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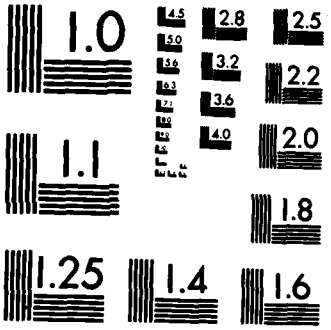

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This project was an interdisciplinary effort attempting to quantify the relationships between the electrical and magnetic properties of transition metal oxides and their local defect arrangements. Highly specialized x-ray techniques were applied to establish defect structures in materials where electrical properties or magnetic properties were also studied. Quantum theoretical modelling of defect structures was also initiated.

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DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING
THE TECHNOLOGICAL INSTITUTE
NORTHWESTERN UNIVERSITY
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Final Report to

U. S. Army Research Office

for Research on

LOCAL DEFECT ARRAYS AND PROPERTIES OF OXIDES

Grant No. DAAG29-80-C0035

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February 28, 1983

STATEMENT OF THE PROBLEM STUDIED

As stated in the original proposal, this project was an interdisciplinary effort attempting to quantify the relationships between the electrical and magnetic properties of transition metal oxides and their local defect arrangements. Highly specialized X-ray techniques were applied to establish defect structures in materials where electrical properties or magnetic properties were also studied. Quantum theoretical modelling of defect structures was also initiated.

IMPORTANT RESULTS

A. Techniques.

Via simulation of EXAFS patterns for FeO, VO, stabilized ZrO_2 and W-doped VO_2, it was found that it is generally not possible to distinguish defect clusters from random arrays of defects. This is an important result, due to the great interest in the community for employing EXAFS to probe local defect arrays in oxides. It implies that, at this moment, we can rely only on analysis of diffuse scattering to provide detailed information on local defect arrays in oxides. In the predecessor to this grant, we had derived for the first time the general equations for diffuse scattering from oxides. We have now learned to solve these equations without approximation directly from measurements. This is a unique capability, not presently possible elsewhere, which allows as complete information on oxide defect arrays as has only heretofore been possible for binary metallic systems.

Another highlight of our research has been the development of a technique to discriminate conduction mechanisms in transition metal oxides. The technique involves analysis of conductivity at fixed thermopower as opposed to fixed stoichiometry. It permits an activated mobility (characteristic of small

polaron conduction) to be unambiguously established.

B. Studies of Oxides

1. $Zr(Ca,Y)O_{2-x}$

Via diffuse X-ray scattering we have shown that the two main features of the local ionic arrangements in these materials are "rods" of stabilizing cations along <332> directions and the fact that oxygen vacancies are near-neighbors to these cations. The high anionic conduction may be due to the "guiding" of the anions along the rods of solute cations.

2. W-doped VO_2

Earlier work by M. E. Fine and co-workers had shown that the curvature in M-H data at low fields might be interpreted as due to W-rich clusters. Our high field data mitigates against this interpretation. Subsequent small angle X-ray scattering showed no evidence of clustering. What the magnetic data does suggest is that each W atom breaks a V^{4+}-V^{4+} homopolar bond along the c-axis and transfers two 3d electrons to its two nearest V^{4+} neighbors, forming V^{3+}-W^{6+} and V^{3+}-V^{4+} pairs. This has since been confirmed via near-edge V_K and W_L X-ray absorption studies. The change in bonding may explain why the semiconductor-insulator transition temperature decreases with W doping.

3. CoO

High precision thermopower measurements confirm V'_{Co} and V''_{Co}, charge compensated by electron holes, to be the majority defects. However, at the larger deviations from stoichimetry, significant departure from point defect ideality occurs. This may indicate the same type of clustering as seen in FeO, and which has been predicted for vacancy concentrations exceeding 0.1 percent. In addition, our analyses show CoO to be a band-type semiconductor. Both findings are important when it is recalled that CoO has long been believed to

be a small polaron conductor exhibiting "ideal" point defect behavior.

4. FeO

Our re-analysis of existing conductivity and Seebeck coefficient data showed that the electrical behavior could be explained by small polaron conduction of electron holes along networks of near-cluster iron cations. When analyzed at constant Seebeck coefficient, the electrical conductivity exhibits a composition-independent activation energy of hopping.

C. Theoretical Studies

Theoretical studies have been carried out on the electronic structure, optical and X-ray spectra, and chemical bonding of selected transition metal oxides. The effects of both oxygen and metal-site vacancies on the metal valency have been studied, and the nature of potential vacancy-site bound states has been explored. The modification of X-ray emission near the K-edge of the metal due to first and second neighbor vacancies has been calculated and compared with experiment for VO_x and TiO_x rocksalt-structure compounds. The variability of metal valency in the inverse spinel Fe_3O_4 has been studied, using molecular cluster techniques. Although the iron A-site and B-site magnetic moments are calculated in good agreement with neutron and magnetic susceptibility data, we find that the classical Fe(2+) and Fe(3+) free ion configurations are not a very good description of the effective atomic configurations. It appears that covalent charge-sharing between metal-3d and ligand-2p states is an essential feature of the bonding mechanism. Theoretical algorithms are being developed to help to determine the energy of formation, and activation energies for diffusion of lattice vacancies.

Participating Scientific Personnel

Co-Principal Investigators:	J. B. Cohen D. E. Ellis M. E. Fine T. O. Mason
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Degrees Earned

H.-C. Chen, "Seebeck Coefficient Measurements in Cobaltous Oxide", M.S., June 1981

C. Tang, ""Local Atomic and Electronic Arrangements in $W_xV_{1-x}O_2$", Ph.D., June, 1983

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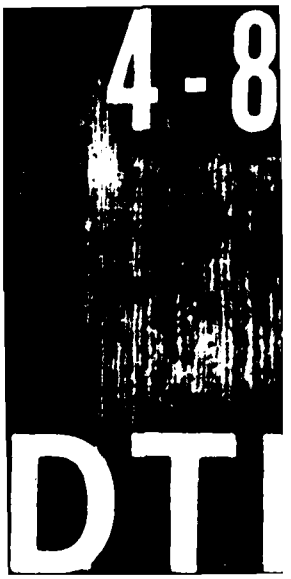
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