4.04.5-10 ENERGY ANALYSES FOR THE ALKALINE-EARTH FORMATES

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The structures of the alkaline-earth formates have been investigated in terms of lattice energy calculations. The lattice energy was approximated to be the sum of repulsive and potentials terms, where the repulsive potential used was in the form: \( U(r) = \frac{1}{12} f (r(r_{0})^{13} - r_{0}^{12}) \) where: \( r \); interatomic distance, \( f \); arbitrarily chosen standard force constant, \( r_{0} \); repulsive radius of an atom. The formate ions were treated as rigid bodies. The repulsive radius of atom concerned and the net charge on each atom of the formate ion were derived using the three known crystal structures, \( \alpha\)-Ca(HCOO)\(_{2}\), \( \alpha\)-Sr(HCOO)\(_{2}\), and \( \alpha\)-Ba(HCOO)\(_{2}\), by a least-square fit.

The results are as follows: \( R_{Ca}(\alpha)=1.591\, \text{Å}, R_{Sr}(\alpha)=1.802\, \text{Å}, R_{Ba}(\alpha)=2.025\, \text{Å} \). \( q_{Ca}(\alpha)=-0.86, q_{Sr}(\alpha)=-0.87, q_{Ba}(\alpha)=-0.15 \). \( R_{H} \) was fixed at 1.397 Å and \( q_{C} \) was assumed to be equal to \( q_{O} \). The reliability of these potential parameters were tested by the calculations of energy minimised structures for the above three structures and for the structure of \( \alpha\)-Ca(HCOO)\(_{2}\), with the results that the observed structures were all well reproduced. The potential and potential parameters proposed were successfully used for the determination of the structure of \( \alpha\)-Sr(HCOO)\(_{2}\), for the differentiation of the structures of \( \alpha\)-Sr(HCOO)\(_{2}\) and \( \alpha\)-Ba(HCOO)\(_{2}\), and for the interpretation of the large anisotropy of thermal vibrations in \( \alpha\)-Ba(HCOO)\(_{2}\),

4.04.5-11 POTENTIAL-ENERGY CALCULATIONS IN CRYSTALS: CARBON DIOXIDE, CO\(_{2}\), AND 9,10-ANTHRACQUINONE, C\(_{14}\)H\(_{8}\)O\(_{2}\).

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In 1970, carbon...oxygen and oxygen...oxygen potentials of the Buckingham L-exp type were derived from crystal and molecular data for carbon dioxide (Ktitogrodsky, Mirkaya, Nauchitel, Soviet Physics-Crystallography (1970) 16,769). The lattice energy of CO\(_{2}\) was represented as a sum of the van der Waals (vdW) and electrostatic terms. The C...O empirical parameters were transferred to CO\(_{2}\) from hydrocarbons. Later, the C...C parameters were refined (Mirkaya, Kozlova, Bereznitzkaya, Phys.Stat.Sol. (1974) 62B,291) and the electrostatic term, which provides most of the calculated lattice energy of carbon dioxide, was reexamined (Hirshfeld, Mirkaya, Acta Cryst. (1979) A35, 366). We have recently revised the 0...0 parameter values.

We are now making crystal-structure and energy calculations for another oxygen-containing compound, 9,10-anthracquinone, using the same 0...0 potential in combination with the C...C and H...H ones. The electrostatic-energy contributions, due to the interactions of the CO groups, are not expected to be as significant here as in CO\(_{2}\), but they might be responsible for the pseudoorthorhombic molecular arrangement and the negative thermal expansion coefficient along the \( c \) axis (Lonsdale, Milledge, El Sayed, Acta Cryst. (1986) B42). We consider this calculation a further test of the assumption of transferability of the vdw potential functions, one of the basic assumptions of the atom-atom approach to the investigation of non-bonded intra- and intermolecular interactions.

The computations are made using the WKIN computer program (Busing, Acta Cryst. (1972) A28, 525). The research is supported by NSF grants CHE77-18745 and CHE80-22526.