

10-Physical and Chemical Properties of Materials in Relation to Structure (Superconductors, Fullerenes, etc)

(3) In reduced and used catalysts, we found a Cu-O coordination peak ($R=0.190\text{nm}$, $N=1$) in RSF. But another peak at $R=0.196\text{nm}$, belonging to Cu-Cu coordination in CuO, was not found in the same RSF. We consider that this is evidence of a strong interaction between metal and $r\text{-Al}_2\text{O}_3$.

(4) Because of $r\text{-Al}_2\text{O}_3$, the reasons of deactivation are different for CZ and CZA. For CZ, deactivation is caused by enlargement and increase of crystalline Cu. For CZA, the $r\text{-Al}_2\text{O}_3$ may prevent the enlargement of Cu crystals, and stabilize in this way the activity of CZA. The reason of deactivation is the change of the dispersed Cu to the crystalline phase in the catalytic reaction, which leads to the loss of active regions.

XRD graphics and RSF figures are shown below.

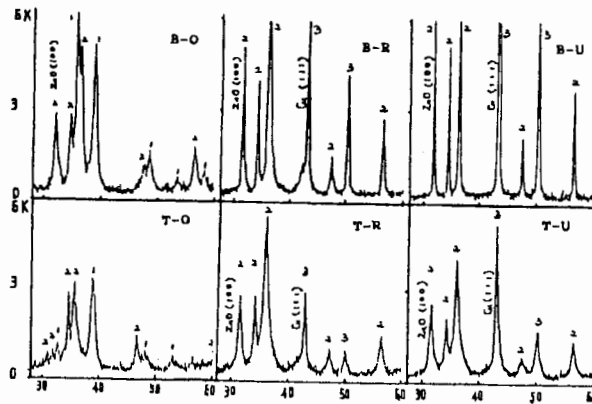


Fig.1 X-ray diffraction diagrams of the binary catalysts the ternary catalysts 1.CuO 2.ZnO 3.Cu

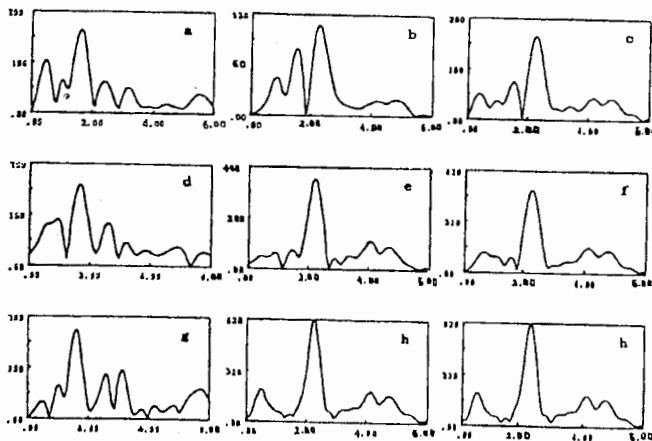


Fig.2 Cu-EXAFS a.T-oxidized b.T-reduced c.T-used d.B-oxidized e.B-reduced f.B-used g.CuO h.Cu

PS-10.03.07 ELECTRON DIFFRACTION STUDY OF THE SUBSTITUTION DISORDER OF THE Ti IONS IN $\text{Li}_{1-x}\text{Ti}_2\text{O}_4$.

By C. Chaillout, E. Moshopoulou, P. Bordet and J.J. Capponi, Laboratoire de Cristallographie, CNRS-UJF, BP 166, 38042 Grenoble cedex 09, France

The LiTi_2O_4 compound (spinel structure, space group $\text{Fd}\bar{3}\text{m}$, $a=8.41\text{Å}$, $Z=8$) is known to be superconducting with $T_c=11\text{K}$. In the spinel oxides containing lithium, it has been observed that the small Li^+ cations can move easily through vacant sites generated by the

titanium-oxygen network. Therefore, by removing or inserting lithium, the stoichiometry of the compound can be varied. In the case of LiTi_2O_4 , Capponi et al. have shown (Physica C, 1991, 185-189, 2721), that it is possible to extract lithium in a "soft" and controlled way by immersion in an HCl solution. In order to see if such a treatment induces any kind of disorder, crystals treated in HCl solution for several days have been studied by electron diffraction. A Philips EM 400T microscope operating at 120KV was used.

Besides Bragg reflections, the presence of pronounced diffuse scattering was readily observed, and its geometry was studied by tilting around a^* and a^*+b^* directions from the $[001]$ zone axis. Figure 1a shows an example of the diffuse scattering observed on the $[001]$ zone axis.

To interpret the diffraction patterns we have applied the theory of invariant clusters proposed by Brunel et al. (J. Phys. Chem. Solids, 1972, 33, 1927) and developed by Sauvage et al. (Acta Cryst., 1974, A30, 239). This theory establishes that, if the diffuse scattering is confined to a geometric locus in reciprocal space, the ordering state can be described by the regular arrangement of identical polyhedra having the average composition of the sample. In the present case, we suppose that the diffuse scattering is due to the substitution disorder of Ti ions over the two types of octahedral sites in the spinel structure (16d and 16c), the displacement of Ti ions from a full 16d site to an empty 16c one being possible after the departure of the two neighboring Li ions. Then, the relevant polyhedron is a cube of edge dimension $a/2$ whose corners and centers of the faces correspond to the center of the octahedral sites occupied either by a Ti atom or by a vacancy. The composition of the sample implies that the numbers of vacancies and Ti atoms in one such cube are equal. With this description, the equation of the surface of diffuse intensity is given by $\cos(\pi X/2)+\cos(\pi Y/2)+\cos(\pi Z/2)+4\cos(\pi X/2)\cos(\pi Y/2)\cos(\pi Z/2)=0$

The calculated intersections of this surface with different reciprocal planes are in agreement with the experimental diffraction patterns as shown in Figure 1b. This observation confirms the presence of a Ti cation disorder between the 16d and 16c octahedral sites in the case of large lithium deficiencies.

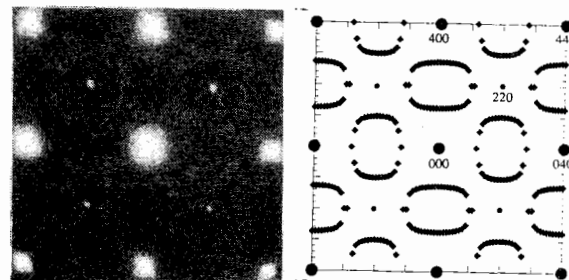


Figure 1. (a) Electron diffraction photograph along the $[001]$ zone axis showing the diffuse scattering due to Ti cation network disorder. (b) The intersection of the diffuse scattering surface calculated with the model described in the text and the $[001]$ reciprocal plane.

PS-10.03.08 STRUCTURAL ASPECTS OF THE CRYSTALLOGRAPHIC-MAGNETIC TRANSITION IN LaVO_3 AROUND 140 K by P.Bordet^{1*}, C. Chaillout¹, M. Marezio^{1,2}, Q. Huang^{3,4}, A. Santoro³, S-W. Cheong², H. Takagi², C.S. Oglesby², and B. Batlogg². ¹ Laboratoire de Cristallographie CNRS-UJF, BP 166, Grenoble Cedex 9, France. ² AT&T Bell Laboratories, Murray Hill, NJ07974, USA. ³ Reactor Division, NIST, Gaithersburg, MD 20899, USA. ⁴ Dept. of Physics, University of Maryland, College Park, MD 20742, USA

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The perovskite-like compound LaVO_3 undergoes a crystallographic-antiferromagnetic transition at about 140 K. Recently, it has been shown that under a magnetic field of a few hundreds Oe the crystallographic transformation occurring in LaVO_3 is accompanied by a magnetic transition into a large diamagnetic state below 135 K. In order to gain insight into the nature of this anomalous behavior, we have determined the structure of LaVO_3 at room temperature and just above (150 K) and below (100 K) the transition. Synchrotron x-ray and neutron powder diffraction techniques were used. The lattice parameter variation vs. temperature and the structural refinements revealed that, above the transition, the structure of LaVO_3 is of GdFeO_3 type, namely it is orthorhombic with lattice parameters at room temperature: $a = 5.55548(4)$, $b = 7.84868(6)$, and $c = 5.55349(5)$ Å and space group $Fm\bar{m}a$. The orthorhombic distortion of the structure is very similar to that of isostructural LaFeO_3 . At 100 K, below the transformation temperature, the structure is monoclinic with lattice parameters: $a = 5.59360(4)$, $b = 7.75951(5)$, $c = 5.56490(3)$ Å, $\gamma = 90.1251(4)^\circ$ and space group $P2_1/a$. In the orthorhombic structure all V sites are equivalent, but two independent sites, V1 and V2, are observed in the monoclinic structure. These two sites form alternate layers along the b axis. Above the transition all the V octahedra are tilted around the three crystallographic axes and are elongated along the [110] direction. The elongation increases at the transition and occurs in different directions, 90° apart, in the V1 and V2 octahedra. The low temperature magnetic structure and the results of field-cooling synchrotron x-ray and neutron powder diffraction experiments will be presented at the conference.

PS-10.03.09 TWO STRUCTURAL FORMS OF DI(DIMETHYL)TETRASELENAFULVALENIUM) TETRAFLUOROBORATE. By N. Thorup*, Chemistry Department B, The Technical University of Denmark, Lyngby, Denmark, I. Johansen, NKT Research Center, Brøndby, Denmark, K. Bechgaard, CISMI, University of Copenhagen, Denmark, M.A. Beno, U. Geiser and J.M. Williams, Argonne National Laboratory, Illinois, USA.

The unsymmetrical organic donor 2,3-dimethyl-1,4,5,8-tetraselenafulvalene forms cation radical salts with inorganic anions. The 2:1 salt with tetrafluoroborate can be prepared by electrocrystallization, and two crystalline phases have been found. One form is tetragonal, space group $I4_2d$, $a = 18.336$ Å, $c = 7.226$ Å. The structure contains stacks of cations along the c axis. Within a stack the cations are shifted along the long molecular axis in a zig-zag manner. The electrical conductivity is metallic at room temperature but at about 80 K a transition into semiconducting behavior is observed. A Peierls type transition is a likely explanation and a structure determination below this temperature has been attempted. The other crystal form is triclinic, $P\bar{1}$, $a = 7.284$, $b = 12.810$, $c = 13.826$ Å, $\alpha = 83.44$, $\beta = 80.16$, $\gamma = 73.96^\circ$. This structure contains two independent cations which are rotated approximately 90° with respect to each other and no pronounced stacking is present. These crystals are semiconducting in the temperature range studied. Polymorphism has been observed for many organic conductors (including superconductors) and as expected the physical properties are strongly related to the packing of the constituents in the crystal structure.

PS-10.03.10 EUROPIUM (III) MOSSBAUER SPECTRUM AS PROBE OF MAGNESIUM (II) SITES IN LITHIUM NIOBATE CRYSTAL.** By Hongxi Zhang*, Liangsheng Qiang and Chongquan Xu, Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150006, P. R. China.

Because of the advantages of magnesium (II) doped lithium niobate (Mg:LiNbO_3) crystal as electro-optic material, the local sites of Mg^{2+} in LiNbO_3 have been widely investigated by various methods (D. A. Bryan et al., Opt. Eng., 1985, 24, 138 and L. Arizmendi et al., Phys. Rev., 1985, B31, 7138) and several models were proposed (Zhang Qiren et al., Phys. Rev., 1991, B43, 12022, Zhou Yiyang et al., Phys. Rev. 1991, B43, 11374 and Zhang Hongxi et al., J. Chinese Ceramic Soc., 1991, 19, 523). But no direct evidence can be used to confirm the position of Mg^{2+} . In the present paper, we report the Mössbauer spectra of Eu^{3+} in Eu:LiNbO_3 and Eu:Mg:LiNbO_3 crystals. Based on the Mössbauer parameter changes, the local site of Mg^{2+} is discussed.

Mössbauer absorbers were prepared from Czochralski-grown Eu:LiNbO_3 (2.5mol% Eu_2O_3) and Eu:Mg:LiNbO_3 (2.5mol% Eu_2O_3 , 6.0mol% MgO) and Eu^{3+} density was about 20mg/cm³. Mössbauer spectra were recorded at room temperature on an OXFORD MS-500 constant acceleration Mössbauer spectrometer with a 1024 multi-channel analyzer. The radiation source was solid state $\text{SmF}_3(^{152}\text{Sm})$, about 100 mCi (^{152}Eu). A xenon proportional counter was used as detector. Eu_2O_3 as standard absorber.

Based on L. Arizmendi's spectroscopic measurement, we fitted the spectra with two Lorentzian lines and obtained the isomer shifts (IS) of Eu^{3+} in Eu:LiNbO_3 and Eu:Mg:LiNbO_3 . The result is listed in the following table and it indicates that Eu^{3+} can occupy both Li^+ site (Eu(Li)) and Nb^{5+} site (Eu(Nb)).

Table Isomer shifts of Eu^{3+} in Eu:LiNbO_3 and Eu:Mg:LiNbO_3 .

Sample	IS	Line 1	Line 2
Eu:LiNbO_3	0.3675, Eu(Nb) , 56%	-0.6182, Eu(Li) , 44%	
Eu:Mg:LiNbO_3	0.2745, Eu(Nb) , 48%	-0.9143, Eu(Li) , 52%	

IS is very sensitive to Eu-O distance and increases with decreasing Eu-O distance (B. H. Oconnor et al., Acta Cryst., 1969, B25, 2140). In LiNbO_3 , average Nb-O distance is shorter than average Li-O distance (S. C. Abrahams et al., Acta Cryst., 1986, B42, 61) and XRD analysis showed that Eu_2O_3 doping does not cause structure changes. When Eu^{3+} replaces Nb^{5+} and Li^+ , Eu(Nb)-O distance is shorter than Eu(Li)-O . Therefore, it is deduced that, for Eu:LiNbO_3 or Eu:Mg:LiNbO_3 , the lower IS corresponds Eu(Li) and the higher IS to Eu(Nb) . From the relative integrated intensities of the two subspectra, we can estimate that about 56% (48%) Eu^{3+} occupy Nb^{5+} sites, 44%(52%) Eu^{3+} occupy Li^+ sites in Eu:LiNbO_3 (Eu:Mg:LiNbO_3) respectively, also listed in the table. The results indicate that Eu^{3+} and Mg^{2+} compete in Nb^{5+} sites and the doping of Mg^{2+} into Eu:LiNbO_3 decreases the ratio of Eu(Nb) . That means Mg^{2+} is preferred to occupy Nb^{5+} site. From the conclusion, we also analyse the mechanism of the increased anti-photorefractivity of Mg:LiNbO_3 .

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