

05.2-7 OBSERVATION OF MAGNETOSTRICTIVE ATOMIC SHIFTS IN  $MnF_2$  FROM  $\gamma$ -RAY DIFFRACTION DATA.

By W. Jauch, J.R. Schneider and H. Dachs, Hahn-Meitner-Institut für Kernforschung, Glienicke Str. 100, D-1000 Berlin 39 (FRG).

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).

$\gamma$ -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  $\mu$ 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.