

05.1-23 THERMAL VIBRATIONS IN BARIUM TITANATE.

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The crystal structure of BaTiO₃ (BT) has been investigated by X-ray (H. Bock, Diplomarbeit Saarbrücken 1979) and neutron-diffraction (R. Schollmayer, Dissertation Saarbrücken 1976) in the cubic and tetragonal phases. Two models have been used for refinement: the displacive model (J. Harada, T. Pedersen, Z. Barnea, AC A26, 566 1970) and the order-disorder-model (od) (R. Comes, M. Lambert, A. Guinier, AC A26, 244 1970). In these models the thermal vibrations of the atoms are described in a different manner. Fitting the displacive model yields a Debye-Waller-Factor (DWF) with the following characteristic features: in the cubic phase the DWF is nearly twice as large as in the tetragonal phase (c-direction). This tetragonal value corresponds to the theoretical one, calculated from the elastic constants. The jump of the DWF at the transition point and its temperature dependence in the cubic phase can hardly be explained by a harmonic theory. Anharmonic effects are introduced in the structure analysis by means of the od-model. In this model the data for the cubic phase can be fitted by a DWF which agrees with the theoretical one and "split-atom position" parameters corresponding to the spontaneous displacements of the atoms in the ferroelectric phase. From the refinement procedure alone neither model can be preferred because both R-values are of the same order of magnitude. The advantage of the od-model lies in the fact that the data can be interpreted quantitatively in a simple manner.

05.1-24 INCOMMENSURATE PHASES OF Rb₂WO₄ AND RELATED COMPOUNDS. By F. Tuinstra and A.J. van den Berg, Lab. voor Technische Natuurkunde, Technological University Delft, The Netherlands.

The incommensurate phases of K₂MoO₄ and Rb₂WO₄ were previously reported to display hexagonal symmetry. Careful analysis of diffraction data, however, discloses orthorhombic symmetry. The spacegroup of the average structure is Cmcm. (van den Berg, A.J., Tuinstra, F. & Warczewski, J. (1973) *Acta Cryst.* B29, 586-589). In both compounds the modulation wave vector \vec{k} is perpendicular to the pseudo-hexagonal c-axis. Both k-vectors change in length as a function of temperature; in K₂MoO₄ \vec{k} keeps a value close to 0.3b* down to 305K, while in Rb₂WO₄ \vec{k} changes from 0.35b* at 750K to 0.37b* at 680K. At 680K the structure locks in at $k = \frac{b^*}{2}$ on cooling. The resulting structure is isomorphous with β -K₂SO₄. In view of this behaviour the incommensurate phase can be looked at as having a structure analogous to β -K₂SO₄ only the k-vector being shorter. The main mechanism in the modulation is an alternation between opposite orientations of the anionic tetrahedra.

Related compounds seem to prefer a rational wave vector: in K₂WO₄, $k = \frac{b^*}{4}$; in Rb₂MoO₄, $k = \frac{b^*}{2}$. The phase transitions are of the order-disorder type, as in β -K₂SO₄ (van den Berg, A.J. & Tuinstra, F. (1978) *Acta Cryst.* B34, 3177; Miyake, M., Morikawa, H. & Iwai, S. (1980) *Acta Cryst.* B36, 532).

It should be noted that, though belonging to the same basic structure, the incommensurate phases of K₂SeO₄ and Rb₂ZnCl₄ have their k-vectors along the pseudo-hexagonal c-axis.

05.1-25 POLYMORPHISM IN THALLIUM(I) THIOCYANATE.

By Robert Lippman and Reuben Rudman, Department of Chemistry, Adelphi University, Garden City, N.Y., 11530, U.S.A.

A differential scanning calorimetry investigation of TlSCN revealed a solid-solid phase transition at 90°C, with a melting point of 230°C. Single-crystal XRD diffractometer data were collected on a small crystal at room temperature and refined (after absorption and extinction corrections) to $R_1=0.040$ and $R_2=0.053$, using the results of Bussem, Gunther, and Tubin [*Z. Physikal. Chem.*, B24, 1(1934)] as starting parameters. Pertinent data are: Orthorhombic, Pbcm, $a=6.783(1)\text{Å}$, $b=6.816(1)\text{Å}$, $c=7.606(1)\text{Å}$, $Z=4$, $D_x=4.96\text{ g/cm}^3$, $D_m=4.96\text{ g/cm}^3$, $S-C=1.62(1)\text{Å}$, $C-N=1.17(1)\text{Å}$, $S-C-N=178.7(7)^\circ$, with the shortest Tl interatomic distance (to S)= $3.306(1)\text{Å}$, based on 25 variable parameters and 313 unique reflections.

At 130°C, the high-temperature phase is tetragonal, with $a=6.821(1)\text{Å}$, $c=7.779(2)\text{Å}$, $Z=4$, $D_x=4.82\text{ g/cm}^3$. The systematic absences are compatible with several space groups, but the data given by Yamada and Watanabe [*Chem. Soc. Jpn. Bull.* 36, 1032 (1963)] for the apparently isostructural KSCN were used as starting parameters. Since $\Delta S_{tr} = 0.15\text{ e.u./mole}$, while $\Delta S_m = 9.56\text{ e.u./mole}$, TlSCN is not a true plastic crystal. However, the SCN⁻ ion is disordered, and studies of similar materials indicate a dynamic, rather than static, disorder. Inasmuch as volume constraints seem to preclude a complete reorientation of the SCN⁻ ions, the 60 independent high-temperature reflections have been refined in terms of a unique model which may be characteristic of this class of disordered compounds. The results of refinements of both phases and a description of their structural relationship and phase transition in terms of a dynamic disordered model will be presented.

05.1-26 PRESSURE INDUCED STRUCTURAL TRANSFORMATION IN RARE-EARTH FORMATES. By K. Satyanarayana Murthy, P. Kistaiah, Leela Iyengar and K.V. Krishna Rao, Department of Physics, Osmania University, Hyderabad - 500 007, India.

The high-pressure behaviour of the formates of some rare-earth elements, Lanthanum, Cerium and Gadolinium has been studied by X-ray diffraction at room temperature using a diamond anvil apparatus. These compounds are isomorphous and crystallize in the trigonal system, space group R3m, with one molecule per unit cell. Pressure induced structural transformations were observed in these compounds at about 40 Kbar and the new phase of these compounds could be indexed basing on the cubic lattice, with lattice constants $a = 7.46, 7.42$ and 7.18 Å for Lanthanum, Cerium and Gadolinium formates, respectively. They are isomorphous under pressure at room temperature. The details of the results and the nature of phase transition will be discussed.