Strain-Induced Bond Buckling and Its Role in Insulating Properties of Cr-Doped V_2O_3

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Structural transformations around both V and Cr atoms in $(V_{1-x}Cr_x)_2O_3$ across its metal-insulator transition (MIT) at $x \sim 0.01$ are studied by extended x-ray absorption fine-structure technique. Our new results for Cr made possible by the use of a novel x-ray analyzer that we developed reveal the substitutional mechanism of Cr doping. We find that this system has a buckled structure with short Cr-V and long V-V bonds. This system of bonds is disordered around the average trigonal lattice ascertained by x-ray diffraction. Such local distortions can result in a long range strain field that sets in around dilute Cr atoms in microscopic regions. We suggest that such locally strained regions should be insulating even at small x. The possibility of local insulating regions within a metallic phase, first suggested by Rice and Brinkman in 1972, remains unaccounted for in modern MIT theories.

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The metal-insulator transition (MIT) in Cr-doped V_2O_3, from paramagnetic metal (PM) to paramagnetic insulator (PI) at room temperature [Fig. 1(a)], has attracted much attention since it was discovered in 1969 [1]. This interest is partly because both PM and PI phases were predicted to be metallic by band structure calculations [2,3], and in part because all known Mott insulators were antiferromagnetic. Mattheiss [3] offered one plausible explanation for the contradiction between band theories and experiment by proposing that Cr does not substitute for V but occupies "vacancy" sites of the parent NiAs structure. Mattheiss furthermore suggested using extended x-ray absorption fine-structure spectroscopy (EXAFS) to investigate the actual location of Cr dopants [3]. Among other factors playing an important role in the MIT of this system, strongly correlated electrons [4], their Fermi liquid behavior [5], electron-phonon [6], and electron-lattice [7] interactions, as well as short range dynamic spin correlations [8] have been proposed. The Mott-Hubbard mechanism of the MIT requires that electron density decreases and, consequently, V-V distances increase in the insulating phase. Experimental evidence of such elongation in pure and Cr-doped V_2O_3 was first discussed by McWhan and Remeika [9] in terms of the changes in the crystal lattice associated with decreasing temperature or increasing Cr concentration. Indeed, crystal structure studies of insulating samples of pure V_2O_3 at low temperature [10] and Cr-doped ($x = 0.038$) samples at room temperature [11] demonstrated that both materials have larger volumes relative to the conducting phase of pure V_2O_3 at room temperature (RT) [11]. In both cases, structural changes could be directly translated to the changes in V-V distances, either via the monoclinic distortion (pure V_2O_3) or an "umbrella distortion" (Cr-doped V_2O_3).

There are many analogous systems with structural phase transitions where the local structure (within a few interatomic distances from a given atom) is different from the average; the one ascertained by x-ray or neutron diffraction [12–14]. When measured by the EXAFS technique, which is sensitive to the local structure (LS) of the first several neighboring shells of atoms surrounding the x-ray excited atom, the lower symmetry low temperature LS in these systems is found to either preserve or change less dramatically during the transitions to the higher temperature and symmetry phase, contrary to what can be inferred from the average structure measurement using diffraction methods. The actual structure can then be obtained from the self-consistent interpretation of these two complementary measurements by taking into account disorder. By applying these methods to pure and Al-doped V_2O_3, Frenkel, *et al.* [15], and Pfalzer, *et al.* [7,16], found that the LS around V remained monoclinically distorted in the metallic phase (RT, $x = 0$) as well as in the insulating phase (RT, $x_{Al} = 0.06$). In the case of the pure V_2O_3, those results imply that V-V distances change by 0.04–0.05 Å across the MIT as opposed to a much larger change (0.11 Å) as inferred from x-ray diffraction technique (XRD) measurements [10]. Frenkel *et al.* [15] reconciled these results in the framework of an order-disorder model by proposing that the average trigonal structure is obtained by disordering of locally monoclinic regions. An additional advantage of EXAFS is its elemental selectivity, which allows one to separately probe the structure around V and Cr in a sample, even for dilute doping. For comparison, standard XRD is not capable of separately solving V and Cr environments in $(V_{1-x}Cr_x)_2O_3$ due to both the similarity in their electron densities and the diluteness of Cr. Such analysis of V and Cr environments in $(V_{1-x}Cr_x)_2O_3$ has not been done prior

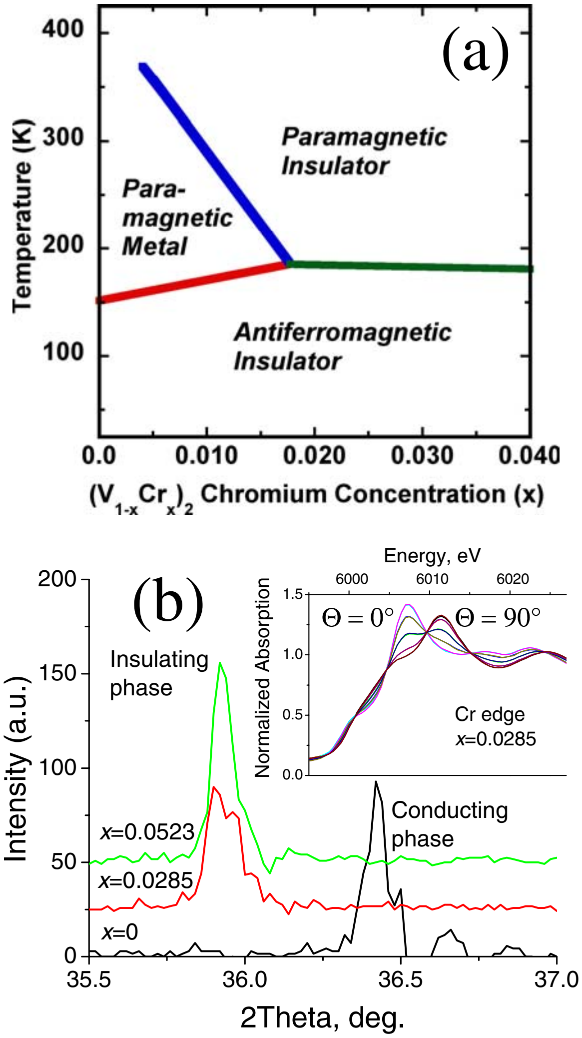

FIG. 1 (color online). (a) The generalized phase diagram for $(V_{1-x}Cr_x)_2O_3$, as a function of temperature and chromium dopant concentration at 1 atm pressure. Since a hysteresis effect is encountered in resistivity measurements across the phase transition in crystals, the phase diagram depicts the results of measurements taken upon sample cooling. (b) Powder XRD spectra of $(V_{1-x}Cr_x)_2O_3$. Shown are the 110 reflections which differ in conducting and insulating phases due to different c/a ratios. The inset shows 10 Cr K edge XANES spectra measured at different Θ (from 0° to 180°, with a 20° increment) for $x = 0.0285$.

to this work due to a major experimental difficulty caused by a low concentration of Cr dopant in the V-rich host. We have recently fabricated a novel fluorescence log-spiral of revolution analyzer that allowed us to measure LS around Cr. This Letter is the first report of a systematic EXAFS study of the LS around Cr and V in single crystals $(V_{1-x}Cr_x)_2O_3$. The use of single crystals allows 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. We propose a new mechanism of structural transformations across the MIT. The changes in the electronic structure in the local vicinity of Cr and V are independently measured by polarized x-ray absorption near-edge structure (XANES) as a function of Cr concentration and temperature, and will be reported elsewhere.

For this study, single crystals of $(V_{1-x}Cr_x)_2O_3$ with $x = 0$ (PM), 0.0116 (PI), 0.0285 (PI), and 0.0523 (PI) were prepared by the skull-melting crystal growth technique; details of the procedure have been specified elsewhere [17]. Chromium content analyses were carried out by energy dispersive spectroscopy and verified by electrical transport measurements. We also observed that the $x = 0.0116$ sample is a mixture of two phases with different c/a ratios, in agreement with earlier reports [9].

EXAFS measurements were performed at beam line X11A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (V K edge) and at PNC/XOR ID beam line, the undulator insertion device at Sector 20 of the Advanced Photon Source (APS) at Argonne National Laboratory (Cr K edge). Self-absorption effects in V K edge data were eliminated by taking measurements in grazing exit angle geometry [18]. Since for low Cr concentration in a V-rich sample neither an energy dispersive detector nor ionization chamber/filter combination can adequately separate Cr K_α fluorescence photons from the otherwise overwhelming V signal, we used a novel log-spiral of revolution analyzer [19], designed and built for detection of Cr K_α photons. This device has now been markedly improved by the addition of a custom built (by E. Stern) annular ion chamber [20]. Both V and Cr K edge measurements were done in two perpendicular orientations: $\Theta = 0°$ and $\Theta = 90°$, where Θ is the angle between the x-ray polarization and the c axis. The samples were first oriented using a gas area detector diffractometer, and a flat was ground on all samples parallel to the (110) plane. At the synchrotrons (NSLS and APS), we repeatedly rotated the crystals around the normal to the flat with 20° increment and measured x-ray absorption coefficients $\mu(E, \Theta)$ at each angle for V and Cr K edges, respectively, using the method applied in Ref. [15]. For a perfect single crystal,

$$\mu(E, \Theta) = \mu_{\|}(E)\cos^2\Theta + \mu_{\perp}(E)\sin^2(\Theta), \qquad (1)$$

where $\mu_{\|}(E)$ and $\mu_{\perp}(E)$ are the absorption coefficients corresponding to $\Theta = 0°$ and $\Theta = 90°$, respectively. Thus, using Eq. (1), we could find the angles corresponding to the two perpendicular orientations, $\mu_{\|}(E)$ and $\mu_{\perp}(E)$, and thus independently obtained two EXAFS signals, $\chi_{\|}(k)$ and $\chi_{\perp}(k)$, where k is the photoelectron wave number. Figure 1(b) (inset) demonstrates this method for orienting the $x = 0.0285$ sample for Cr K edge measurement at the APS. The presence of multiple isosbestic points in the XANES region of this and other samples proves that this signal is a two-component mixture [$\mu_{\|}(E)$ and $\mu_{\perp}(E)$] and, therefore, the samples are high quality single crystals.

EXAFS data were processed with the IFEFFIT package [21]. The fits of FEFF6 theory [22] to the V(Cr) data were performed in r space concurrently for $\chi_{\|}(k)$ and $\chi_{\perp}(k)$, by constraining the V(Cr)-O distances to have the same length and disorder as measured in each orientation (Fig. 2). Visual examination of the Fourier transform magnitudes shows that the V and Cr data are similar for each orientation ($\Theta = 0°$ and $\Theta = 90°$). Such similarity suggests that Cr substitutes for V in the lattice at all concentrations, in contradiction to the hypothesis of Mattheiss. Therefore, the substitutional model was used to fit Cr K edge EXAFS data (Fig. 2, inset). The finding of substitutional Cr was further verified by testing the alternative model of Cr doping (vacancies in NiAs structure) proposed by Mattheiss [3]. Such a model is ruled out based on the poor fit quality. Fit results are summarized in Fig. 3, which demonstrates that the local structure around V and Cr deviates from the average structure measured by XRD. In the PM phase ($x = 0$) the average V-V distances in axial and basal planes are systematically longer than those predicted from XRD results alone. Such elongation confirms the presence of local monoclinic distortions in the trigonal lattice of V_2O_3 at RT obtained previously [15,16]. However, the behavior of the V-V and Cr-V distances in the PI phase is completely unexpected: V-V distances are found to be longer than Cr-V distances both in the axial and basal plane directions (Fig. 3). This difference, in turn, requires the V-V bond to be longer and V-Cr bond to be shorter than the average metal-metal distance, ascertained by XRD [11]. This trend can be also observed in Fig. 3.

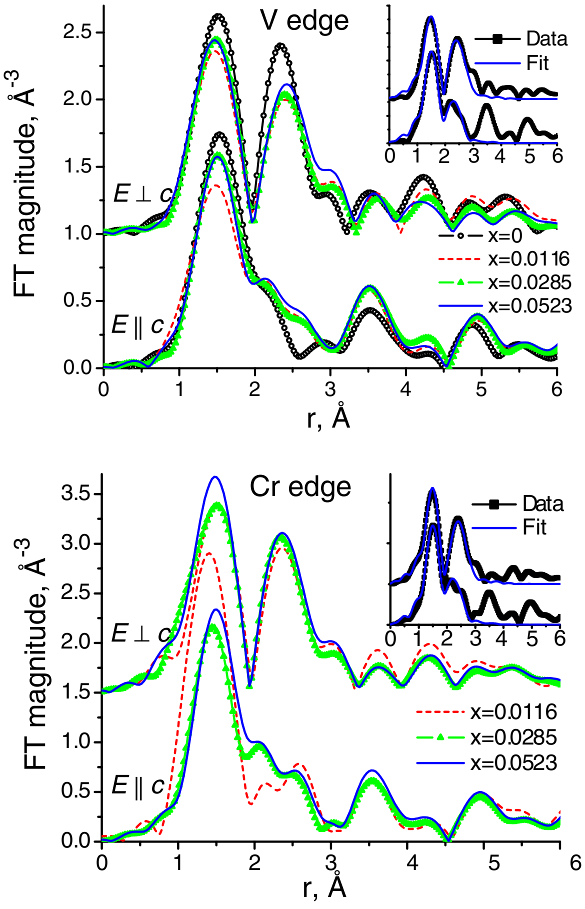

FIG. 2 (color online). EXAFS data and theoretical fits (insets, for $x = 0.0523$) for single crystals $(V_{1-x}Cr_x)_2O_3$.

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 [23] of the crystal structure of $(V_{1-x}Cr_x)_2O_3$ due to the Cr and V size mismatch. Since our measurements have proven this system to be a substitutional alloy, Cr atoms play the role of "strain defects" [24] and, being the smaller atoms, locally contract the V_2O_3 host lattice. As a result, adjacent V atoms relax toward Cr defects, and V-V distances involved in such relaxation expand relative to pure V_2O_3 (Fig. 4). 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 [24]. It should be emphasized that when disorder is present, as in this case, the actual relative atomic distances are given by the LS and not by those inferred from diffraction and should be employed in all theoretical models of MIT of these the materials exhibiting metal-metal bond length changes across the transition. The presence of "exceptionally large scattering centers" around Cr impurities was hypothesized by Rice and Brinkman in order to explain the anomalously large rise in residual resistivity per at. % Cr in this system [25]. However, no mechanism was offered as to the origin of these "large scattering centers". In addition, Castellani,

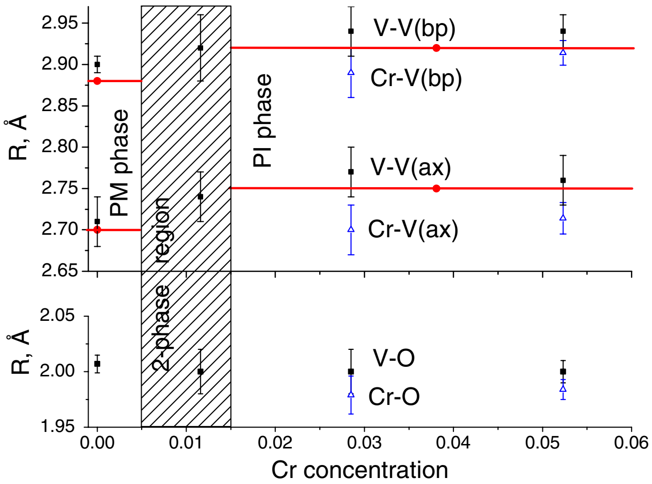

FIG. 3 (color online). First nearest neighbor distances in $(V_{1-x}Cr_x)_2O_3$ measured by EXAFS (symbols) and inferred from x-ray diffraction results for an average structure (solid lines). XRD results for metal-oxygen distances are less reliable due to the oxygen atoms' disorder and are not shown.

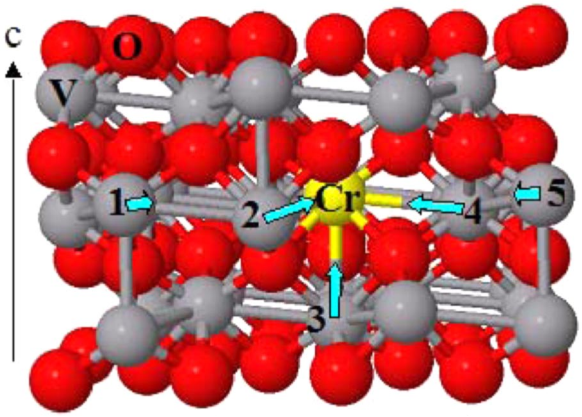

FIG. 4 (color online). Model of local structural distortions around Cr in $(V_{1-x}Cr_x)_2O_3$. Some V atoms which are displaced toward Cr dopants (in the direction of arrows) are denoted by numbers. This model illustrates the dopant-induced strain causing Cr-V (e.g., Cr-V2 and Cr-V3) bonds to contract, 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.

et al. [26], stated that "each Cr-occupied site... has to be counted as a site onto which the V-3d electrons cannot jump...." These authors go on to state "in other words, we are confronted with a type of percolation problem...." Castellani's hypothesis, however, does not explain why these regions should be large. 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 PI regions (with longer V-V distances and, therefore, lower electron densities than in the PM V_2O_3 host) analogous to those proposed by Rice and Brinkman.

In summary, we used polarized Cr and V *K* edge EXAFS spectroscopy measurements, made possible by the novel log-spiral of revolution x-ray analyzer, on single crystal $(V_{1-x}Cr_x)_2O_3$ to answer the question central for the theory of its MIT, namely, the role of Cr dopants. Our results indicate that Cr atoms create substitutional strain defects in the V-rich host, causing long range strains centered on Cr atoms and the concomitant elongation of V-V bonds causing large insulating regions. As the concentration of Cr increases, such regions can effectively block conductivity above the percolation threshold, which suggests a percolative nature of the MIT in $(V_{1-x}Cr_x)_2O_3$.

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