

PS09.01.27 ELECTRON DENSITY DISTRIBUTION IN γ -CuBr BY THE MAXIMUM ENTROPY METHOD. H. Ishibashi, J. Tamura and K. Nakahigashi, College of Integrated Arts and Sciences, Osaka Prefecture University, Sakai, Osaka 593, Japan

The electron density distribution of γ -CuBr with sphalerite structure was determined by the maximum entropy method (MEM) with the aid of powder X-ray data at room temperature and 9 K. The electron density map of lower-density region for the $(\bar{1}10)$ plane at room temperature is shown in figure. Covalent bonding between Cu and Br due to the strong admixture of Cu $3d$ and Br $4p$ states is clearly recognized. Further the valence electron density of Cu is elongated along the three directions indicated by arrows. These elongations originated from the anharmonic thermal motions. On the other hand, the thermal motions of both atoms were reduced at 9 K, particularly the spread of Cu along the arrows disappeared. The root mean square displacement of Cu and Br at room temperature and 9 K was 0.222 Å, 0.158 Å and 0.089 Å, 0.074 Å, respectively, and agreed well with those determined by the neutron diffraction studies (F. Altorfer *et al.*, *J. Phys.: Condens. Matter*, 1994, 6, 99499962).

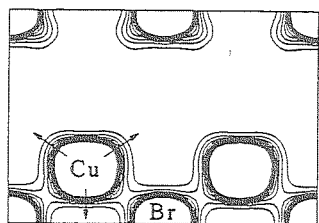


Figure. The MEM map of γ -CuBr for the $(\bar{1}10)$ plane at room temperature. Contour lines (e^{-3}) are drawn from 0.3 to 2.1 with 0.2 intervals.

PS09.01.28 CHARGE AND NUCLEAR DENSITY DISTRIBUTION OF THE PYROCHLORE $Y_2Sn_2O_7$ BY MEM. C.J. Howard and D.J. Cookson, Australian Nuclear Science and Technology Organisation, Menai, NSW 2234, Australia. B.J. Kennedy, School of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia, T. Ikeda, M. Takata and M. Sakata, Department of Applied Physics, Nagoya University, Nagoya 464-01, Japan

A Maximum Entropy Method (MEM) has been used to obtain accurate charge and nuclear density distributions in the stoichiometric pyrochlore $Y_2Sn_2O_7$. The cubic pyrochlore structure with the general formula $A_2B_2O_6O^A$ is formed by a wide variety of ions, and tolerates a high degree of non-stoichiometry on the O^A anion and the A cation sites. The crystal structure can be viewed as two networks, the rigid B_2O_6 framework of vertex sharing BO_6 trigonal anti-prisms and the A_2O^A chains. A great number of materials adopt the structure and these display a large range of physical properties. The aim in this study was to derive the charge and nuclear densities in the typical pyrochlore, $Y_2Sn_2O_7$, by MEM analysis from X-ray and neutron powder diffraction data, so as to reveal details of the bonding. The synchrotron X-ray data were recorded at the Australian National Beamline Facility at the Photon Factory, Japan, and the neutron data were collected using the high resolution powder diffractometer at ANSTO. The R-factors for the MEM charge and nuclear densities were 4.3% and 4.8%, respectively. The MEM charge density indicates weak covalency in the Y-O(1) bonding, and relatively strong Sn-O covalency. The charge density also shows a slight charge delocalisation between Y and O(2), this being the first experimental confirmation of the theoretically assumed weak electron transfer between the Y_2O and Sn_2O_6 sublattices which partially explains the predisposition of pyrochlores to non-stoichiometry. The MEM nuclear density shows the anisotropic deformation due to thermal

motion of atoms, and confirms that the features observed in the charge density analysis are in fact due to electron delocalisation rather than atomic displacements.

PS09.01.29 ELECTRON-DYNAMICAL CHARACTERISTICS AND STABILITY OF METAL HYDRIDES. R.P. Ozerov, A.V. Sazonov, A.V. Bochkarev, S.A. Samoilov and VI. Khleskov, Mendeleev University of the Chemical Technology of Russia, Miusskaja Sq 9, 125047 Moscow, Russia

The X-ray diffraction data treatment, atomic and electronic structure as well as vibrational characteristics calculation have been attempted to be used in linking together the structure and stability of hydrides. The later represent the model matrices for hydrogen storage systems (in ecologically pure energetic) which must be stable enough not to loose hydrogen at room temperature and to let hydrogen go out at elevated temperatures.

There are 2 ways of the electron structure investigations. First, electron density can be measured using the accurate X-ray diffraction data. The experimental data [1,2] has been treated for LiH. The Hansen-Coppens multipole model has been used. Another way consists of the quantum chemical calculations. The iterative extended Huckel method with special parameterization for metal atoms has been employed for the calculation of zone structure and charge transfer in LiH, NiH and AlD₃. The cluster approach has been used with the maximum cluster size approximately 100 atoms.

The coincidence of the results was found to be good. The charge transfer of about 0.8 electron has been found.

The isotope exchange coefficient b in the reaction $LiH(D)-H_2$ has been calculated using the previous data. The method of moments of the frequency function has been worked out. The comparison of the calculated temperature dependence of b shows the good agreement with experimental one.

1. Calder, R.S., et al 1962, *J.Phys. Chem. Sol.* 23, 6212
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PS09.01.30 CHARGE DENSITY STUDIES OF ORGANIC NON-LINEAR OPTICAL MATERIALS J. M. Cole^{†*}, J. A. K. Howard[†], G.J. McIntyre^{*}, R. C. B. Copley[†], A. E. Goeta[†], M. Szablewski[†], G. H. Cross[†] [†]University of Durham, U.K.; ^{*}Institut Laue Langevin, France.

Recent developments in organic non-linear optical (NLO) materials over the last 20 years have triggered a prolific interest into this area of research. Second harmonic generation (SHG) measurements of organic NLO materials have already produced results which, by far, supersede those obtained from all known inorganic alternatives.

It has been found¹⁻² that a deeper understanding of the nature of (a) charge transfer (CT) processes and (b) intermolecular forces in these compounds is the key to the optimization of the SHG effect. In light of these findings, we are currently pursuing an extensive program of charge density (CD) analysis since this provides an ideal route to improved understanding in both of these areas. Moreover, recent work³ has shown that one can use CD experimental results in order to determine the values of all (hyper)polarizability coefficients in the solid state. No other accurate *solid state* method to calculate these values exists.

A series of five zwitterionic tetracyanoquinodimethane (TCNQ) derivatives have been studied by single-crystal X-ray diffraction at 150K.⁴ More recently, neutron experiments at 20K have been performed in conjunction with more extensive single-crystal X-ray diffraction experiments at 20K using our in-house F_{dd} cryodiffractometer (10-300K). Results of such 20K X/N CD studies will be the prime subject of this presentation.

References

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