

MODEL STRUCTURE OF ALKALI METAL CHLORIDE MELTS

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As it was established in works [1,2], the best agreement between the calculated and experimental X-ray data for alkali metal (AM) halide melts is achieved by employing notions based on Zarzycki's model. The most acceptable for most of the AM fluorides and chlorides are quasicrystalline clusters with the structure of the NaCl type limited by the second-fourth coordination spheres (CS). This work takes a more close look at model structures containing Cl₃ clusters limited by the third CS. Clusters with this size have a minimal charge in comparison with clusters of other sizes, which ensures them the least far-ranging interaction. At the same time, the experience of working with the autocomplex model [3,4] suggests that in order to account for the transport properties of AM halide melts it is necessary to postulate the existence of weaker outer-sphere interactions between clusters and elementary ions such as M⁺, X⁻, M₂X⁺, MX₂⁻. This work deals with model structures incorporating Cl₃⁺ or Cl₃⁻ clusters and, respectively, MX₂⁻ or M₂X⁺ ions. Formally, these model structures may be regarded as laminated. Inside the layer the cluster is surrounded by four outer sphere (OS) ions, whereas between the layers these ions are missing. In the adjacent layers Cl₃ are shifted to the value of d(M-X). The parameters of these structures are distances d(M-X) in cluster - d(cl), inside the layer (between Cl₃ and OS ions) - d(os) and d(l) between layers. Based on experimental mole volumes V_m(m) for AM chloride melts the parameters d(os) and d(l) were calculated for four variants: d(os) equal to d₁(m) or d₂(m), and d(l) equal to d₁(m) or d₂(m), where d₁(m) and d₂(m) correspond to the locations of the first and second maxima on curves of correlation functions G(r) obtained with X-ray data [5]. For evaluation of the d(cl) values and the values of the potential energy of interaction between cluster and OS ions Pauling's potential was used. The accuracy of this potential is sufficient for a quality analysis [6].

According to these calculations, the crystal lattice parameter in Cl₃ clusters changes nonuniformly, i.e. d(cl) diminishes from the first to the third CS of the cluster. Moreover, the energy values of (Cl₃-Cl₃)- and (Cl₃-OS ion)-interactions for "experimental" d(os) and d(l) (namely, for those that were calculated from experimental V_m(m)), as well as the values of minimal energies, i.e. those at minimum points of potential curves for the aforementioned types of interactions were calculated. As it turned out, for all AM chlorides at d(os)=d₁(m) the values of these energies are highly close for (Cl₃-OS ion)-interaction. The same takes place for (Cl₃-Cl₃)-interaction at d(l)=d₁(m). And for the (C₃⁻· M₂X⁺) structure in the latter variant the values of the second parameter, i.e. d(os), are the closest to the experimental ones.

These findings allows to suggest that within the given model the formation of the melt structure is controlled either by (Cl₃-Cl₃)-interaction or by (Cl₃-OS ion)-bond. Selection between the possibilities (or joining them into a more complex model) requires further calculations.

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