The Influence of A-Site Magnetism in AV_2O_4 Spinels Approaching Itinerant Electron Limit

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Introduction

The spinel system AV_2O_4 (A = Cd, Mg, Zn, Mn, Fe, and Co) has been studied extensively due to its physical properties which emerge from the interplay among the spin-lattice coupling from its 3*d* localized electrons, orbital degrees of freedom, and its geometrically frustrated structure. This spinel system is also a model system for studying an insulator-metal transition, which results from the overlap between the orbitals of its V^{3+} ions. The chemical substitution on the *A*-site of AV_2O_4 changes the V^{3+}-V^{3+} distance ($R_{V\text{-}V}$) systematically. Goodenough found the critical $R_{V\text{-}V}$ distance to be R_C = 2.94 Å [1]. In the insulator-metal transition studies, the inclusion of spinels with magnetic *A*-site ions is justified due to the dominant V-V interactions [2]. In this work, we present our study on the effects of magnetism in AV_2O_4 in approaching R_C by comparing the physical properties of AV_2O_4 (*A* = Cd, Mg, Zn) with nonmagnetic *A*-site ions and $Mn_{1-x}Co_xV_2O_4$ with magnetic *A*-site ions.

Experimental

Temperature dependent powder x-ray diffraction measurements down to T = 10 K were performed on single crystals of $Mn_{1-x}Co_xV_2O_4$ and MgV_2O_4 and polycrystalline samples of AV_2O_4 (A = Cd, Zn).

Results and Discussion

Fig 1. shows the $R_{V\text{-}V}$ dependence of the structural and transport properties for both AV_2O_4 (*A* = Cd, Mg, Zn) and chemical substitution compound $Mn_{1-x}Co_xV_2O_4$. The plot shows a weakening of the Jahn-Teller effect and decreasing activation energy (E_a) as the system approaches the itinerant electron limit. However, there are two paths that the system follows, which we assert as a result of the *A*-site magnetism. There is an indication that the structural transition temperature (T_S) is dependent on the magnetic field [3], where T_S decreases with decreasing field. This is consistent with Fig. 1(b), where T_S decreases with Co-substitution on the Mn-sites.

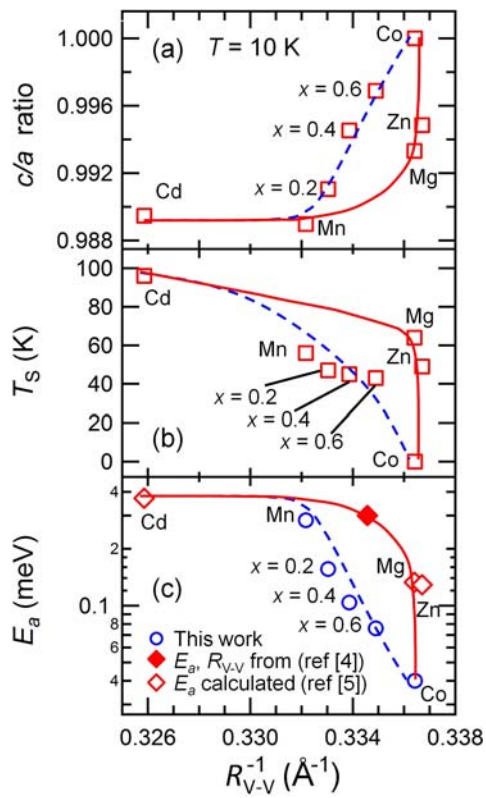

Figure 1. The variation with $R_{V\text{-}V}$ of (a) the *c*/*a* ratio at T = 10 K; (b) the structural transition temperature (T_S); (c) the transport activation energy for AV_2O_4 (solid red line) and $Mn_{1-x}Co_xV_2O_4$ (dashed blue line)

Conclusions

$Mn_{1-x}Co_xV_2O_4$ spinel system with magnetic A-site ions shows a more rapid approach towards the itinerant electron limit compared to AV_2O_4 (*A* = Cd, Mg, Zn) as evident from the disappearance of the Jahn-Teller effect and a more rapid decrease of E_a. This shows that while $R_{V\text{-}V}$ is a critical parameter controlling the physical properties of AV_2O_4 spinels, *A*-site magnetism plays an additional role in the insulator-metal transition.

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