Experimental report

13/12/2018

Proposal: **4-01-1579** **Council:** 4/2017

Title: Neutron scattering studies of transition metal pyrovanadates M2V2O7 (M = Ni, Co, Mn)

Research area: Physics

This proposal is a new proposal

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Samples: Mn2V2O7
Co2V2O7
Ni2Vi2O7
Mn2-xZnxV2O7

Instrument	Requested days	Allocated days	From	To
IN4	6	4	22/05/2018	26/05/2018

Abstract:

The family of transition metal-pyrovanadate systems with general formula M2V2O7 (M =Cu, Ni, Co, Mn) have attracted much interest due to their intriguing crystal structures where the main building blocks are various extended units of M-O and V-O polyhedra. The origin of their interesting physical properties lies closely related to the structural and electronic aspects of the compounds. Recently, our group has systematically investigated the magnetic and electric properties of these pyrovanadates in their polycrystalline form. We have investigated the compound á-Cu2V2O7 using powder inelastic neutron scattering on MARI which shows that the third nearest neighbour exchange interaction playing a dominant role. It would be interesting to estimate the exchange interactions in M2V2O7 (M =Ni, Co, Mn) compounds to find out whether it is general trend that third neighbour exchange interactions are dominate in these compounds also. We therefore propose to investigate magnetic excitations in these compounds using IN4.

Experimental Report: Neutron Scattering Studies of Transition Metal pyrovanadates $M_2V_2O_7$ (M = Ni, Co, Mn)

Experiment No. – 4-01-1579

In order to study the nature of magnetic ground state explicitly, we performed inelastic neutron scattering on IN4 spectrometer on the 3*d* transition metal based pyrovanadate systems with general formula $M_2V_2O_7$. This group of compound has attracted lots of interest for their fascinating and diverse crystal structures where main building blocks are various extended units of M-O and V-O polyhedra exhibiting low dimensional chain, sheet like structure to more complex three dimensional structure. It consists of magnetic M^{2+} ($3d^9$ to $3d^5$) and nonmagnetic V^{5+} ($3d^0$, S = 0) metal ions, making it a system having both partially filled and empty d shells. Although V is nonmagnetic, it can expedite the magnetic interaction by electron transfer via its empty 3*d* level. The magnetic interaction can be quite intriguing due to the interaction pathways. Ground state magnetic structure of this series of compound is also versatile depending on the transition metal. From neutron diffraction study we observed canted antiferromagnetic correlation within the Co^{2+} spins for $Co_2V_2O_7$ and a complex incommensurate configuration is found in case of $Mn_2V_2O_7$. Therefore to get insight in the nature of magnetic ground state of these compounds, inelastic neutron scattering experiments have been performed on the powder sample of $Co_2V_2O_7$ and $Mn_2V_2O_7$ compounds. $Mn_2V_2O_7$ has paramagnetic to antiferromagnetic transition at around 20 K and it goes to more complex incommensurate phase below 11 K. To find out the reason behind this complicated ground state of $Mn_2V_2O_7$, we also performed inelastic neutron scattering study in the Zn doped samples where Mn is substituted partially by nonmagnetic Zn. Non-magnetic $Zn_2V_2O_7$ has also been studied to find out the phonon contribution. In the following section, experimental result obtained from IN4 instrument is briefly stated.

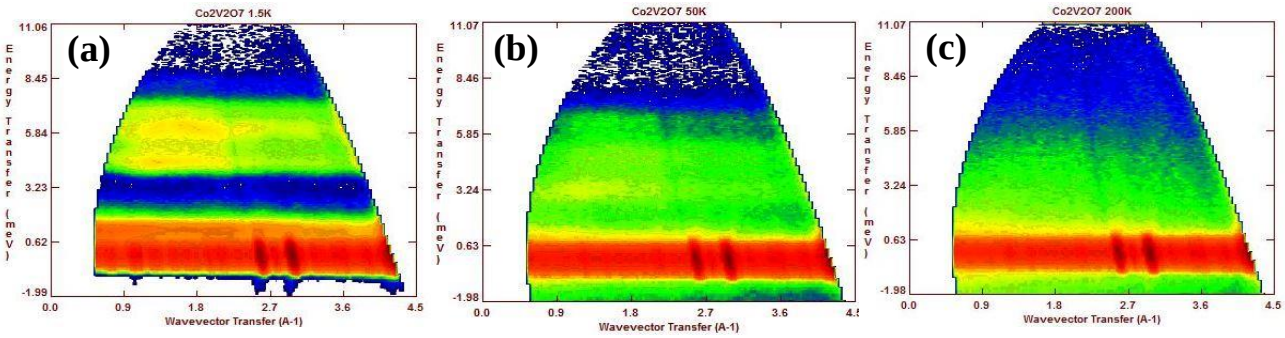

Figure1. 2D colour plot of INS data measured on $Co_2V_2O_7$ at (a) 1.5 K, (b) 50 K and (c) 200 K.

$Co_2V_2O_7$: $Co_2V_2O_7$ has canted antiferromagnetic ground state where interaction is mostly antiferromagnetic along *c* (along skew chain of Co1 and Co2) with the presence of small moment along *b* which forms cycloidal type spin configuration. INS experiment has been performed on 5.46 g of powder sample of $Co_2V_2O_7$ on IN4 spectrometer with an incident wavelength of 2.6 Å at different temperatures. INS study at 1.5 K shows clearly two bands of scattering intensities around the energy transfer $\hbar\omega$ = 4.8 meV and 5.8 meV in the low-Q regime which signifies the magnetic origin. These scattering intensities started to diminish above T_C = 8 K. But up to 50 K there some scattering intensities exist which may be due to

short range spin correlation before the long range ordering. Temperature dependent magnetic susceptibility also deviates from Curie-Weiss type behaviour below 100 K signifying the presence of some short range correlations. Figure 1 (a), (b) and (c) show the 2D colour coded intensity maps, energy transfer vs momentum transfer inelastic neutron scattering measured at 1.5 K, 50 K and 200 K.

$Mn_2V_2O_7$: INS study has been performed on 6.91 g of powder sample of $Mn_2V_2O_7$ with incident wavelength of 3.36 Å on IN4 spectrometer. A broad band of scattering intensity started to appear below T_C = 20 K at around 4 meV energy transfer in the low-Q regime. Low-Q scattering is related to the long range magnetic ordering and it arises from the spin wave excitations in the ordered state of material. Below 11 K, where commensurate to incommensurate transition set up, appearance of feature is observed in the 2D colour plot of energy transfer versus momentum transfer around very low energy transfer regime of approximately 1.8 meV. Though this second scattering intensity below 11 K is not resolved completely, but it signifies the presence of another magnetic ordering below 11 K. Some broad scattering is also present just above the T_C because of some short range ordering present in this system above T_C. 2D colour plot of energy transfer versus momentum transfer of this INS study is shown in figure 2 (a), (b) and (c) respectively for 1.5 K, 14 K and 50 K.

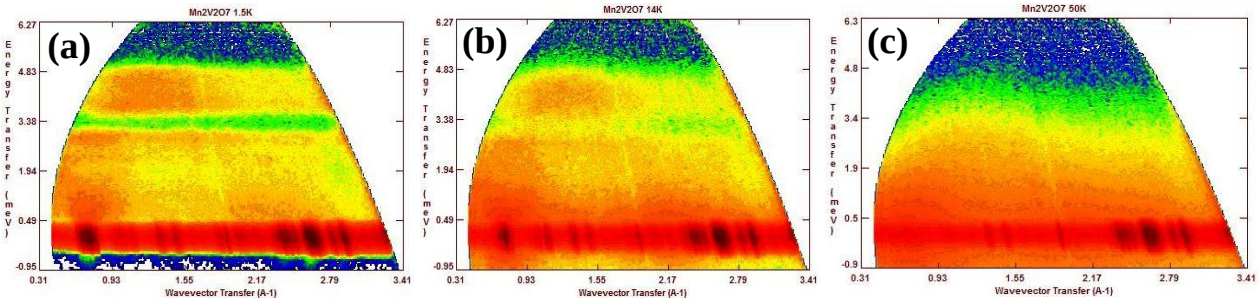

Figure1. 2D colour plot of INS data measured on $Mn_2V_2O_7$ at (a) 1.5 K, (b) 14 K and (c) 50 K.

$Mn_{(1-x)}Zn_xV_2O_7$ [x = 0.2, 0.4, 1, 2]: To understand the complex magnetic ground state of $Mn_2V_2O_7$, we studied INS on nonmagnetic Zn substituted compounds at different temperatures below and above magnetic ordering. All measurements are performed on 8-9 g powder sample on IN4 spectrometer with incident wavelength of 3.36 Å. With 10% Zn doping the behaviour is almost same like $Mn_2V_2O_7$. We observe a clear band of scattering intensity around 4 meV energy transfers in the low-Q regime at low temperature and a broad scattering is also present above T_C. 2D colour plot of INS data measured at 1.5 K, 14 K and 50 K on $Mn_{0.8}Zn_{0.2}V_2O_7$ are shown in figure 3(a), (b) and (c) respectively. With further Zn doping (20%), we clearly observed the two band of scattering intensities at $\hbar\omega$ = 4.7 meV and 3.0 meV in the low-Q regime. This is shown in figure 3(d), (e) and (f) respectively for 1.5 K, 10 K and 50 K for $Mn_{1.6}Zn_{0.4}V_2O_7$ compound. But, in case of $MnZnV_2O_7$ (50% Zn doping) no band like feature is observed in the energy transfer versus momentum transfer colour plot. Only a broad scattering is observed in the low-Q regime. 2D colour plots of these scattering intensities are shown in figure (g) and (h) respectively for 1.5 K and 50 K. Nonmagnetic $Zn_2V_2O_7$ has also been studied to find out the phonon contribution which is shown in figure 3(i) measured at 1.5 K with incident wavelength of 3.36 Å.

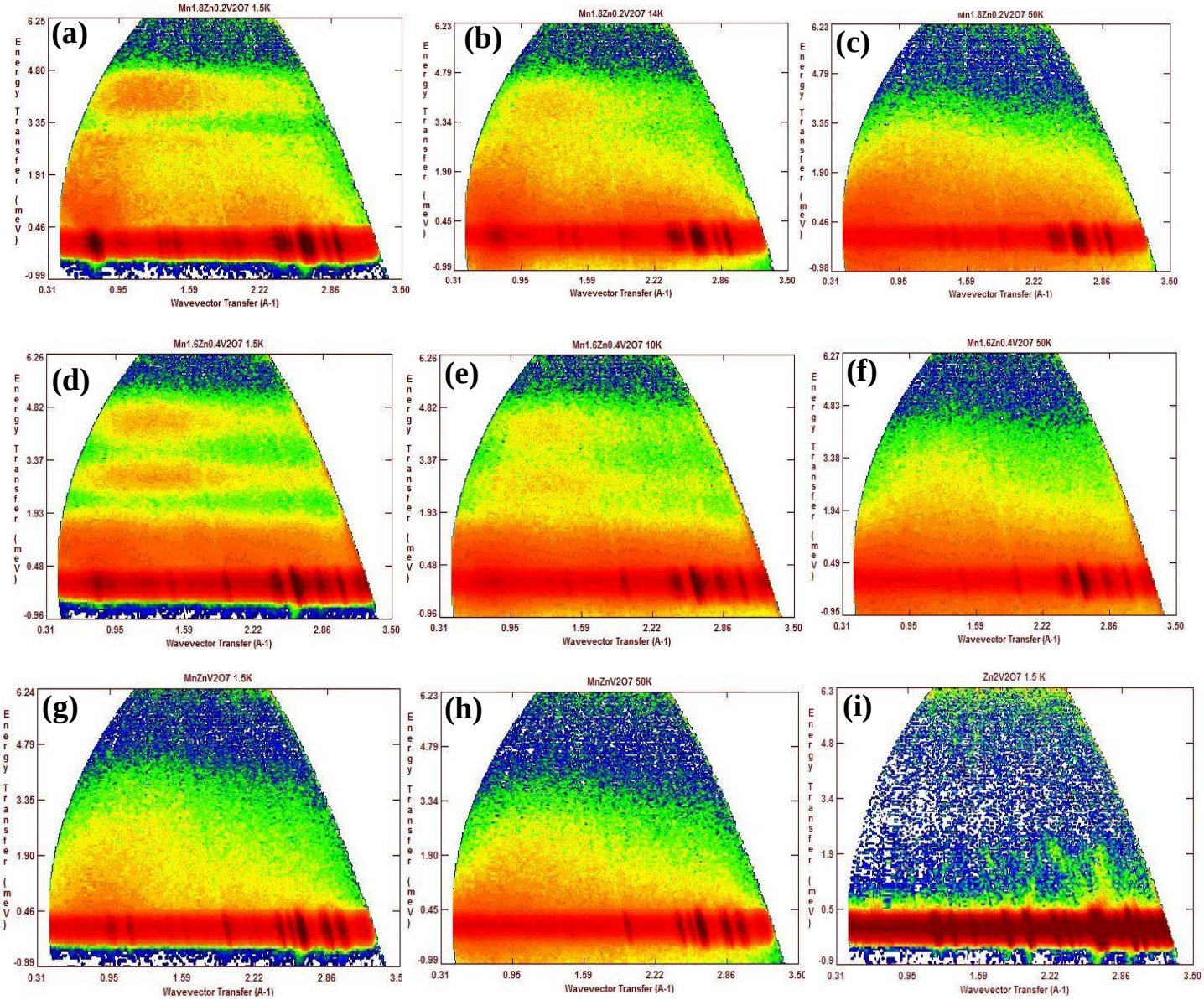

Figure3. 2D colour plot of INS data measured on $Mn_{1.8}Zn_{0.2}V_2O_7$ at (a) 1.5 K, (b) 14 K and (c) 50 K; on $Mn_{1.6}Zn_{0.4}V_2O_7$ at (d) 1.5 K, (e) 10 K and (f) 50 K; on $MnZnV_2O_7$ at (g) 1.5 K and (h) 50 K. (i) displays the same for $Zn_2V_2O_7$ at 1.5 K

Further analysis of these data is ongoing. We are trying to do the spin wave simulation using SpinW software package to understand the underlying physics in the fascinating ground state of these