Comments on a new class of ionic materials*

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(Received 13 June 1975)

We consider the cohesion and electronic structures of a new class of ionic compounds including $Na_2C_{18}H_{36}N_2O_6$ and $NaC_{18}H_{36}N_2O_6I$.

Dye *et al.*[1,2] have recently reported a crystalline salt of the Na anion (Na^-) of the stoichiometry $(NaC)^+$. Na^-, where C stands for the bicyclic polyoxadianine crypt $C_{18}H_{36}N_2O_6$. The Na bound within the crypt to form $(NaC)^+$ and the Na^- are arranged in a typical ionic structure. A series of questions immediately came to mind concerning this interesting compound.

(1) What is the origin of its thermodynamic stability?

(2) What are the low-lying electronic excitations?

(3) How do these affect its electronic properties? We address ourselves briefly to these questions in this note.

The total energy of the crystal per ion pair may be written in a very crude approximation as:

$$E_{\mathrm{TOT}} = I - A - E_{\mathrm{crypt}} - E_{\mathrm{pol}} - E_{\mathrm{MAD}} + E_{\mathrm{S.R}} \ , \tag{1}$$

where I and A are the ionization energy and electron affinity of Na, E_{crypt} is the binding energy of Na^+ to the crypt molecule, E_{pol} is the sum of the polarization energies of the two ions, E_{MAD} is the Madelung energy, and $E_{\mathrm{S.R.}}$ other short-range contributions to the cohesive energy. For Na, $I = 5.19$ eV and $A = 0.54$ eV.[3] The Madelung energy may be very crudely estimated as 3.1 eV as follows. The Na^+–Na^- nn separation is 7.1 Å. The coordination is six-fold as in the NaCl structure. However, the Na^-–Na^- distance is[2] 8.8 Å compared with the 10 Å expected for the NaCl structure. We have therefore reduced the 4 eV expected for an NaCl structure to 3.1 eV on the basis of the changes in the next nearest neighbor contributions to E_{MAD}, giving

$$I - A + E_{\mathrm{MAD}} \cong -1.5 \text{ eV} \ . \tag{2a}$$

We can estimate $E_{\mathrm{S.R.}}$ as follows. The first three terms in (1) are independent of the lattice constant Na^+–Na^-. E_{MAD} scales as a^{-1}. E_{pol} scales as a^{-4}. The equilibrium condition $\partial E_{\mathrm{TOT}}/\partial a = 0$ permits us to relate $E_{\mathrm{S.R.}}$ to E_{MAD} and E_{pol} if we suppose E_{SR} to scale as a^{-n}:

$$E_{\mathrm{S.R}} = (1/n)E_{\mathrm{MAD}} + (4/n)E_{\mathrm{pol}} \ . \tag{2b}$$

For the alkali halides, the elastic constants indicate that n should be about 10. For the present material, in which the separations are large, we can expect n to be significantly larger, and we select 20. We obtain

$$E_{\mathrm{TOT}} = -(E_{\mathrm{crypt}} + 0.8\, E_{\mathrm{pol}} - 1.4 \text{ eV}) \ . \tag{2c}$$

There are two possible charge transfer processes:

$$(NaC)^+ + Na^- \rightleftharpoons NaC + Na \tag{3}$$

$$(NaC)^+ + Na^- \rightleftharpoons (NaC)^- + Na^+ \ . \tag{4}$$

In (3) recombination takes place, leaving neutral entities on each sublattice. This involves a one-electron transfer from Na^- to $(NaC)^+$. In (4) two electrons are transferred from Na to NaC^+ via a Coulomb and exchange interaction or via a two-step process with (3) as the intermediate state. Both excitation mechanisms lead to "conduction" and "valence" bands separated by a band gap. Equation (3) corresponds to a hole in the valence band on the Na^- sublattice and an electron in the conduction band on the $(NaC)^+$ sublattice. Equation (4) corresponds to a novel two-electron excitation moving on the $(NaC)^+$ sublattice.

For Eq. (3), the band gap would be, approximately,

$$\Delta E_3 \cong A - I + \Delta E_{\mathrm{crypt}} + E_{\mathrm{pol}} + E_{\mathrm{MAD}} \ . \tag{5}$$

For simplicity, we shall assume that the change in the energy of interaction between Na and crypt upon transferring the electron is equal to the binding energy E_{crypt}, leaving

$$\Delta E_3 \cong E_{\mathrm{crypt}} + E_{\mathrm{pol}} - 1.5 \text{ eV} \ . \tag{6}$$

Correspondingly, for Eq. (4), the gap would be

$$\Delta E_4 \cong E_{\mathrm{crypt}'} + \Delta E_{\mathrm{pol}} + 2\,E_{\mathrm{MAD}} \ , \tag{7}$$

where $E_{\mathrm{crypt}'}$ and ΔE_{pol} are the change in the interaction of the crypt with the enclosed ion and the change in the polarization energy, respectively. Supposing that Na^- would be weakly bound within the crypt and ignoring the changes in polarization energy leads to

$$\Delta E_4 \cong E_{\mathrm{crypt}} + 6.2 \text{ eV} \ . \tag{8}$$

Comparing (6) and (8) shows that

$$\Delta E_3 < \Delta E_4 \quad \text{if } E_{\mathrm{pol}} < 7.7 \text{ eV} \ . \tag{9}$$

Since polarization energies can hardly be expected to exceed 4 eV, it seems highly probable that the thermally generated excitations important for conductivity are holes in the Na^- "valence" band and electrons in the $(NaC)^+$ "conduction" band, with a band gap given approximately by (6).

The resistivity is $5\times10^{13}\,\Omega$ cm at 275 K and $7\times10^{9}\,\Omega$ cm at 335 K.[1] Ignoring any preexponential temperature dependence and supposing the activation energy to be temperature independent yields a value of 1.2 eV for the latter. As a decrease in activation energy would increase the rate of change of resistivity with temperature, 1.2 eV must be regarded as an upper limit. This activation energy E_a contains two parts,

$$E_a = E_\mu + \tfrac{1}{2}E_g\,, \qquad (10)$$

where E_μ is the mobility activation energy and E_g is the band gap, which we have identified with ΔE_3. Comparing (10) with (6) gives us

$$\begin{aligned} E_g &\cong 2E_a - E_\mu = 2.4\text{ eV} - E_\mu \\ &\cong E_{\text{crypt}} + E_{\text{pol}} - 1.5\text{ eV} \end{aligned}$$

or

$$E_{\text{crypt}} + E_{\text{pol}} = 3.9\text{ eV} - E_\mu\ . \qquad (11)$$

Because E_μ originates in part from the distortion of the crypt in bonding Na^+ and in part from the distortions attendant to the loss of polarization energy, we can make a very rough estimate of E_μ as

$$E_\mu \simeq \xi(E_{\text{crypt}} + E_{\text{pol}}) \qquad (12)$$

with $\xi \lesssim \frac{1}{2}$, giving

$$\begin{aligned} &E_{\text{crypt}} + E_{\text{pol}} \simeq 2.6\text{–}3.9\text{ eV}\,, \\ &E_\mu \simeq 1.3\text{–}0\text{ eV}\,, \qquad (13) \\ &E_g \simeq 1.1\text{–}2.4\text{ eV}\,. \end{aligned}$$

Equation (13) must be regarded as only schematic.

Two other striking observations can be understood crudely within the above picture. First, the crystals appear gold at −190 °C, bronze at 40 °C, and brown at 83 °C.[1] Our picture would explain the observed color at −190 °C if the gap were close to its upper limit, $E_g \simeq 2.4$ eV, $E_\mu \ll E_g$. The change to bronze and then brown can be attributed to band tailing associated with small polaron and exciton effects, which we discuss below. Secondly, the observed decomposition[1] of the material at 83 °C can be understood by comparing the value of E_{TOT} from (2) and our estimated value of $E_{\text{crypt}} + E_{\text{pol}} \simeq 3.9$ eV with the cohesive energy of Na and crypt. The resulting value of E_{TOT} is $-2.4\text{ eV} + E_{\text{S.R.}}$. The cohesive energy of Na for 2 atoms is 2.3 eV. The difference, ΔH, between the cohesive energy of the solid compound and its constituents is

$$\begin{aligned} \Delta H &\simeq 2.3\text{ eV} + E^c_{\text{crypt}} - 2.4\text{ eV} + E_{\text{S.R.}} \\ &\simeq 0.1 + E^c_{\text{crypt}} + E_{\text{S.R.}}\,, \end{aligned} \qquad (14)$$

where E^c_{crypt} is the cohesive energy of crypt. From (2b) and (2c) we can estimate that $E_{\text{S.R.}} \sim 0.3$ eV so that

$$\Delta H \simeq E^c_{\text{crypt}} + 0.2\text{ eV} \simeq 0.4\text{ eV}\ . \qquad (15)$$

We see that these rough estimates of the cohesive energy of the compound and of its constituents differ by 0.4 eV. The latter is too small to be taken seriously, given the roughness of our estimates. Nevertheless, it indicates the relative instability of the compound, as observed.

We now consider the characteristics of the conduction band. We note that effective masses at the bottom of the conduction bands of related insulators such as alkali halides,[4] rare gas solids,[4,5] and simple molecular crystals[6] (H_2, CF_4, etc.) fall in the range 0.2–0.5. The reason for these low values is that conduction electrons are excluded from a substantial part of the space within the material by Madelung potentials, repulsive pseudopotentials, or both. The same factors operate in the present case so that we can anticipate a value of m^* as low as 0.1 to 0.2. For the above materials the width ΔE_c of the conduction band is well estimated by the formula

$$\Delta E_c \simeq \hbar^2/2ma^2\,, \qquad (16)$$

where a is the lattice constant. Equation (16) gives results in agreement with those of band structure calculations and photoemission measurements[4] on the alkali halides and solid rare gases. Accordingly, we use it in the present case and obtain a width of 0.6–0.8 eV for the conduction band.

There is an appreciable configurational change inside the crypt upon the incorporation of the Na^+ ion. We should expect corresponding configurational changes between (Na^0C) and (Na^+C). Together with the relatively small bandwidth obtained above, these configurational changes should give rise to significant polaron effects[8] on the conduction band: (a) The conduction bandwidth will be narrowed. (b) Interband transitions will be smeared out due to vibrational overlap effects, possibly accounting for the color changes observed upon heating. (c) Vibrational structure of molecular type can appear in the optical spectrum if the coupling is strong enough. Mobility determinations are required for an assessment of the role of polaron effects.

Excitons occur in the alkali halides.[4] They will probably also occur in these materials below the interband transition. The extent to which they give rise to sharp peaks in the absorption spectrum depends on how strong the polaron effects are. While consideration of the color and stability of the crystals militate against a large mobility activation energy, it is still too early to assess the polaron effects.

Similar considerations can be applied to other ionic solids of this class. For example, $(\text{NaC})^+\text{I}^-$ has roughly equal placement of atoms.[9] The electron affinity of the iodine atom[10] is $A = 3.1$ eV so that

$$E_{\text{TOT}} = -1.0 - E_{\text{crypt}} - E_{\text{pol}} + E_{\text{S.R.}} \qquad (17)$$

and

$$\Delta E_3 = +1.0\text{ eV} + E_{\text{crypt}} + E_{\text{pol}}\ . \qquad (18)$$

Using the upper limit of our estimate for $E_{\text{crypt}} + E_{\text{pol}}$, 3.9 eV, gives

$$E_{\text{TOT}} = -4.9\text{ eV} + E_{\text{S.R.}} \qquad (19)$$

and, more interestingly,

$$E_g \cong 4.9\text{ eV}\ . \qquad (20)$$

Thus, the interband transition should be located in the near uv somewhere around 2500–3000 Å. Exciton states are likelier to be exhibited; if so, they should reveal the halogen doublet (two excitations split by $\xi = 0.9$ eV for 1).[3] The exciton binding energy should be less than in the alkali halides,[4] where it is less than ξ. Thus, the first component should be a stable, bound exciton, whereas the second should be metastable, in resonance with interband transitions.

These considerations should apply as well to many ionic crystals containing relatively large organic donors and organic or inorganic acceptors.[11]

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*Supported by the L. Block Fund and the Materials Research Laboratory of the National Science Foundation at The University of Chicago; by the U. S.-Israel Binational Science Foundation at Tel-Aviv University; and by the R. A. Welch Foundation and the NSF at the University of Texas.

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