

05.2-7 OBSERVATION OF MAGNETOSTRICTIVE ATOMIC SHIFTS IN MnF_2 FROM γ -RAY DIFFRACTION DATA.

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Rutile-type MnF_2 was chosen to study the relationship between optical birefringence and structural change as a function of temperature in a simple antiferromagnet ($T_N=67$ K). It was previously inferred, on the basis of the Ewald-Born theory of structural birefringence, that a very small displacement of the fluorine ions would be sufficient to account for the observed magnetic contribution to the birefringence (Jauch and Dachs, Solid State Comm. (1974), 14, 657).

γ -radiation ($\lambda = 0.03 \text{ \AA}$) was used to collect selected Bragg diffraction intensity data on an absolute scale at room temperature and 11 K from a single crystal plate (counting statistical precision of J: 0.4%-1%). The fluorine positional parameter u was determined by least-squares refinement (weights based on counting statistics alone, no extinction correction, anisotropic temperature factors). Result: $u = 0.30523(7)$ at room temperature, $u = 0.30471(6)$ at 11 K with goodness-of-fit parameters not significantly different from 1. The observed magnetostrictive atomic shifts agree in both magnitude and sign with predictions from the Ewald-Born theory.

05.2-8 NONLINEAR OPTICAL PROPERTIES AND STRUCTURE OF ORGANIC CRYSTALS. By V.D. Shigorin General Physics Institute, the USSR Academy of Sciences, Moscow, USSR.

In recent years a great number of organic crystals have raised great interest due to their large optical nonlinearities. As most of such crystals are molecular ones, it is possible, at first approximation, to relate nonlinear optical properties of a given crystal to the hyperpolarizability of its constituent molecules and their orientation within the unit cell. The use of molecular hyperpolarizability tensorial additivity allows to simplify the consideration of structural aspects of organic crystal optical nonlinearities. The relationships between molecular hyperpolarizabilities and second- and third-order optical susceptibilities for all point symmetry groups are presented. It is deduced that if the number of nonzero independent components of nonlinear susceptibility tensor is greater than the number of such components of molecular hyperpolarizability tensor, then additional structural relations between susceptibility tensor components appear. By means of numerous examples it is shown that quantitative estimation of nonlinear susceptibility tensor components for any crystal with the known structure is possible on the basis of structure data and measured nonlinearities of related compounds. Molecular and crystal structure peculiarities of organic materials with large optical nonlinearities are analysed.

05.2-9 THE ELASTIC CONSTANTS OF TARTARIC ACID. By H. Küppers and M. Pies, Mineralogisches Institut, Universität Kiel, Germany.

The elastic constants and their temperature coefficients of monoclinic tartaric acid were measured by an improved Schaefer-Bergmann method. A pulsed argon laser (50 Hz) was used, and the ultrasound was fed into the crystal only for a short time (100 μ s) before the laser was triggered. This minimizes the warming up of the specimen by absorption of ultrasound.

The measured values $c_{11} = 75.4$, $c_{22} = 16.0$, $c_{33} = 35.2$, $c_{12} = 8.4$, $c_{13} = 16.0$, $c_{23} = 11.1$, $c_{44} = 8.0$, $c_{55} = 12.7$, $c_{66} = 8.9$, $c_{15} = -20.3$, $c_{25} = -0.5$, $c_{35} = -3.8$, $c_{46} = 0.2 \cdot 10^{10} \text{ dyn/cm}^2$ differ considerably from those determined by Mason (Piezoelectric crystals, 1950) by resonance techniques.

The elastic behaviour is characterized by an extreme anisotropy. The ratio of maximum to minimum elastic stiffness is 5.9 : 1. This anisotropy can be correlated with the crystal structure (Okaya et al., Acta Cryst. (1966) 21, 237). The maximum stiffness is found parallel to the preferential direction of the hydrogen bonds. From spectroscopically determined molecular force constants a rough quantitative estimate of the maximum stiffness can be made which reasonably agrees with the value experimentally determined.

05.2-10 RELATION BETWEEN STRUCTURE AND PHYSICAL PROPERTIES OF NON-STOICHIOMETRIC TRANSITION METAL CARBIDES. By J. Hauck, Institut für Festkörperforschung, Kernforschungsanlage Jülich, D-5170 Jülich, W. Germany.

The transition metals M of group III-VI can form carbides MC_x with NaCl lattice which are non-stoichiometric within the range $0.5 < x < 1$. Short range order in the disordered high temperature solid solutions and ordered phases at $x = 0.88$ (V), 0.83 (V,Nb), 0.63 (Ti) and 0.5 (Ti,Zr,RE) can be described by a structure model considering repulsive interactions of carbon vacancies. Each carbon vacancy exhibits the same number of first, second and third nearest neighbors at compositions $x = 1-n/24$ ($n = 0, 1 \dots 12$). The comparison of lattice energies for the resulting different structure models shows that short and long range ordering at $x = 0.83$ is favoured by a maximum of Coulomb energy, while covalent bond energy with a decrease of all M-C bonds favours $x = 0.5$ and $x = 1$ compositions.

Some physical properties which are unusual for compounds with NaCl lattice can be described by the present structure model. The maxima of melting temperature, lattice constants, critical resolved shear stress and activation energies of diffusion at $x \approx 0.8$ can be correlated to the maximum Coulomb energy at $x = 0.83$.

a) Transition metal carbides with small lattice constants like VC_x order at $x = 0.83$ and exhibit a large deviation from $x = 1$ stoichiometry because of the strong Coulomb interactions of carbon vacancies. The short range order parameters are close to those calculated for the structure model: $\alpha_1 = \alpha_2 = -0.2$, $\alpha_3 = 0.2$. The maximum carbon content of $x = 0.89$ can only be achieved by $\sim 1\%$ vacancies in the V sublattice similar as in TiO_x . The carbon vacancies of $VC_{0.88}$ cannot be filled with hydrogen atoms.

- b) Transition metal carbides with large lattice constants and strong covalent bond energy exhibit small deviations from $x = 1$ stoichiometry and form low temperature phases at $x = 0.5$ and $x = 1$. $ZrCo_{0.65}$ e.g. orders in Ti_2C structure rather than in a M_2C_3 structure because of the gain of covalent bond energy for a reduction of Zr-C bond distance by 0.03 Å (Hauck, Larson, Gruzalski, Darken & Barhorst, unpublished). $ZrC_{0.65}$ can be charged with hydrogen.
- c) Transition metal carbides with both strong Coulomb and strong covalent interactions like HfC_x and TaC_x exhibit the highest melting points of solids with about 4000 °C but exhibit very little tendency for ordering because of the small differences between Coulomb energies favouring $x = 0.83$ and covalent bond energies favouring $x = 0.5$ and $x = 1$ compositions.

05.2-12 PULSED NEUTRON DIFFRACTION STUDY OF A15

COMPOUNDS. By J.-E. Jorgensen, Aronne National Laboratory, U. S. A., A. N. Christensen and S. E. Rasmussen, Aarhus University, Denmark.

The three A15 compounds Mo_3Si , non stoichiometric Nb_3Ge and Nb_3Sn have been studied by pulsed neutron powder diffraction. These compounds represent high, medium and low temperature superconductors. The aim of the experiments was to study the relationship between superconductivity and structural instability at low temperature. The martensitic transformation (cubic to tetragonal) was observed in Nb_3Sn .

The mean squares displacements of the thermal vibrations were measured as a function of temperature. The degree of anisotropy of the transition metal vibrations will be related to structural and superconducting properties.

05.2-11 THERMAL EXPANSION OF SOME RE T_4B_4 TYPE RARE EARTH METAL BORIDES. By K. Damodar Reddy, B. Appa Rao, K. Satyanarayana Murthy and Leela Iyengar, Department of Physics, Osmania University, Hyderabad - 500 007, India

The ternary metal borides of RE T_4B_4 - type (RE=rare earth metal, T = Os, Ir) crystallize in a tetragonal structure with the space group $P4_2/n$ and are isotypic with $NdCo_4B_4$. The tetragonal unit cell parameters 'a' and 'c' of RE Os_4B_4 (RE = La, Ce, Pr, Nd and Sm) and of RE Ir_4B_4 (RE = La, Pr, Nd and Sm) have been determined accurately over the temperature range 300-800 K by X-ray powder diffraction techniques. Using the high temperature lattice parameter data the axial thermal expansion coefficients α_a and α_c have been evaluated at different temperatures. It has been found that the thermal expansion coefficients are anisotropic ($\alpha_a > \alpha_c$) and this anisotropy increases with decreasing axial ratio c/a. These results are discussed in relation to the structure and other physical properties of these materials.

05.2-13 FINE POWDER SHG-TECHNIQUE FOR THE DETERMINATION OF POLAR DISTORTION IN SUBSTANCES AND ITS APPLICATION TO THE STUDY OF SYSTEMS WITH FERROELECTRIC PHASES ($SbNbO_4$ - $BiNbO_4$ AND $SbNbO_4$ - $SbSbO_4$). By S. Yu. Stefanovich, A. P. Leonov and Yu. N. Venevtsev. L. Ya. Karpov Institute of Physical Chemistry, Moscow, USSR.

Quantitative estimations of noncentrosymmetric distortions in crystals by means of the Second Harmonic Generation (SHG) in powders are usually unsatisfactory because of the strong dependence of the intensity of the signal ($I_{2\omega}$) on the coherent length (L_C) which for various crystals varies considerably. However in the case of SHG in fine powders with the size of particles $\leq 2 \mu$ it is possible to exclude L_C from the expression for $I_{2\omega}$. Then the only parameter, on which the intensity depends, becomes the nonlinearity of the sample (d). For ferroelectrics this dependence is $I_{2\omega} \sim d^2 \sim P_s^2$, where the spontaneous polarization P_s is a measure of polar distortion of the structure.

For the detection of very weak SHG-signals, reflected from a fine-powder or ceramic sample we use a high-sensitive measuring system which also enable us to follow the changes of $I_{2\omega}$ (and P_s) vs. temperature. The results obtained by this technique when combined with the data of the usual X-ray powder analysis prove to be especially useful for the investigation of phase diagrams when ferroelectric or other non-centrosymmetric phases are present.

We have considered two systems of solid solutions based on ferroelectric $SbNbO_4$, the