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Strain Defects and Their Role in Metal-Insulator Transition in Cr-Doped V_2O_3

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Investigating the origin of the metal-insulating transition (MIT) in $(V_{1-x}Cr_x)_2O_3$ at $x \sim 0.01$ at room temperature is a challenging task mostly because of too dilute Cr concentration within a concentrated V matrix. Lacking experimental information about Cr and V local environments, the MIT theories, including the most popular Mott-Hubbard model, rely on the average structure of this system ascertained by neutron and x-ray diffraction. We applied a novel x-ray analyzer to discriminate between local environments of V and Cr in the $(V_{1-x}Cr_x)_2O_3$ single crystals by Cr K-edge and V K-edge XAFS at the range of concentrations across the MIT. We observed that a small number of Cr atoms serve as strain defects, generating long-range strain in the lattice and form large regions with long V-V bonds. Our finding supports the hypothesis of Rice and Brinkman, proposed in 1972, that large insulating regions should exist in this system.

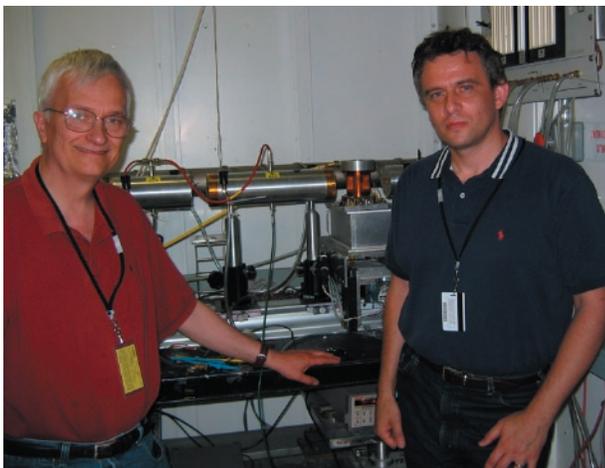
The metal-insulator transition (MIT) in Cr-doped V_2O_3 , from paramagnetic metal (PM) to paramagnetic insulator (PI) at room temperature (**Figure 1**), has attracted much attention since it was discovered in 1969. Among many puzzles this system offers is the lack of electronic instability at $x(\text{Cr}) \sim 0.01$ in theoretical calculations of the density of states. Another peculiarity is the structural transformation at the same concentration, ascertained by diffraction, leading to the elongation of the V-V distances both in the ab plane and along the c-axis of the trigonal lattice. The latter observation led many to believe that the MIT in this system is the classical example of Mott-Hubbard type, with V-V distance increase causing delocalization of 3d-electrons and, hence, the MIT. The natures of both the structural and electronic instabilities have long remained unknown.

XAFS analysis of Cr environments in $(V_{1-x}Cr_x)_2O_3$ around the MIT concentra-

tion could not be done prior to this work due to the dominating V fluorescence XAFS background. We have recently fabricated a novel fluorescence log-spiral of revolution analyzer where a highly oriented pyrolytic graphite (HOPG) layer was deposited on a Plexiglas support. The LSR parameters were optimized for reflecting Cr K_α photons whose wavelengths satisfied the Bragg condition at the LSR surface. Since the V K_α fluorescence was effectively sup-

pressed, this method allowed us to obtain XAFS measurements at the Cr edge. The use of single crystals prepared by Patti Metcalf at Purdue allowed us to take advantage of linearly polarized (in the plane of synchrotron orbit) x-ray photons to separately probe metal-metal (V-V and V-Cr) bonds in the directions parallel and perpendicular to the trigonal c-axis. Cr K-edge measurements were done at the PNC-CAT (undulator beamline) at the Advanced Photon Source. V K-edge measurements were done at beamline X11A at the NSLS.

Fit results are summarized in **Figure 2**, which demonstrates that the local structure around V and Cr deviates from the average structure measured by XRD. The behavior of the V-V and Cr-V distances in the insulating phase is completely unexpected: V-V distances are found to be longer than Cr-V distances both in the axial and basal plane directions. This difference, in turn, requires



Authors (from left) Douglas Pease and Anatoly Frenkel

the V-V bond to be longer and V-Cr bond to be shorter than the average metal-metal distance, ascertained by XRD. This trend can be also observed in **Figure 2**.

We explain these new structural details (shortening of Cr-V and elongation of V-V bonds relative to the "average" structure) in terms of local buckling of the crystal structure of $(V_{1-x}Cr_x)_2O_3$ due to the Cr and V size mismatch. Cr atoms play the role of "strain defects" first studied by Eshelby in the 1950s, when he studied inhomogeneities in elastic media. Being the smaller atoms,

Cr impurities locally contract the V_2O_3 host lattice. As a result, adjacent V atoms relax toward Cr, and V-V distances involved in such relaxation expand relative to pure V_2O_3 (**Figure 3**). For the low concentration of strain defects (i.e., in our case of $x < 0.1$) the strain fields produce an average volume change with distortions from the average centered at the Cr site and decaying slowly in three dimensions (as $1/r^3$). Our findings allow us to conclude that, due to the long range nature of the strain field, even a small concentration of Cr (ca. 1%) may be sufficient

to form large insulating regions (with longer V-V distances and, therefore, lower electron densities than in the PM V_2O_3 host) analogous to those hypothesized by Rice and Brinkman in their Phys. Rev. B article in 1972. As concentration of Cr increases, strain defects begin to interact, triggering structural instability that causes the drastic changes in c/a ratio at $x=0.01$. Furthermore, such insulating regions, whose size is amplified by long range strain fields, may effectively block conductivity, which suggests a percolative nature of the MIT in $(V_{1-x}Cr_x)_2O_3$.

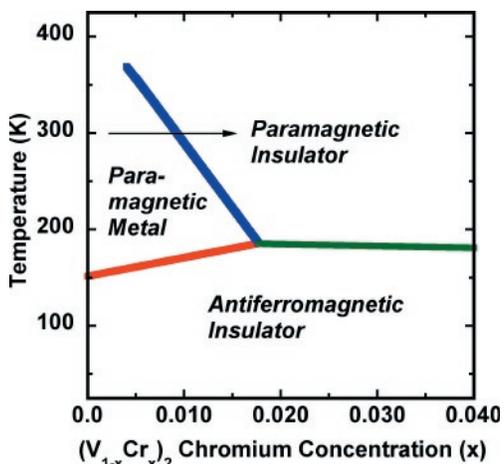


Figure 1. The generalized phase diagram for $(V_{1-x}Cr_x)_2O_3$ as a function of temperature and chromium dopant concentration at 1 atm pressure. The samples' compositions ($x = 0, 0.00365, 0.0116, 0.0285$ and 0.0523) span the diagram across the MIT as shown by the arrow.

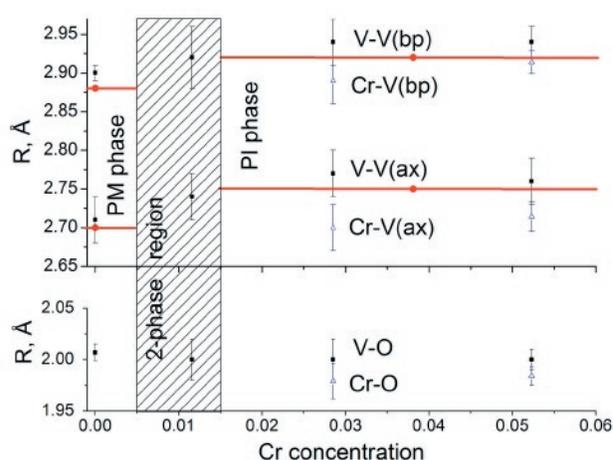


Figure 2. First nearest neighbor distances in $(V_{1-x}Cr_x)_2O_3$ measured by EXAFS (symbols) and inferred from x-ray diffraction results for an "average" structure (lines).

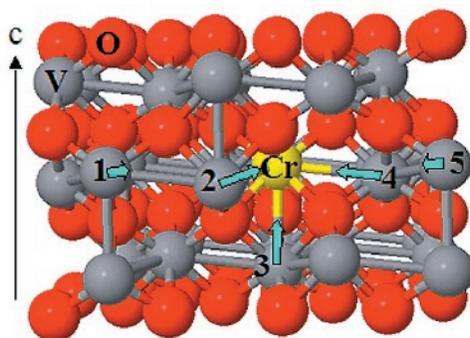


Figure 3. Model of local structural distortions around Cr in $(V_{1-x}Cr_x)_2O_3$. Some V atoms that are displaced toward Cr dopants (in the direction of arrows) are denoted by numbers. This model illustrates the dopant-induced strain causing Cr-V (e.g., Cr-V2 and Cr-V3) bonds to contract, and V-V (e.g., V1-V2 and V4-V5) bonds to expand relative to the average M-V distances measured by x-ray diffraction.