11.4–11 DIFFUSE X-RAY SCATTERING OF NaTl SINGLE CRYSTALS. By J.Schneider

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Non rotating monochromatic single crystal x-ray (NOROMOSIC) investigations of the Zintl-phase intermetallic compound NaTl were undertaken for the first time. They show unusual and temperature dependent diffuse patterns. In addition to anisotropic thermal diffuse scattering close to Bragg peaks, extended off-Bragg regions of diffuse scattering are observed. (Fig.1)
The interpretation is performed on the basis of lattice dynamical models which assume weak bonding of adjacent [110] zig-zag chains consisting of Na and Tl atoms respectively.

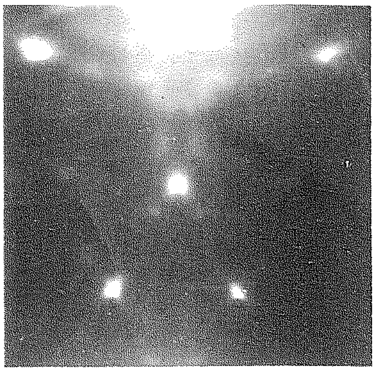

Fig.1 NOROMOSIC x-ray pattern of NaTl single crystal [110]-axis

11.4–12 THE TEMPERATURE DEPENDENCE OF THERMAL VIBRATIONS IN OXYGEN-OCTAHEDRAL FERROELECTRICS. By S.A.Ivanov, G.B.Ter-Mikaelyan, V.E.Zavodnik and Yu.N.Venevtsev.

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The study of the character of thermal vibrations is the important part in the dynamics of crystal lattice and is of principal value in the clearing up the nature and real mechanisms of many physical phenomena in ferroelectrics.
Taking the above into consideration the temperature dependence of thermal vibrations U^2 for several ion sublattices is observed for a number of polycrystalline samples with perovskite and pyrochlore structures in the wide temperature range. The kind of obtained dependences of $U^2(T)$ allowed in the some cases to make certain conclusions about the presence of the anharmonicity of the vibrations of some ions and thereby to consider them to be ferroelectrically active. In the case of $KTaO_3$ the particularities of thermal vibrations of ions were also defined with very high accuracy with the help of the precise X-ray experiment which was carried out on the perfect single crystal. The results obtained by this experiment on the whole confirmed the qualitative conclusions which were made in the course of studing the polycrystalline samples of $KTaO_3$. The analysis of the further possibilities of studing of the anharmonicity of the thermal vibrations on polycrystalline samples and single crystals of the above mentioned structural families was made.

11.4–13 THERMODYNAMIC FUNCTIONS FOR SULFUR FROM CRYSTAL STRUCTURE AND LATTICE DYNAMICS.

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From the X-ray diffraction data on orthorhombic sulfur (Abrahams, Acta Cryst. (1955) 8, 662; Pawley & Rinaldi, Acta Cryst. (1972) B28, 3605) a suitable model for lattice-dynamical calculations has been derived, using the Born-von Kármán procedure, and a non-rigid molecular model (Gramaccioli & Filippini, Acta Cryst. (1983), A39, 784). The van der Waals force field has been taken from Rinaldi & Pawley (J.Phys.C (1975) 8, 599), and the internal force field was initially taken from Steudel & Mäusle (Z.Naturforsch. (1978) 33a, 951). The difference between the calculated and the observed values for the lowest internal frequencies are however high if a rigid model is assumed, as it was in previous calculations of thermodynamic functions for the vapour phase, where the influence of packing in the crystal upon internal frequencies was neglected (Guthrie et al., J.Amer.Chem.Soc. (1954) 76, 1488): this involves differences of about 2 cal/mole.°K for entropy at room temperature, which are much larger than other corrections for existence of several molecular species. Because of this, the internal field has been modified by essentially lowering the torsional constants. From these calculations, a satisfactory agreement is obtained for vibrational frequencies, and an excellent match with experimental data is obtained for thermodynamic functions in the crystal and temperature factors.

11.5–1 LATERAL AND ANGULAR PARAMETERS OF THE UNIT-CELL OF A HIGHLY PURE SILICON CRYSTAL. By H. Siegert and P. Becker, Physikalisch-Technische Bundesanstalt, Braunschweig, Federal Republic of Germany.

The redetermination of the Avogadro constant currently in progress at the Physikalisch-Technische Bundesanstalt requires a relative uncertainty of less than 5×10^{-7} in the determination of the unit-cell volume in a silicon single crystal. From precision measurements of lattice spacings (Ando, Bailey, Hart, Acta Cryst. (1978) A 34, 484) it is known that the shape of the unit-cell, even in highly pure silicon crystals, is not exactly cubic. Thus the unit-cell volume, calculated from the knowledge of only one lattice plane spacing may exhibit a systematic error of up to $\Delta v/v \approx 1 \times 10^{-6}$.

Using a whole set $\{h\ k\ l\}$ of equivalent lattice planes with $\sqrt{h^2 + k^2 + l^2}$ = const., the axial lengths a, b, c, axial angles α, β, γ and the volume v of a "real" unit-cell were calculated, assuming that the unit-cell is slightly deformed by internal or external forces.

By crystal-to-crystal comparison measurements, relative aberrations from the cubic shape in the order of $\pm 2 \times 10^{-7}$ were found. The results are listed in the table. In order to study the differences in lattice plane spacings, thin crystal wafers in a double crystal arrangement and consecutive Laue reflections were used. Provided both wafers were of almost the same thickness, the rocking curves show a detailed fine structure which allows the differences in angular position to be detected to better than 10^{-8} rad.

In future work the mean unit-cell volume of a cube of silicon one kilogram in weight will be determined. Further investigation will be aimed at clarifying whether, as Ando, Bailey and Hart have surmised, the unit-cell volume in a highly pure silicon crystal remains almost unchanged even when the crystal lattice is slightly deformed.

Table: Lateral and angular parameters of the unit-cell of a highly pure silicon crystal at 22.50°C and vacuum.

$a = (543\ 101.915 \pm 0.049)$ fm

$b = (543\ 102.116 \pm 0.049)$ fm

$c = (543\ 102.007 \pm 0.049)$ fm

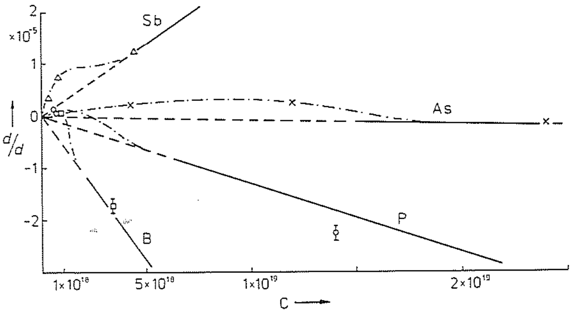
$\alpha = \pi/2 - (10 \pm 10) \times 10^{-8}$

$\beta = \pi/2 + (22 \pm 10) \times 10^{-8}$

$\gamma = \pi/2 - (5 \pm 10) \times 10^{-8}$

$V = (0.160\ 193\ 259 \pm 0.000\ 000\ 044)\ \mathrm{nm}^3$

Figure : Lattice parameter changes $\Delta d/d$ versus (low) impurity concentration c (atoms cm^{-3}) in silicon. The individual confidential limits of each measurement are of the order of 10^{-7} $\Delta d/d$, except the two limits marked in the figure.



11.5–2 LATTICE DISTORTIONS INDUCED BY B, P, As AND Sb IN SILICON. By P. Becker and M. Scheffler, Physikalisch-Technische Bundesanstalt, Braunschweig, Federal Republic of Germany.

The lattice parameters of silicon crystals doped with B, P, As and Sb have been measured as a function of impurity concentration using a highly accurate X-ray diffraction technique (Becker, Seyfried, Siegert, Z. Physik B (1982) 48, 17). This method allows the change of lattice parameters for doping concentrations even below 10^{18} atoms cm^{-3} to be studied. Some of the results are shown in the figure. For low concentration all samples show a dilatation of the lattice if compared with a highly pure Si crystal (dotted (-·-·-) curves in the figure). For higher concentration the B, P and As doped samples show a reduced lattice parameter and only Sb gives rise to an expansion.

In order to elucidate the discrepancies between the lower and higher concentration data, parameter-free calculations of the lattice distortions at substitutional and interstitial impurities in Si are performed using the self-consistent Green's functions method (Scheffler, Vigneron and Bachelet, Phys. Rev. Lett. (1982) 49, 1965 and Phys. Rev. B to be published). In a good accordance between theory and experiment, all impurities in the sample with high doping concentrations essentially occupy substitutional sites. The amount of the lattice parameter change and the trends between different impurities quantitatively confirm the concept given by the covalent radii of the atoms (straight lines in the figure). The low concentration results, on the other hand, indicate the presence of a considerable percentage of interstitial defects.

11.5–3 MEASUREMENT OF DISORDER-DIFFUSE X-RAY SCATTERING USING A DIFFRACTOMETER. By T.R.Welberry, Research School of Chemistry, Australian National University, CANBERRA, Australia. & A.M.Glazer, Clarendon Laboratory, Parks Rd., OXFORD, England.

Substitutional or orientational disorder occurs widely throughout many branches of crystallography. But while conventional structure solution using Bragg reflections has become more or less a routine operation, the measurement and interpretation of diffuse x-ray scattering for problems involving disorder is still done largely on an ad hoc basis. Recently we have sought to develop methods, using conventional Weissenberg equipment, to make the systematic study of disorder problems in molecular crystals a more routine process. (Epstein et al, Acta Cryst.A38, 611-618 (1982);Welberry et al, Acta Cryst. B38, 1518-1525 (1982); Epstein & Welberry, Acta Cryst. A39, 882-892.(1983)). In this paper we present the results of a comparative study of these film-based methods with experiments we have recently carried out on a diffractometer, which were undertaken in order to assess the reliability of the film-based methods.

In order to make the comparison as close as possible the diffractometer (Stoe Stadii-2) was set up to correspond in resolution to the Weissenberg camera. With the detector 125mm from the sample a vertical detector slit-width of 4mm. gave comparable resolution to a 1mm. layer-screen gap on a 30mm. radius Weissenberg camera. The horizontal detector-slit width, which corresponds to resolution in theta and which has no counterpart on the Weissenberg camera, was set at 2mm. For an example run, stationary counts of 100 secs. were made at points in reciprocal space on a grid a*/10 by c*/5 for the h0l section of the chosen sample: 1,4-dibromo-2,5-diethyl-3,6-dimethylbenzene; Space Group $P2_1$, a=9.084, b=4.459, c=17.940 Å, β = 122.82. Data was collected for one half of