conference abstracts

s9'.m1.p13 **The crystal structure of soda at 110 K and 270 K.** E. Libowitzky, G. Giester, *Institut für Mineralogie und Kristallographie der Universität Wien – Geozentrum, Althanstr. 14, A-1090 Wien, Austria.*
Keywords: disorder, hydrogen bond, carbonate.

Crystals of soda, $Na_2CO_3 \cdot 10H_2O$, were grown by slow evaporation of a saturated sodium carbonate solution at room temperature. Because the compound dehydrates immediately to the monohydrate at room temperature, a crystal fragment of 0.35 x 0.35 x 0.40 mm in size was separated carefully from a larger crystal working within apiezone grease. The grease-covered crystal was measured on a single-crystal CCD X-ray four-circle diffractometer. A whole sphere of data ($N_{unique} > 4\,\sigma(F_o) = 3565$ and 3084) was collected at 110 and 270 K, respectively, using a commercial Oxford Cryostream system operating with LN_2.

Whereas the crystal structure of soda had been published in rather old literature[1] with $R = 18$ %, in the present investigation the acentric structure was solved by direct methods (SHELXS-97) and refined subsequently using full-matrix least-squares techniques (SHELXL-97) to $R1 = 1.9$ % (110 K) and 2.5 % (270 K). In contrast to the previous structure description[1], even the hydrogen atoms were located and refined with isotropic displacement parameters. Space group is Cc, lattice parameters are $a = 12.740(1)\ /\ 12.763(1)$, $b = 8.816(1)\ /\ 8.955(1)$, $c = 12.571(1)\ /\ 12.593(1)$, $\beta = 115.966(2)\ /\ 115.892(2)$ at 110 / 270 K, $Z = 4$.

The structure is composed of pairs of edge-sharing $Na(H_2O)_6$ octahedra forming $Na_2(H_2O)_{10}$ units and CO_3 molecules. These units are connected by hydrogen bonds ($d_{O\cdots O} > 2.73$ Å) in a NaCl-like arrangement. The structure is pseudo-centric, only the carbonate groups and four H atoms violating the centric symmetry. Test refinements in space group $C2/c$ resulted in $R1$ values of more than 6 % at both temperatures.

Unlike the room temperature structure with disordered carbonate groups[1], the CO_3 molecules are perfectly ordered at 110 K and show almost isotropic ADPs of the carbonate O atoms. The CO_3 position is constrained by hydrogen bonds, involving at least two H bonds per acceptor oxygen atom.

At 270 K the carbonate groups still hold the former low-temperature position to 60 %, whereas 40 % are disordered into at least two different positions with large and strongly smeared ADPs of the carbonate O atoms. However, a centro-symetric equivalent of the low-temperature CO_3 position is occupied to only ~ 10 %.

A definite phase transition was not observed in differential scanning calorimetry measurements between 120 and 278 K. Hence, it appears that the process from (partially) disordered to perfectly ordered carbonate groups takes place over a wide temperature interval and without change of the space group symmetry Cc. This behavior may be promoted by the weak forces of the hydrogen bonds that hold the CO_3 groups in place.

[1] Taga T. "Crystal structure of $Na_2CO_3.10H_2O$.", Acta Cryst., (1969), B25: 2656 – 2658.

s9'.m1.p14 **Anharmonic thermal motion of a rigid molecule.** D. Schwarzenbach, *Institute of Crystallography, Physics Department, University of Lausanne, CH-1015 Lausanne, Switzerland.*
Keywords: thermal motion, anharmonicity, rigid-body libration.

The rigid-body TLS model of Schomaker and Trueblood [1] approximates the atomic displacements by rectilinear movements, and assumes a harmonic isolated-molecule potential for the translational and librational movements of the entire molecule. This model may be generalized with two kinds of anharmonicity, arising respectively from the curvilinear motions of the atoms, and from an anharmonic translation-libration potential.

A correction for the first kind, the skewness of the atomic probability density functions arising from harmonic angular large-amplitude librational oscillations, has been proposed by Willis & Pawley [2]. These authors include third-order cumulant terms in the displacement factor expression. The number of adjustable parameters is thereby not increased since all these cumulant terms are functions of the L tensor elements. The resulting atomic parameters do not need to be corrected for the effects of the curvilinear motion. The refinement is carried out with respect to the elements of the T, L and S tensors, *i.e.* the rigid-body motion is imposed by constraints. The leading terms arising from this anharmonicity are: (*i*) the libration correction of atomic coordinates proportional to the temperature T; (*ii*) third-order cumulants varying with T^2 which modifiy the atomic *p.d.f.* along the radius-vector from the center of libration to the atom.

We present here the theory of the second type of anharmonic motion due to an anharmonic libration potential, requiring the introduction of additional adjustable parameters. The leading term arising from this anharmonicity are: (*i*) a correction of the orientation of the molecule varying with T which is analogous to thermal expansion; (*ii*) third-order cumulants varying with T^2 which modify the atomic *p.d.f.* perpendicular to the radius-vector. The presence of this type of anharmonic terms may generally be inferred from harmonic refinements of diffraction data measured at different temperatures. Firstly, they result in a variation of the apparent equilibrium orientation of the molecule as a linear function of T. Secondly, harmonic mean-square libration amplitudes are proportional to temperature, but the presence of anharmonic terms results in a steeper increase with temperature (e.g. $L \approx aT + bT^2$). As an example, we present refinements at four different temperatures of the disordered molecule of C_{60} in the clathrate structure of $(hydroquinone)_3C_{60}$.

[1] Schomaker V., Trueblood K.N. "On the Rigid-Body Motion of Molecules in Crystals", Acta Crystallogr., (1968), B24: 63-76.
[2] Willis B.T.M., Pawley, G.S. "The Temperature Factor of an Atom in a Rigid Vibrating Molecule. II. Anisotropic Thermal Motion", Acta Crystallogr., (1970), A26: 260-262.