Model of Sodium Chloride Premelting

Vyacheslav G. Kremenetsky, Vladimir V. Sidelnikov, and Sergey A. Kuznetsov

Institute of Chemistry, Kola Science Centre RAS, 14 Fersman Str., Apatity, Murmansk Region, 184209, Russia

Reprint requests to Prof. S. A. K.; Fax: +7 81555 61658; E-mail: kuznet@chemy.kolasc.net.ru

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A model for the premelting of alkali chlorides is proposed. It is shown that diminishing of the free length of phonons under temperature increase may bring about the instability of the crystal lattice near the melting point. A probable structure of a lattice near this temperature been examined.

Key words: Alkali Chlorides; Premelting Anomalies; Clusters.

As is known, a number of physicochemical properties of alkali chlorides varies anomalously when reaching the melting point from below. In particular, there occurs an abnormal increase of the lattice constant and heat conductivity [1 – 3]. Nowadays, the opinions still differ as to what causes this abnormal behaviour. This work suggests an approach to explain these anomalies, taking into account some features of the crystal lattice NaCl.

Our model is based on the following facts. First, it is known that the free length of phonons, Λ, is about 1 nm [4, 5]. In particular, for the NaCl crystal the value of Λ decreases from 10 nm at 83 K to 2.3 nm at 273 K. At high temperatures $\Lambda \sim 1/T$, that is, on rising the temperature, the crystal lattice is likely to promote a further Λ decrease. It is necessary to note that the free length of phonons determines the size of that area where the vibrational motion of ions is completely correlated. Third under certain conditions, diminishing of the correlation radius may result in instability of the crystal lattice and its transfer to another state. One of the variants of structural reorganization is, for instance, the occurrence of dissipative cellular structures.

Now let us look at the NaCl-type structure from the crystallochemical viewpoint. It becomes evident that among the clusters consisting of several coordination spheres of an M^+ or X^- central ion, the cubic clusters, limited by the third coordination sphere, are the most interesting ones. Among the particles with the local structure of the NaCl type, these clusters have the minimum charge. For instance, a cluster consisting of the central ion M^+ and its first coordination sphere, i. e. an ($M^+ \cdot 6X^-$) cluster, has a charge of -5. If the second coordination sphere of the M^+ ion is also included, we obtain a cluster ($M^+ \cdot 6X^- \cdot 12M^+$) with the charge of $+7$. By adding sequentially the following coordination spheres, we obtain a series of clusters with summary charges -5, $+7$, -1, $+5$, -19, $+5$, $+17$, -13, $+11$, etc. The minimum charge (-1) belongs to the aforementioned cluster of the ($M^+ \cdot 6X^- \cdot 12M^+ \cdot 8X^-$) composition. Let us designate it as an $M3^-$ cluster. A similar cluster for the central X^- ion has the charge of $+1$, and its composition is ($X^- \cdot 6M^+ \cdot 12X^- \cdot 8M^+$). It is designated as $X3^+$. Both $M3^-$ and $X3^+$ clusters consist of 27 ions.

Existence of stable clusters of another size is less probable, since their formation requires greater energy consumption due to their larger charges.

It is easy to see that the structure of the NaCl type constructed from the $M3^-$ and $X3^+$ cubic clusters is identical to the initial structure. This type of structure has the property of self-similarity. In other words, the ($M3^- \cdot X3^+$) structure is similar to the initial structure of the NaCl type, consisting of M^+ and X^- ions, and formally on this basis it is possible to generate complicated hierarchical structures.

The NaCl crystal lattice parameter, d(s), is 0.282 nm at 298 K. Consequently, the size of the cubic cluster M^+ or X^- has the value $2 \cdot 0.282 \cdot \sqrt{3} = 0.98$ nm. At the melting point of 1043 K, the experimental d(s) value becomes equal to 0.295 nm, with the cluster size increasing to 1.02 nm. It can be assumed that during a temperature rise the path length of phonons becomes closer to the size of the cluster, which makes the crystal lattice unstable. As the result, the structure may break up to a number of M3$^-$ and X3$^+$ "superions". This means that there occurs some cross-disordering of the M3$^-$ and X3$^+$ clusters, which in turn promotes the clusters compression and increases their internal energy. For a limiting case (which is unlikely to arise), that is for isolated clusters, the number of parameters is available in [6]. Note that the described structure defragmentation is a specific way of response for such structures like those of the NaCl type and cannot be considered as the universal mechanism suitable for all types of structures.

As was mentioned before, Λ is in inverse proportion to the temperature [5]. By using the value of Λ at 298 K, it is possible to measure the temperature at which Λ becomes approximately equal to the cluster size: $T = 298 \cdot 2.3/1.00 \approx 685$ K. Here we have used the average size of the cluster parameter, equal to 1.00 nm. So, it can be assumed that temperatures around 700 K generate the processes of crystal lattice decay to fragments consisting of the aforementioned "superions". At this stage, the heating of a crystal lattice is not accompanied by any anomalies. But at the last stage, the mechanism of structure relaxation changes. Namely, clusters of that type, with less stability, are destroyed. More exactly, we have in view the relative stability of not isolated clusters, but structures consisting of one sort of clusters (M3$^-$ or X3$^+$) and additional particles with compositions, discussed in [7]. As it has been shown, the rigidity of such structures is still preserved. Additional particles (let us name them outersphere particles) appear to replace the destroyed clusters and have the composition MCl$_2^-$ (or MCl and Cl$^-$) for structure type (X3$^+$·MCl$_2^-$) and ClM$_2^+$ (or MCl and M$^+$) for the (M3$^-$·ClM$_2^+$) type. Their formation fosters the occurrence of additional freedom degrees.

Our reasons for choosing this initial model structure were as follows. For instance, let us join the M$^+$ and Cl$^-$ ions located in the NaCl-type lattice nodes to M3$^-$ clusters so that the distance d(M-X) between these clusters is the least possible. The only way to achieve it is by translating a cluster in one of the coordinate planes to the distances $\boldsymbol{r} = d(\text{M-X})^{\min} \cdot \boldsymbol{i} \pm 3d(\text{M-X})^{\min} \cdot \boldsymbol{j}$, where $\boldsymbol{i}$ and $\boldsymbol{j}$ are single vectors of axes lying on this plane. The resulting layer will contain clusters of the desired type. In this case the adjacent layer, created in the same manner, will be spontaneously shifted to the crystal lattice parameter d(s). This parameter is equal to the minimal distance between the M$^+$ and Cl$^-$ ions: $d(\text{s}) \equiv d(\text{M-Cl})^{\min}$. In addition to clusters, each layer contains free ions – three for each cluster (Fig. 1). For a structure containing M3$^-$ clusters they are two M$^+$ cations and one Cl$^-$ anion; for a structure with X3$^+$ clusters they are two Cl$^-$ anions and one M$^+$ cation. These ions are located parallel to one of the cluster's ribs (see Fig. 1). In Fig. 1 they separate into two particles, but in first approximation we may consider them as one complex ion ClM$_2^+$ or MCl$_2^-$. The ratio of M3$^-$ clusters and outersphere ClM$_2^+$ ions (or X3$^+$ and MCl$_2^-$) is unity. A structure like this contains the greatest possible share of isolated clusters. Thus, the cluster inside the layer is surrounded by four outersphere ions, whereas between the layers these ions are missing. Clusters located in neighbouring layers are shifted relative to each other.

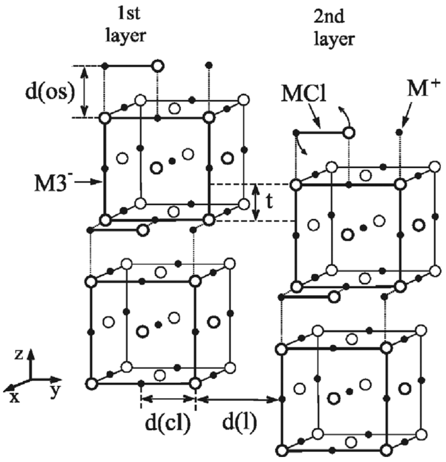

Fig. 1. Model structure (M3$^-$·ClM$_2^+$).

The three parameters of these model structures specified in the figure are distances d(M-Cl): 1) in cluster – d(cl), 2) inside the layer (between the ions of the third coordination sphere of the cluster and outersphere ions) – d(os), and 3) between the layers – $d(1)$. The fourth parameter t characterizes the relative displacement of clusters and does not influence the molar volume.

Calculations were carried out with the use of the computer program ChemObjects (on C++) developed by the authors. The calculation procedure is given in [6, 7]. The geometry of clusters was optimized without accounting for their interactions (isolated clusters) and further did not vary. Thus, our calculation describes a limiting case of weak influence of the environment on the cluster's geometry, which certainly cannot be realized, but allows determining the tendency of structural change. Physically, the disruption of atom movement correlation in adjoining clusters is caused by shortening of the free length of phonons discussed above.

The general conclusions from these calculations are the following. Repulsion of clusters placed into a layer has the minimum value at their relative displacement along the *x*-axis not equal to the lattice parameter $d(\mathrm{s})$ (in this position ions with different charges are opposite), but it is displaced by a small value in comparison with $d(\mathrm{s})$. This displacement can generate the development of dislocations. At the same time, the clusters of neighbouring layers store the relative position which is typical of an ideal crystal lattice. In other words, the viewed model structure is actually not layered. As to the outersphere particles, their positions are capable of changing appreciably, generating dot defects.

In comparison with [6, 7], the calculations in this work were more complicated. Instead of the outersphere particle with rigid bonds, we accounted for a free ion and MCl molecule capable of rotating in space. The total number of parameters optimized was fifteen. As anticipated, the calculated optimal values were somewhat different from those reported in [7]. In the new calculations, $d(\mathrm{os}) = 0.30$ nm, $d(\mathrm{l}) = 0.31$ nm, $t = 0.26$ nm. The $d(\mathrm{cl})$ parameter was the same. Distorted ideal geometry of clusters and changed distances between the adjacent layers, resulting from the structure optimization, led to a spread in values $d(\mathrm{M\text{-}X})$ and $d(\mathrm{s})$. The calculated weighted average value of this parameter $\overline{d(\mathrm{s})}$ is 0.295 nm, precisely coinciding with the experimental $d(\mathrm{s})$ value for the melting temperature [8]. So, the model considered here predicts the correct $d(\mathrm{s})$ value near the melting point.

Increasing the $d(\mathrm{s})$ parameter near T_{melt} leads, in turn, to an increase in the free phonon length, since they are proportional to each other [9]:

$$\Lambda = \frac{d(\mathrm{s})}{\beta\gamma T}, \tag{1}$$

where β is the coefficient of thermal expansion, γ the Grunaizen parameter, and T the temperature. The heat conductivity, δ, is proportional to Λ [9]:

$$\delta = 1/3 \cdot C_v v \Lambda, \tag{2}$$

where C_v is the heat capacity, v the speed of phonons. It should be noted that changes in Λ near T_{melt} are affected not only by the anomalous growth of $d(\mathrm{s})$ but also by the changes in β. Taking into account [10] that

$$\beta = \gamma C_v \chi, \tag{3}$$

where χ is the adiabatic condensability, (1) can be rewritten as:

$$\Lambda = \frac{d(\mathrm{s})}{\gamma^2 C_v T \chi}. \tag{4}$$

As was experimentally established [1], the χ value in the temperature range from $(T_{\mathrm{melt}} - 40)$ to T_{melt} decreases dramatically. In other words, the irregular increase in the heat conductivity is a summary effect of two factors: 1) fast growth of $d(\mathrm{s})$ near T_{melt} (from physical considerations, this growth should have an exponential dependence on temperature), and 2) a decreasing χ value. Apparently, these are the reason for the changes of Λ transformations from monotonous decreasing with temperature growth to an anomalous increase near T_{melt}.

Evidently, a similar structure should be unstable (probably metastable) as it consists of particles with very different compositions and sizes, and even a small rise in temperature (by 4 – 6 K) brings about melting of the crystal lattice of alkali chlorides. But this point needs further consideration.

Thus, the model may explain both the anomalous change of the lattice constant and heat conductivity, and the abnormal increase of vacancies.

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