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Strong hysteresis near solidification points of alkali halides with high ionic-radii ratios

A. Voronel, E. Shasha, D. Linsky, and S. Feldberg
School of Physics and Astronomy, Raymond and Beverly Sackler Faculty of Exact Sciences,
Tel-Aviv University, 69978 Ramat-Aviv, Israel

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A series of conductance measurements of alkali halides NaCl, NaBr, and NaI was performed in a range of 600–1100 K including liquid and solid states for both cooling and heating regimes. The hysteresis phenomenon is observed to be more pronounced for salts with higher ionic-radii ratio (200 K for NaI) with relaxation time exceeding hundreds of hours. At the cooling regime the conductivity drops slowly from a high value typical for liquids at the freezing point to a solid-salt value defined by a Na^+ migration energy at the end of the hysteresis interval instead of an abrupt jump expected at the usual first-order transition. A sort of glassification is assumed to be present at the solidification interval of the salts with high ionic-radii ratios.

Alkali halides are rather simple objects to deal with and seem to have been investigated properly in their both liquid and solid states.[1,2] However, an investigator, who probes deeper may find it interesting to follow the very crystallization process of these interesting substances. Indeed, published data on the resistance of alkali halides[3–5] were obtained by extensive measurements during a heating process within the crystalline state and not in cooling. Single-crystalline samples as a rule were not prepared from a melt but from a solution. That is why published data may be indicative of melting only but not of the crystallization. One will be able further on to see a drastic difference between these two processes depending on the substance and its prehistory.

Our ac measurements[6] were performed in both cooling and heating regimes with a HP LCR meter (0.1–20 kHz frequency region) within a 600–1100 K temperature range. Pt-PtRh thermocouples for temperature and temperature-gradient measurements were used simultaneously as leads for the ac current within the measuring cell. The hermetized cell was surrounded by additional alumina tubes for thermal isolation within a computer-regulated furnace. The size of the liquid sample varied from 0.1 to 1 cm^3 without a noticeable change of the result. Also a change in the arrangement geometry was not reflected in the shapes of the curves or positions of singular points. The temperature stability within the measuring cell was about 0.1 K. The resistance stability at any particular temperature was better than 0.15%. The temperature gradient within the sample never exceeded 1 K.

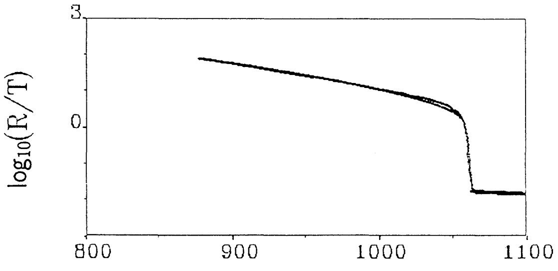

FIG. 1. Temperature dependence of electrical resistance R of NaCl sample (for a temperature cycling rate of 10 K/h). This figure presents two curves: The lower one corresponds to the cooling regime and the higher one to the heating regime. One can see that there is practically no difference between the curves.

Figures 1, 2 (upper part), and 3 present our data[6] for a family of similar salts Na-R, where R is Cl, Br, or I. We have deliberately chosen a family of substances with the same dominating carrier of charge (cation Na^+) to be able to compare the role of their size ratio relative to a larger anion. The logarithmic scale along the vertical axis (impedance of the sample) allows us to see the properties of both the solid and the liquid phases in one graph.

One can immediately notice that, while the cooling curve of NaCl (like that of many other ionic salts with smaller ionic size ratio) basically coincides with the heat-

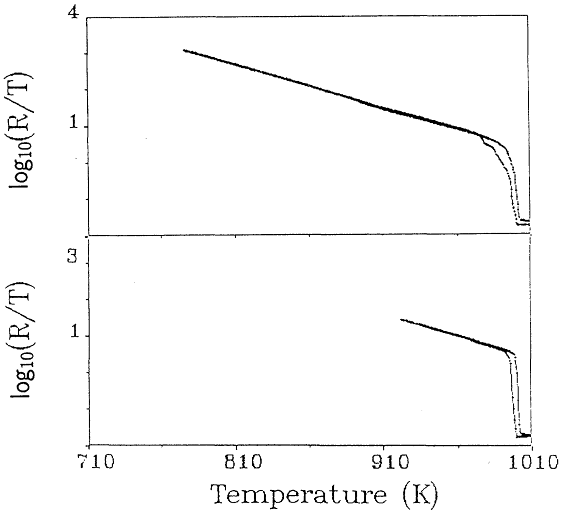

FIG. 2. Temperature dependence of electrical resistance R of NaBr sample (the upper figure corresponds to a temperature cycling of a 10 K/h rate and the lower one to a 1 K/h rate). In both figures the cooling curve is situated below the heating one. One can see a hysteresis of about 20 K in the upper figure and a noticeably smaller in the lower one.

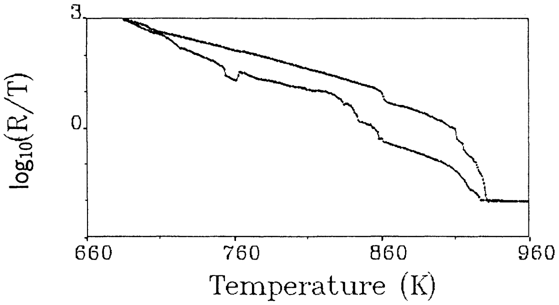

FIG. 3. Temperature dependence of electrical resistance R of NaI sample (for a temperature cycling rate of 10 K/h). The lower curve corresponds to the cooling regime and the higher one to the heating regime. One can see a hysteresis of about 200 K.

ing curve, for NaBr, and even more pronounced for NaI, a strong hysteresis takes place in a temperature range (20 K for NaBr and 200 K for NaI, correspondingly) far wider than any possible experimental uncertainty. Temperature rates here for both cooling and heating were rather slow, 10 K/h. In any case they were considerably slower than those for previously published data.[3–5] Thus one run took no less than a couple of days of continuous measurement. Nevertheless, the curves of Figs. 1, 2 (upper part), and 3 were repeatedly measured many times with different geometries of cells, different arrangements of inserted leads, and different masses of samples. They agree perfectly well, confirming both the persistence (or absence) of the hysteresis and the particular difference between the salts.

In order to understand better the nature of this hysteresis we have slowed the rate down to 1 K/h (10 times).[6] One can only see the result in Fig. 2 (lower part) where the hysteresis for the NaBr salt becomes smaller. This result in principle could be expected if at the slower rate the specimen approaches a more equilibrated behavior.

In drastic contrast to NaBr, for both NaCl (Fig. 1) and NaI (Fig. 3) the results at slower rates remain basically unchanged. Perhaps the reasons for that are the opposite ones for different salts: While for the NaCl the slower rate does not change the sample's quasiequilibrium state all through the interval, for NaI the sample even at the slower rate still is far away from the really quasistatic regime and keeps the NaI system out of equilibrium below its melting point in a sort of metastable state. Since the difference in thermal conductance of these three materials is actually insignificant, one would associate this effect with the nature of a solidification transition and kinetics of the liquid phase in the nearby region.

The ionic radii ratios $r^{>}/r^{<}$ for three salts are roughly equal to 1.8, 2.0, 2.2 consequently. It is interesting to note that a delocalization of smaller particles among a disordered array of larger ones for hard spheres has been predicted by Bosse and Thakur[7] for a radii ratio $r^{>}/r^{<} > 3.5$. The differences between the results displayed in this figure and those for NaI may characterize the deviation of the liquid salt from the hard-sphere model.

The data of Figs. 1, 2 (upper part), and 3 corresponding to the heating regime within the solid phase up to about melting temperature agree well with the data of Refs. 3–5 and expose the results of measurements at 400 Hz frequency. Other frequencies up to 20 kHz were checked as well.[6] This allows one to extract from the impedance a frequency-independent Ohmic resistance in accordance with the standard impedance spectroscopy procedure.[8] The usual interpretation of conductivity of these ionic crystals is based on the idea of the dominating of diffusion of Na^+ ions hopping to vacancies in cation sites created as a result of thermal processes. The theoretical prediction for this kind of conductivity corresponds to an exponential Arrhenius-like formula

$$\frac{R}{T} = A \exp\left(\frac{U}{kT}\right), \tag{1}$$

where R is the sample resistance, A is a constant, and $U = E + \Delta E$, with E being equal to the energy of the vacancy creation and ΔE the migration energy of Na^+. One may find an interval of rather a stable U corresponding to the intrinsic regime expected theoretically.[9] Then the values of activation energy U along the heating regimes in all our three cases are rather close to the data from the literature.[3–5] But the data obtained by the cooling for the NaI samples (Fig. 3) seem to be of a different nature since the activation energy U derived from the cooling curve (Fig. 4) is roughly 2–3 times less and corresponds rather to an energy ΔE of hopping of Na^+ ions through the medium with an unlimited number of vacancies. A more detailed investigation of this interval (Fig. 4) reveals the solidification itself to behave rather like a gradual process spread over an interval of about 200 K than as an abrupt first-order transition. The resistance of liquid grows slowly and at the very beginning of solidification hardly corresponds to the expected exponential formula. Thus it looks like an excess of vacancies from the liquid state being arrested by a slow kinetics nearby the freezing region prevents the system from a complete ordering. For a large vacancy concentration one cannot be sure in the conductivity mechanism since even the very distinction between the Schottky and Frenkel

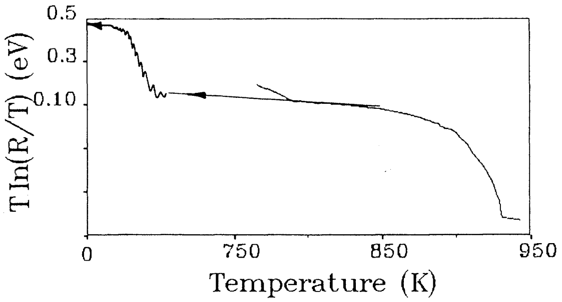

FIG. 4. Activation energy of NaI sample (for cooling with a 1 K/h rate). The interpretation of this curve is as follows. If one accepts the Arrhenius equation [Eq. (1)], then $T\ln(\frac{R}{T}) = T\ln(A) + U$. Assuming that A is constant, then the intersection of the cooling curve with the Y axis at T=0 will give the activation energy U (arrow indicates an extrapolation from a linear part of the curve).

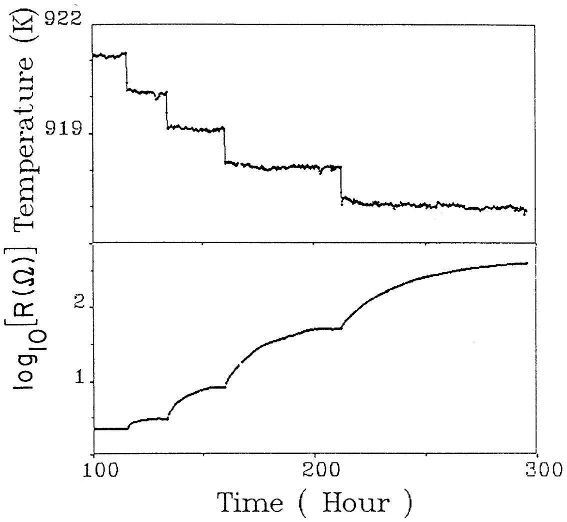

FIG. 5. Temperature (upper part) and $\ln(R)$ (lower part) vs time for NaI sample. One can see that while the temperature has been quickly established the resistance relaxation time is much longer and tremendously increases with decreasing temperature.

TABLE I. Macroscopic relaxation time of NaI.[a]

Temperature (K) ±0.1 K	τ (h)
920.1	3 ± 0.5
919.15	7 ± 1
918.1	15 ± 1
917	28 ± 2

[a] The relaxation time (from Fig. 5) was evaluated using the equation $\ln(\frac{R}{R_0}) = A(1 - e^{-\frac{t-t_0}{\tau}})$, where R is the resistance, $A = \ln \frac{R_\infty}{R_0}$, τ is the relaxation time, and t is the time.

defects is not grounded in such a state. However, an activation energy U=0.45 eV, which one may derive from a low-temperature interval of this intermediate state, fits very well to the migration energy ΔE of this salt known from the literature.[4] This probably suggests a presence of an abnormally high concentration of vacancies in the metastable state obtained by our cooling process.

Thus the conductivity of NaI in the cooling regime near its solidification seems to gradually decrease from its high value in liquid to its extremely low value in solid along an extended range of temperatures in a way rather more typical for a second-order transition than for the usual crystallization. The system seems to achieve its genuine crystalline state at a much lower temperature by an irregular series of jumps (see Fig. 3).

Since the size ratio plays a decisive role here, one can probably find in this experiment a clue to better understanding of solid electrolytes behavior, which usually exhibits close values for their activation energies U. Analogous measurements on AgBr and AgI and corresponding computer simulations are in progress now.

We have also performed (for NaI) preliminary measurements of macroscopic relaxation times. In Fig. 5 one can see the resistance of the sample of NaI as a function of time after cooling at 1 K in the vicinity of the transition point. The relaxation time increases about one order of magnitude within an interval of 4 K (see Table I). Meanwhile the equilibration time for the measured temperatures does not exceed tens of minutes. We are going to derive more detailed information about the relaxation phenomena from future dispersion measurements in a wider frequency range.

All these effects persist also in other salts with a close disparity of radii of their ions defining their packing ($NaNO_3$ and many mixtures).

X-ray-scattering, x-ray-absorption fine-structure (XAFS), Brillouin, and Raman-scattering experiments are in progress now to check up our phenomenological results.

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