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Magnetic Properties of Transition Metal Ion doped $LiCuVO_4$†

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The magnetic properties of Mn- and Zn-doped $LiCuVO_4$ were investigated. With Zn-doping the high temperature region remains antiferromagnetic but with Mn-doping it shows small ferromagnetic ordering. For both transition metal ions doping the intrachain exchange integral decreases. Zn-doping has very minor effect on $LiCuVO_4$ and the long range ordering with very minute ferromagnetic moment has been observed whereas for Mn-doped sample long range ordering with appreciable ferromagnetic moment has been observed.

Key Words: One dimensional spin chain.

INTRODUCTION

The study of low dimensional quantum magnets is one of the most important topics of condensed matter physics because of various interesting quantum magnetic phenomena due to strong quantum fluctuations in the one dimensional structure[1-3]. Recently a new member of the 1D cuprate with the chemical formula $LiCuVO_4$ with spin S = 1/2 (in $x^2 - y^2$ orbital) was synthesized[4-8], which has only one crystallographically distinct Cu site[9]. Moreover, for this system, the exchange interaction between the nearest-neighbour Cu^{2+} ions through Cu-O-Cu exchange path is rather weak, as expected for the Cu-O-Cu angle close to 90º (*ca.* 95º) or even weaker than the next nearest-neighbor interaction[10-12] suggesting the effects of the magnetic frustration are significant in its magnetic properties. This type of magnetic structure is interesting as it satisfies the condition for the occurrence of simultaneous magnetic and ferroelectric transitions to the so called multiferroic state[9-13]. In the present work we have investigated the doping effect on the transition metal ion site on the magnetic properties. To the best of our knowledge this is the first time the evolution of the long range ordering with doping in this low dimensional $LiCuVO_4$ has been shown.

EXPERIMENTAL

The polycrystalline samples were prepared by solid-state reaction from high purity Li_2CO_3, CuO, V_2O_5, ZnO and MnO powders with final sintering temperature 550 ºC. The X-ray powder diffraction has been taken from Rigaku MiniFlex II DEXTOP X-ray diffractometer with CuK_α radiation. Magnetic measurement was done using MPMS SQUID (Quantum design) magnetometer.

RESULTS AND DISCUSSION

Fig. 1, shows X-ray diffraction pattern of $LiCu_{1-x}M_xVO_4$ (M = Zn and Mn and x = 0, 0.05) samples, which clearly indicates the single phase. Fig. 2 shows the magnetization as a function of temperature at different magnetic fields for $LiCuVO_4$ sample. As temperature decreases the magnetization passes through wide peak at T_m *ca.* 26 K and then increases somewhat at 10 K. The T_m value is independent of the magnetic field. The behaviour is consistent with those already reported.[7,14,15] Fig. 3, shows the M(T) behaviour of Zn doped $LiCuVO_4$ sample at different magnetic fields. It is observed that with doping of Zn, M(T) behaviour remain same except slight increased value of magnetization. In Fig. 4 the M(T) curve of Mn-doped $LiCuVO_4$ has been presented. It also shows a broad peak around 21 K and the bifurcation (between ZFC and FC) occur around that temperature. As the magnetic field increases the broad peak diminishes but the signature remains there even at higher magnetic field.

It has been observed by fitting (not shown) with the Curie-Weiss law: $\chi = C/T-\theta$, where χ is the susceptibility M/H, T is absolute temperature, C is the curie constant and θ is the

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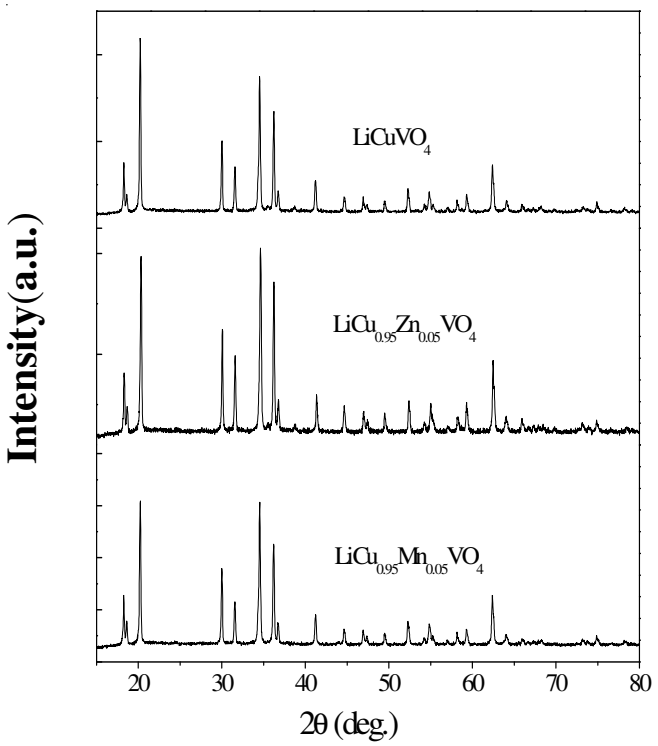

Fig. 1. X-ray diffraction pattern of $LiCuVO_4$, $LiCu_{0.95}Zn_{0.05}VO_4$ and $LiCu_{0.95}Mn_{0.05}VO_4$ samples. The patterns show single phase character

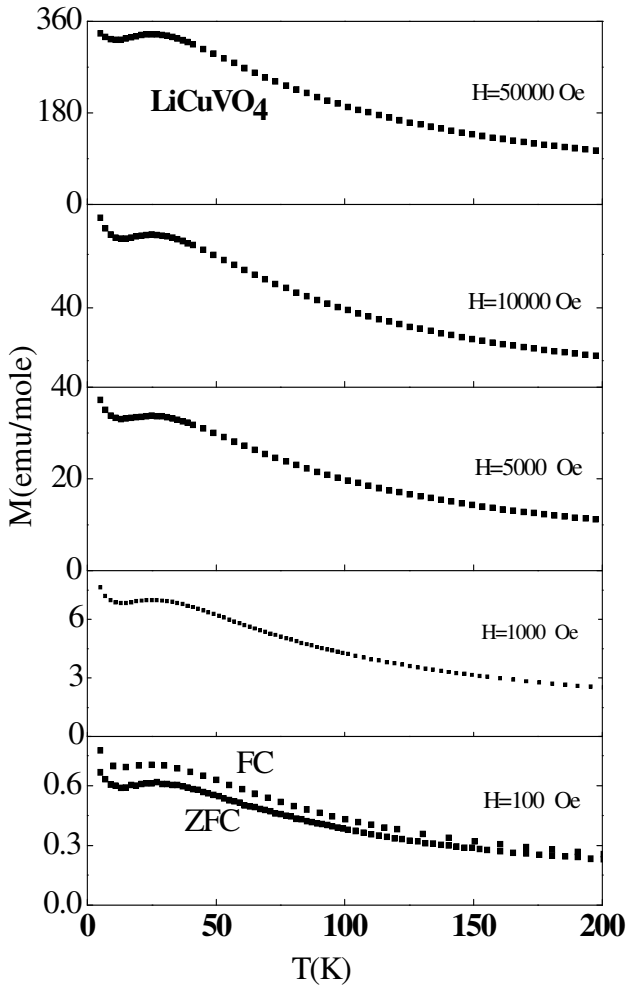

Fig. 2. Magnetization as a function of temperature of $LiCuVO_4$ at different magnetic field (100-50000 Oe)

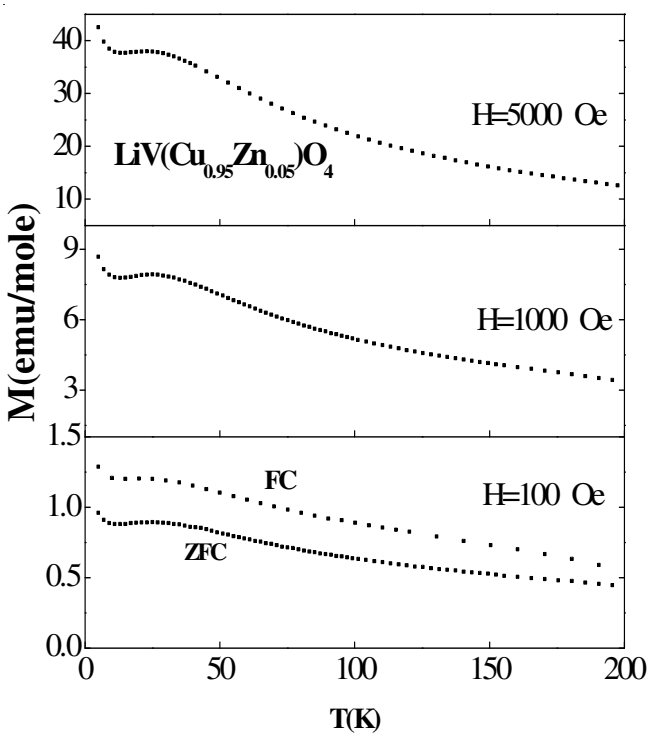

Fig. 3. Magnetization as a function of temperature of $LiCu_{0.95}Zn_{0.05}VO_4$ at different magnetic Field (100-5000 Oe)

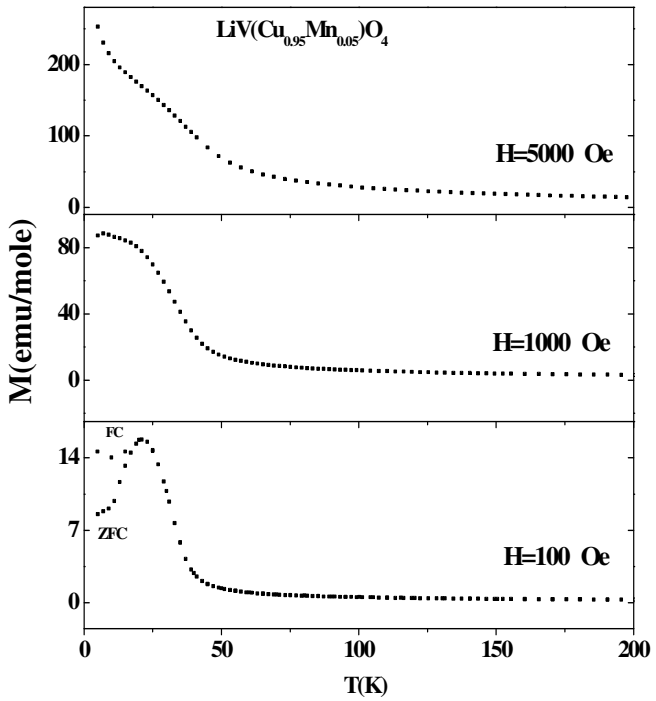

Fig. 4. Magnetization as a function of temperature of $LiCu_{0.95}Mn_{0.05}VO_4$ at different magnetic field (100-5000 Oe)

Weiss constant, that Zn-doped samples show antiferromagnetic coupling with $\theta = 30.5$ K and Mn-doped samples show ferromagnetic (FM) coupling with $\theta = -0.16$ K. It is interesting to mention that with Zn-doping θ value increases and at the same time magnetization value also increases slightly. The reason of simultaneous increasing of both θ and magnetization value is not clear. It might be the fact that we have not obtained the correct value because of choosing very small temperatures

range (100-200 K). Mn-doping induces the ferromagnetic ordering with finite ferromagnetic moment as is observed from the Curie-Weiss law. It might be due to the fact that Mn-doping decreases the angle (from *ca.* 95º towards *ca.* 90º) between Cu-O-Cu in the chain. Moreover, the intrachain exchange integral decreases with doping of Mn as is observed from the shifting of T_m towards lower temperature ($J_1 = T_m/1.282$)[15].

Fig. 5, displays the M-H hysteresis loop of Zn- and Mn-doped samples at 5 K. For Zn-doped sample it is found that the M(H) curve bends very slightly with increase of magnetic field. The extrapolation of the high field linear behaviour to the H = 0 Oe results in the very minute ferromagnetic component. On the other hand the M-H hysteresis loop of Mn-doped $LiCuVO_4$ at 5 K shows relatively larger ferromagnetic component. Therefore, it can be concluded that Mn-doping induce long range ferromagnetic ordering in $LiCuVO_4$. Whereas Zn-doping has only minor effect on $LiCuVO_4$ with slight induced of the ferromagnetic moment. It might be the fact that with Zn and Mn doping on Cu^{2+} (transition metal ion) site the angle between Cu-O-Cu changes, which in effect changes the exchange interaction which may lead the induction of three dimensional long range ferromagnetic ordering. Detail study of transition metal ion doping on $LiCuVO_4$ is under progress and more interesting results are expected.

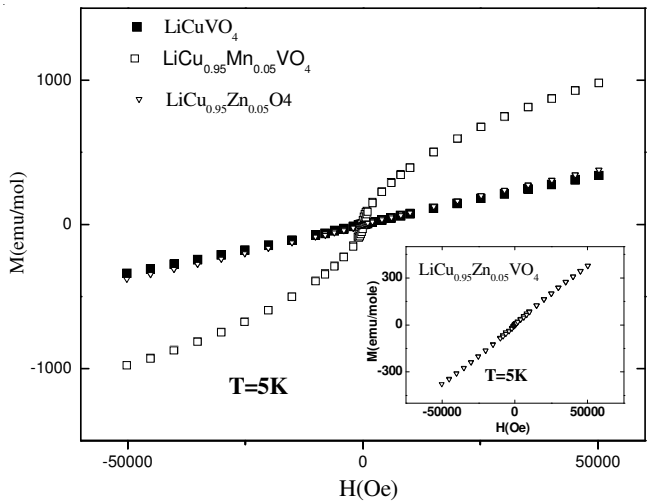

Fig. 5. Variation of magnetization with magnetic field (-5 T to +5 T) of $LiCuVO_4$, $LiCu_{0.95}Zn_{0.05}VO_4$ and $LiCu_{0.95}Mn_{0.05}VO_4$ samples. Inset shows the M(H) behaviour of Zn-doped sample in extended scale

Conclusion

The magnetic properties of Zn- and Mn-doped $LiCuVO_4$ have been investigated. With Zn doping short range antiferromagnetic ordering remains unchanged except slight increase of magnetization value. On the other hand Mn-doping interestingly induce one dimensional small ferromagnetic moment.

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