattice structure of C-type in $RbVF_4$ and G-type in $Cs_{0.5}Rb_{0.5}VF_4$, and that the magnetic structure was $2a_p$ x $2b_p$ x c_p for $RbVF_4$ and $2a_p$ x $2b_p$ x $2c_p$ for $Cs_{0.5}Rb_{0.5}VF_4$. To look for the magnetic phase transition of the layer compounds, we measured the temperature dependence of the integrated intensity (I) of magnetic reflections shown in Figs.1 (a) and (b). The results are represented in Figs.2 (a) and (b) for $RbVF_4$ and $Cs_{0.5}Rb_{0.5}VF_4$, respectively. From these (I-T) curves, it was found that there is the magnetic transition at about 45 K in $RbVF_4$, and at about 36 K in $Cs_{0.5}Rb_{0.5}VF_4$.

Since the magnetic transition of $CsVF_4$ occurs at about 43 K, it is considered that the difference of these transition temperatures results from the slight different circumstance of the inner and inter-plane magnetic interaction among the magnetic moments of V^{+3} ions in the two-dimensional networks of VF_6 octhedra. Thus, we carried out measurements of some magnetic reflections under the 0.8 T field-cooling by appling the magnetic field of 0.8 T on heating up, where the magnetic field was vertical and parallel to the c axis. However, we could not find any change of the magnetic transition temperature and the intensity-modulation of the magnetic reflections. It is therefore expected that the stronger magnetic field than 0.8 T is needed to change the induced magnetic structure as like that in $CsVF_4$. We are now proceeding to study the magnetic structures in $RbVF_4$ and $Cs_{0.5}Rb_{0.5}VF_4$ under the field-cooling of the high magnetic field of 1 to 2 T by the neutron diffraction. The present results suggest that the partial substitution between Rb^{+1} and Cs^{+1} ions intercalated among the networks of the VF_6 octahedra affect the inter-plane magnetic interaction among the anti-ferromagnetic VF_6 networks because of the decrease of the transition temperature.

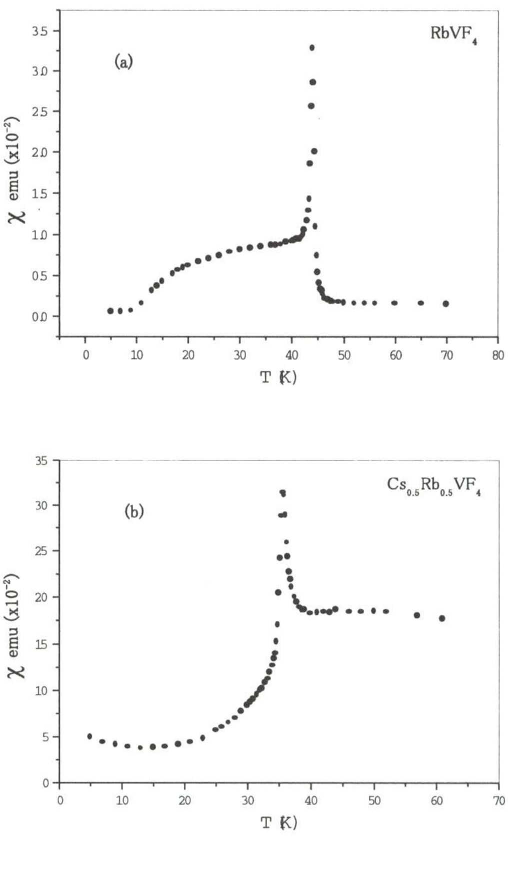


Fig.3. Temperature dependence of the magnetic susceptibility. The applied magnetic field was 1.5 kOe to be parallel to the c axis of the layer compounds; (a) $RbVF_4$, and (b) $Cs_{0.5}Rb_{0.5}VF_4$.

2.2 Magnetic susceptibility

To study the difference of the magnetic properties between $RbVF_4$ and $Cs_{0.5}Rb_{0.5}VF_4$, we measured the magnetic susceptibility of these layer compounds by using highly accurate SQUID magnetometer. The data were taken under zero field-cooling and 0.8 T field-cooling, and by applying the magnetic field of several strength to be vertical and parallel to the c axis. The details of the present susceptibility will be published elsewhere.[7] The representative results are shown in Figs.3 (a) and (b) for $RbVF_4$ and $Cs_{0.5}Rb_{0.5}VF_4$, respectively. In the figures, we measured the susceptibility under the zero-field cooling when the applied magnetic field of 1.5 kOe was parallel to the c axis on heating up. The temperature dependence of the susceptibility indicated under the field-cooling of 0 and 0.8 T that there is the anti-ferromagnetic phase transition at about 45 K in $RbVF_4$ and at about 36 K in $Cs_{0.5}Rb_{0.5}VF_4$, and that the magnetic moments of V^{+3} are aligned to be almost parallel to the c axis below the transition temperature. The susceptibility in $Cs_{0.5}Rb_{0.5}VF_4$ shows the different behavior from about 43 K to 10 K in contrast to those in $RbVF_4$ and $CsVF_4$.[6] It is deduced that, in $RbVF_4$ and $CsVF_4$, there are the weak ferromagnetic components depending on the specimen temperature, while there is no components in its temperature region in $Cs_{0.5}Rb_{0.5}VF_4$. Thus, we considered that the partial substitution between Rb^{+1} and Cs^{+1} ions in $Cs_{0.5}Rb_{0.5}VF_4$ affects the cooperative tilting scheme of the VF_6 octahedra around their primitive axes. Such the localized structural modulation around V^{+3} ions gives slightly changes of the inner and/or inter-plane magnetic interaction among the magnetic moments of V^{+3} ions.

Furthermore, an interested sharp divegence of the susceptibility occurs in the vicinity of the transition temperature as like that in $CsVF_4$. It is well known that such the critical behavior results from an appearance of short-range order among the magnetic moments. However, the intensity of the $(1/2\ 1/2\ 1/2)_p$ and $(1/2\ 1/2\ 0)_p$ magnetic reflections in $RbVF_4$ and $CsVF_4$ did not diverge around to the transition temperature, though the reflections were measured under the field cooling of 0 and 0.8 T and by applying the magnetic field of 0.8 T on heating up. It is therefore considered that such the divergence of the susceptibility is a characteristic property in the layer magnetic compounds having the $TlAlF_4$-type structure. On the other hand, the susceptibility taken under the same condition of the magnetic fields but applied to be vertical to the c axis, did not show the divergence in the vicinity of the transition temperature and sharply increased as decreasing the specimen temperature. It was also found that the susceptibilities taken in the applied magnetic fields to be parallel and vertical to the c axis perfectly consist each other in the region between the transition temperature and the temperature at the maximum value of the susceptibility-divergence.

§3. Discussion

From the present experiments, we found that the magnetic phase transitions occur at about 45 K in $RbVF_4$ and 36 K in $Cs_{0.5}Rb_{0.5}VF_4$, and the magnetic structures are the anti-ferromagnetic order of the V^{+3} magnetic moments to be the C-type in $RbVF_4$ and the G-type in $Cs_{0.5}Rb_{0.5}VF_4$. However, in $RbVF_4$, the weak ferromagnetic components are observed in the peculiar temperature region below the transition temperature as shown in Fig. 3(a). It was considered that the components to be vertical to the c axis result from cants of the magnetic moments aligned along the c axis in the (0 0 1) plane. The structure having the space group $P2_12_12$ gives the large tilts of the VF_6 octahedron around its primitive axes in contrast to those in high-temperature phases; $P2_12_12_1$ ($184K < T < 413K$), $Pmmn$ ($413K < T < 482K$) and $P4/mbm$ ($T > 482K$). At about 30 K, the tilting angles of the octahedra in $RbVF_4$ can be roughly estimated to be about 10 to 15 degrees.[1] Thus, the super-exchange magnetic interaction among V^{+3} ions induces the weak ferromagnetic components in the (0 0 1) plane by largely modulating a linear bonding direction of V^{+3} -F^{-1} -V^{+3} sited in the two-dimensional networks of the VF_6 octahedra. On the other hand, $Cs_{0.5}Rb_{0.5}VF_4$ shows the structural phase transition to the $P2_12_12$ structure at about 123 K and the largely different scheme of the successive phase transition in contrast to those in $RbVF_4$ and $CsVF_4$.[1–3] Therefore, it is expected that the VF_6 octahedra are not largely tilted and the cants of the magnetic moments do not occur below the magnetic transition-temperature of about 36 K, that is no weak ferromagnetic components. In order to study a correlation between the magnetic structure and the inter-plane magnetic interaction among two-dimensional anti-ferromagnetic networks of V^{+3} ions in $RbVF_4$ and $Cs_{0.5}Rb_{0.5}VF_4$, we are now proceeding to carry out the measurements of the lattice parameters by x-ray diffraction and of the localized structural modulation around V^{+3} ions by EXAFS in addition to the neutron diffraction.

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