

Relationship of EXAFS-determined Bond Anharmonicity to Electron Delocalization

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Beamline(s): X23A2, X23B

Introduction: The EXAFS cumulant expansion yields information on the anharmonicity of the pair-distribution function for bonded atoms. We have found that this anharmonicity is correlated with (and hence gives information about) the degree of electron delocalization in specific bonds.

Methods and Materials: We collected temperature-dependent EXAFS transmission data for a number of materials, including Ti_2O_3 , V_2O_3 , Cr_2O_3 , Se, I_2 , Br_2 , *n*-butyl bromide, *sec*-butyl bromide, and *tert*-butyl bromide. Br_2 and the butyl bromides were measured in the gas phase, I_2 in both gas and powder phases, and all other materials as powders. Temperatures from 20 K to 500 K were used.

Results: To facilitate comparison between samples, we defined a dimensionless radial asymmetry parameter for each distinguishable pair of atoms, given by

$$\rho = \frac{\langle (r - \bar{r})^3 \rangle^{1/3}}{\bar{r}}$$

where \bar{r} is the average distance between the atoms. A perfectly harmonic bond thus corresponds to a radial asymmetry parameter of zero.

Ti_2O_3 undergoes a semiconductor-metal transition with onset at 390 K. As can be seen from Figure 1, the radial asymmetry parameter for the shortest titanium-titanium bond increases substantially at that temperature.

Solid iodine, although not a conductor at standard pressure, does have substantial nanoscale delocalization of electrons. The increase in the radial asymmetry parameter for the iodine bond in the transition from vapor to solid reflects this delocalization (Table I).

Finally, *t*-butyl bromide is considerably more reactive than *n*-butyl bromide, primarily because of hyperconjugation. This is also reflected in our data (Table I).

In contrast, the bond between nearest-neighbor vanadiums in V_2O_3 shows no change in anharmonicity at its metal-insulator transition. Investigation continues into this compound.

Table I. Radial asymmetry parameters

Iodine Vapor	Iodine Solid	<i>n</i> -butyl bromide	<i>t</i> -butyl bromide
$\rho = 0.053 \pm 0.022$	$\rho = 0.093 \pm 0.006$	$\rho = 0.027 \pm 0.004$	$\rho = 0.038 \pm 0.004$

Conclusions: EXAFS-determined anharmonicities can be used to probe the degree of electron delocalization in bonds in a wide range of materials.

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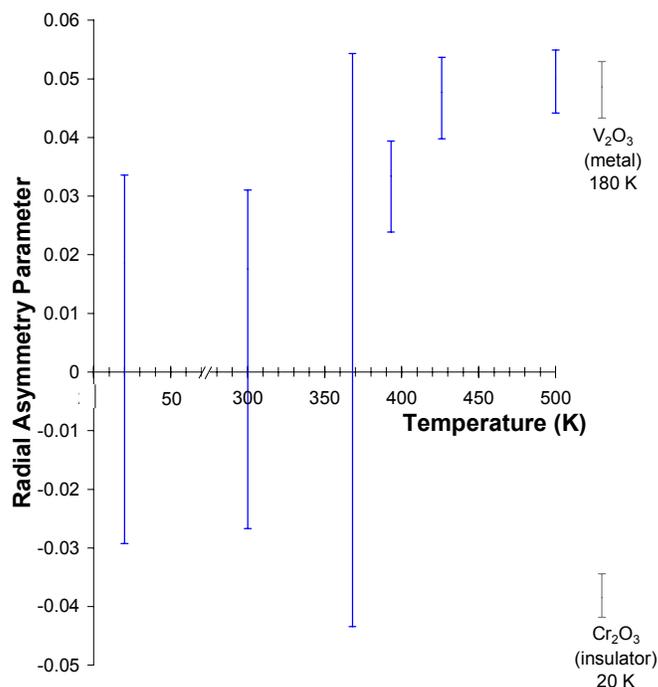


Figure 1. Radial asymmetry parameters for nearest neighbor titanium atoms in Ti_2O_3 as a function of temperature. Representative Cr_2O_3 and V_2O_3 data included for comparison.