Is it possible to make materials with ionic superconductivity?

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Abstract

The basic idea is that we try to find some materials in which bosonic ions with sufficiently small *effective mass* are used as charge carriers instead of Cooper's pairs in order to provide high temperature *ionic* superconductivity.

Among single-charged ions comprising ionic crystals only lithium isotope Li^6 can be used for that purpose. Thus, we consider Li^6Cl, Li^6F, Li^6Br and Li^6I ionic crystals. Assuming that all interactions of lithium ions in crystalline lattice can be described by suitable periodic potential the corresponding Schrödinger equation can be solved using well-known tight-binding approximation. The form of molecular potential used in the calculations is fitted to experimental molecular dissociation energies, as well as their size and elastic properties of ionic crystals.

The results show that Bose-condensation temperature for Li^6-ions is of the order of $10^{-34} \div 10^{-43}$K in all crystals. If, however, the crystal is compressed so that the wave functions of neighboring lithium ions are sufficiently overlapped, then Bose-condensation temperature of Li^6-ions can be increased significantly. Our estimates show that compressing the crystals by 20-22% in all three directions one can rise the Bose-condensation temperature in all crystals considered to *above room temperature*.

Taking into account the well-developed semiconductor heteroepitaxial technologies this high compression (in two dimensions) can be accomplished in practice by MBE-growing the short-period strained-lattice superlattices from very thin (several monolayers) layers of corresponding ionic crystal interdisposed by relatively thick layers of thoughtfully-chosen solid alloys.

Introduction

Ionic crystals, i.e. crystals formed from positive and negative ions, are widely known. As a rule, they are dielectrics due to large electronic band gap and absence of free carriers in the conduction band so that all electronic states in the valence band are occupied almost at all temperatures up to the melting point [1]. Consider, for example, ionic crystals LiF, LiCl, LiBr and LiI with NaCl crystal structure. Obviously, the distribution of lithium ions in the crystal lattice can be described by Schrödinger equation with appropriate translational symmetry. Since the mass of lithium ion is less than that of ions of fluorine, chlorine, bromine and iodine we can write for the lithium ion wave function $\psi(\vec{r})$

$$H\psi(\vec{r}) = E\psi(\vec{r}) \qquad (1)$$

$$H = -(\hbar^2/2m)\Delta + U(\vec{r}) \qquad (2)$$

$$U(\vec{r}) = U(\vec{r}+\vec{n}) \qquad (3)$$

where $\vec{n}$ is translation vector

$$\vec{n} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 \qquad (4)$$

Here, n_1,n_2,n_3 are positive or negative integers, $\vec{a}_1,\vec{a}_2,\vec{a}_3$ are three independent lattice translations,

$\hat{H}$ -is the Hamiltonian with $\Delta = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$, $\hbar$ - is Planck's constant divided by 2π, m is the mass of lithium ion, and $U(\vec{r})$ is potential energy of the ion in the crystal.

Eq.(1) differs from well-known equation for electrons in a periodic potential only by the mass of the particle considered (see, e.g. [2]).As a consequence, one can conclude that ion energy in ionic crystals is a function of wave vector $\vec{k}$ and solutions for real-valued ion eigenenergies exist only for specific energy intervals. In other words there is the ionic energy band structure. The wave-like ionic conductivity, however, is absent in

the known ionic crystals like LiF, LiCl, LiBr and LiI. Using band-structure language, it means that all states in the lower (ionic valence) band are occupied and (ionic) energy band gap is very large. According to Pauli's exclusion principle the redistribution of ions in ionic valence band upon available energy and momentum states is impossible, since no one ion is allowed to take the state occupied by another ion.

It may be of interest to consider a natural question: "Why the wave-like ionic conductivity is absent in common ionic crystals?" Since there is spin - degeneracy for Li^7 ions the number of available states in ionic valence band must be much higher than ion number density. The absence of wave-like ionic conductivity is then possible only if the spin-degeneracy is some how removed. It is easy to see , however, that only one spin state is energetically favorable for ions in ionic crystals. Indeed, in Heisenberg approximation (used in treatments of ferromagnetism) it has been shown that for a system consisting of two atoms or ions the energy change due to spin moment reversal is given by

$$U_{exs} = -2A(\vec{S}_i \vec{S}_j) \tag{5}$$

where U_{exs} is the exchange energy and $\vec{S}_i, \vec{S}_j$ are the spin moments of interacting atoms. All known calculations of exchange integral (A) indicate that it has a positive sign (the only exception being exchange interaction between the atoms with incompletely filled internal electronic shells) and the magnitude of A is about several eV. Under these circumstances the antiparallel spin orientation of lithium and halogen ions will provide the minimum of the system energy and the difference of exchange energy due to spin change by 1 for any ion in the pair will be

$$2A(\vec{S}_i \vec{S}_j - A(\vec{S}_i (\vec{S}_j - \vec{1})) \gg .kT \tag{6}$$

Then all lithium ions in the crystal (or it's part) are forced to have the same spin value, corresponding to the minimum of system energy. That is almost equivalent to completely filled ionic valence band. In our opinion, this is a reason for absence of wave-like ionic conductivity in common ionic crystals. Another reason, however, can be a small ionic wave function overlap in those crystals.

Returning now to the main theme one should mention that Pauli principle is applicable only to particles with half-integer spin. If the ion has integer spin then the redistribution of ions over available energy and momentum states will occur even in completely filled band upon application of electric field, i.e. ionic conductivity is possible. It is well-known that the ion is a "bose-particle" if the sum of electrons, neutrons and protons , comprising the ion, is even, otherwise the ion is a fermion [3]. Note, that naturally-occurring crystals are constructed from single-charge fermionic ions the only exception being the ion of lithium isotope Li^6, which consists of 3 neutrons, 3 protons and 2 electrons.

Now we would like to estimate the main characteristics of interest foe ionic crystals Li^6F, Li^6Cl, Li^6Br and Li^6I using tight-binding approximation (an analysis is quite similar to that for electrons [1]). Let the Hamiltonian of lithium ion in a molecule be

$$H_i = -(\hbar^2 / 2m)\Delta + U_i(\vec{r}) \tag{7}$$

In that case we can take (as a zero order approximation) the linear combination of eigenfunctions of the Hamiltonian

$$H_i \psi(\vec{r}) = E_i \psi(\vec{r}) \tag{8}$$

satisfying the Bloch theorem with amplitude possessing the translation invariance of the lattice

$$\psi(\vec{r}) = \sum_{\vec{l}} e^{2\pi \vec{k} \vec{l}} \psi(\vec{r} - \vec{l}) \tag{9}$$

where $\psi(\vec{r} - \vec{l})$ is an eigenfunctions of H_i operator for lithium ion and $\vec{l}$ is the vector of the lattice site occupied by negative ion.

Denoting by $U_k(\vec{r}) - U_i(\vec{r})$ the difference of potentials seen by lithium ion in the crystal and in the molecule (which is supposed to be formed from positive lithium ion and negative halogen ion) we obtain as a first approximation for ion energy in the crystal

$$E(\vec{k}) = E_i - \sum E(\vec{l}) e^{2\pi \vec{k} \vec{l}} \tag{10}$$

$$E(\vec{l}) = -\int \psi_i^*(\vec{r} + \vec{l})\{U_k(\vec{r}) - U_i(\vec{r})\}\psi_i(\vec{r})d\vec{r} \tag{11}$$

intgration being performed over crystal volume $E(100) = -\int \psi_i^*(\vec{r}+\vec{a})\{U_k(\vec{r})-U_i(\vec{r})\}\psi_i(\vec{r})d\vec{r}$

$$(7)$$

Here, k_1, k_2, k_3 are wave vector projections on different crystallographic axes, a is lattice constant and ψ_i is normalized Li^6 ion wavefunction.

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Taking into account only nearest-neighbor interaction in NaCl-type lattice we have

$$E(\vec{k}) = E(k_1, k_2, k_3) = E_i - E(0) + 2E(100)\{\cos ak_1 + \cos ak_2 + \cos ak_3\} \tag{12}$$

$$E(0) = -\int \psi_i^*(\vec{r})\{U_k(\vec{r})-U_i(\vec{r})\}\psi_i(\vec{r})d\vec{r} \tag{13}$$

$$E(100) = -\int \psi_i^*(\vec{r}+\vec{a})\{U_k(\vec{r})-U_i(\vec{r})\}\psi_i(\vec{r})d\vec{r} \tag{14}$$

where k_1, k_2, k_3 are wave vector projections on crystallographic axes (x,y,z) and a is lattice constant.

For calculation of Li^6 ion effective mass we can use a well-known (in tight-binding approximation) expression

$$m^* = \frac{\hbar^2}{2E(100)a^2} \tag{15}$$

If we choose the molecular potential in the form

$$U_i(r) = -\frac{q^2}{4\pi\varepsilon_0 r} + \lambda\exp(-\frac{r}{\rho}) \tag{16}$$

and calculate the λ and ρ parameters according to [1], then we obtain from (16) potential curves shown in Fig.1.
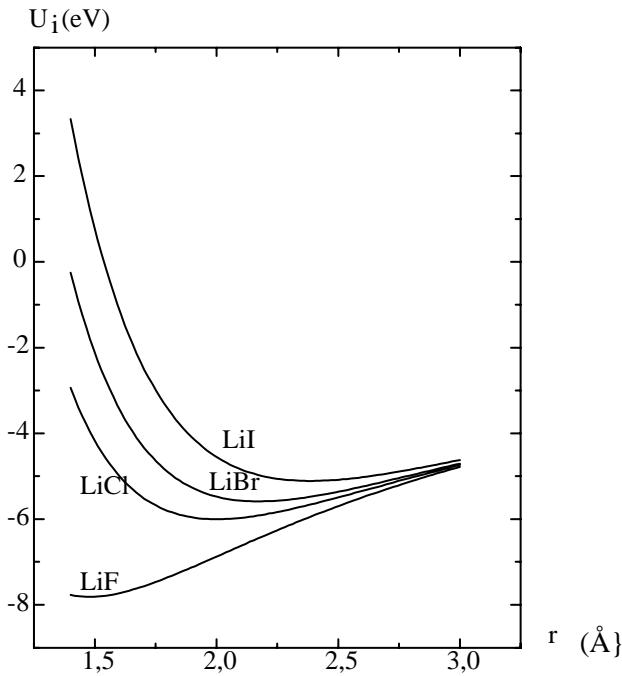

Fig.1. Potential curves for lithium ion in the molecules calculated from eq.(16)

Since minima of potential curves (E_{min}) differ from observed dissociation energies the molecular potential should be refined

$$U_i(r) = -\frac{q^2}{4\pi\varepsilon_0(r-\Delta r)} + \lambda\exp(-\frac{r-\Delta r}{\rho}) + C$$

$C=0$ when $r>r_c$, $C=\Delta U=E_d-E_{min}$, when $r<r_m$, , $C=0,5\Delta U(1+cos[\pi(r-r_m)/(r_c-r_m)])$ when $r_c>r>r_m$

$\Delta r=0$ when $r>r_c$, , $\Delta r =r_m-r_r$, when $r<r_m$, , $\Delta r =0,5(r_m-r_r) (1+cos[\pi(r-r_m)/(r_c-r_m)])$ when $r_c>r>r_m$

Lattice constants ($r_c=a/2$) and parameters λ u ρ are given in [1], inter-ion distances in molecules and their dissociation energies into atoms can be taken from [4] and electron affinity of halogens and lithium ionization potential from [5].

Table 1. Parameters used for the calculation of molecular potential

| material	$a/2$ lattice constant Å	r_m molecular size Å	ΔE difference between halogen electron affinity and lithium ionization potential eV	E_{da} Dissociation energy of the molecule into atoms eV	λ eV	$E_d=E_{da}+\Delta E$ Dissociation energy of the molecule into ions eV	r_r Calculated inter-ion distance in the molecule according to (16) Å	ρ Å	E_{min} eV
LiF	2,014	1,564	-1,9	6,0	308,3	-7,9	1,48	0,291	-7,814
LiCl	2,570	2,021	-1,6	4,8	510,4	-6,4	2,002	0,330	-6,003
LiBr	2,751	2,170	-1,9	4,4	615,6	-5,9	2,168	0,340	-5,589
LiI	3,000	2,392	- 2,2	3,6	624	-5,8	2,39	0,366	-5,109
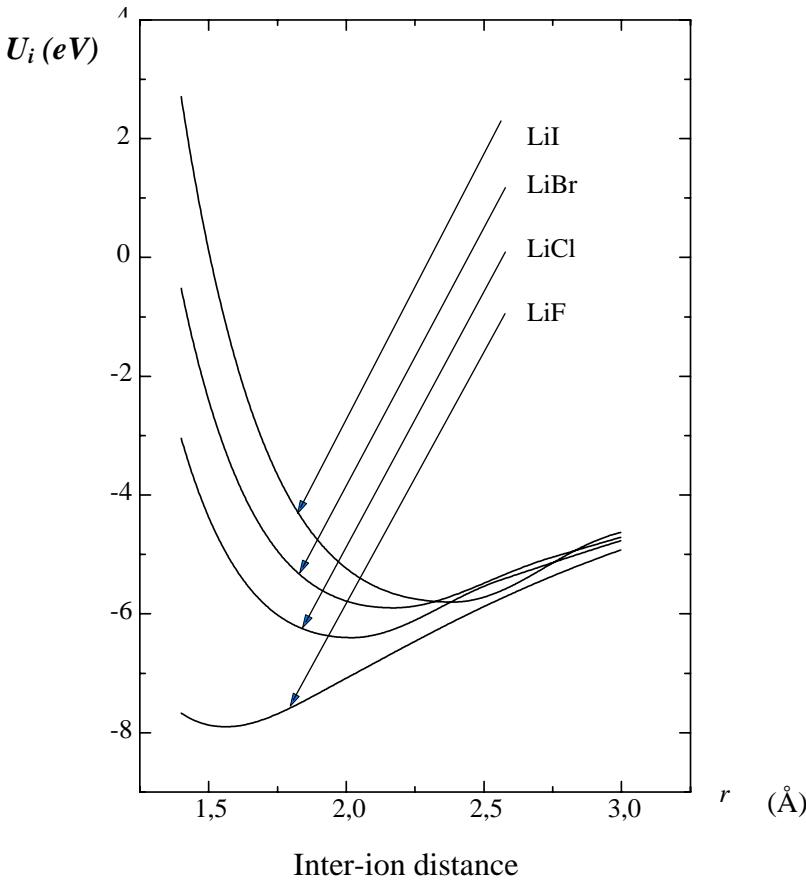
Fig.2. Refined potential for lithium ion in LiF, LiCl, LiBr and LiI molecules

Calculation of molecular wave functions

For the ground state the lithium ion wavefunction in a molecule $\psi(r)$ is spherically symmetric and can be found from corresponding Schrödinger equation

$$\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r} + (E - U_i(r))\psi = 0 \tag{17}$$

where

$$U_i(r) = -\frac{q^2}{4\pi\varepsilon_0(r - \Delta r)} + \lambda\exp(-\frac{r - \Delta r}{\rho}) + C \tag{18}$$

The influence of a mass of an ion of halogen (M_h) on calculated values in further is taken into account, by replacement in (17) m on $mM_h/(m+M_h)$.

For numerical solution we used the following conditions

$$\psi(r) = 1 \text{ when } r = r_m \tag{19}$$
$$\psi(r) = 0 \text{ when } r = 0 \tag{20}$$
$$\psi(r) = 0 \text{ when } r = a = 2r_c \tag{21}$$
$$E = E_d \tag{22}$$

The results obtained are shown in Fig.3.

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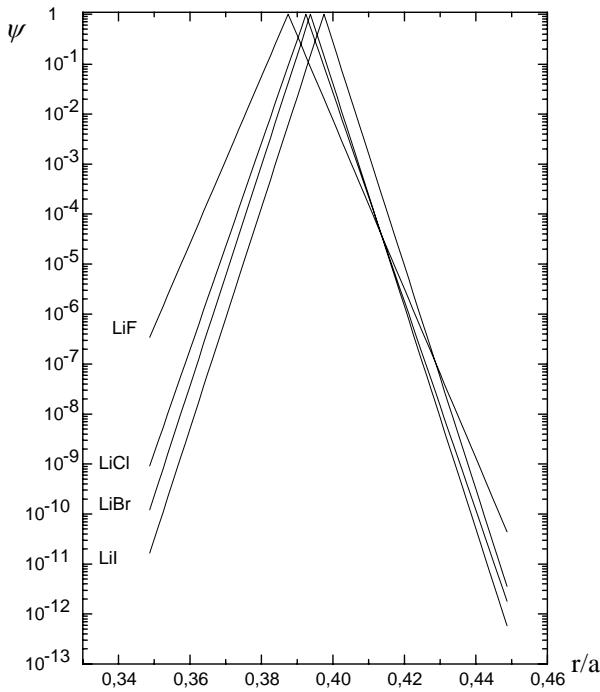
Fig.3. Lithium ion wavefunctions

The normalized wavefunctions can be expressed as

$$\psi_i = \psi / \sqrt{\int 4\pi r^2 \psi^2(r) dr} \qquad (23)$$

and are shown in Fig.4.
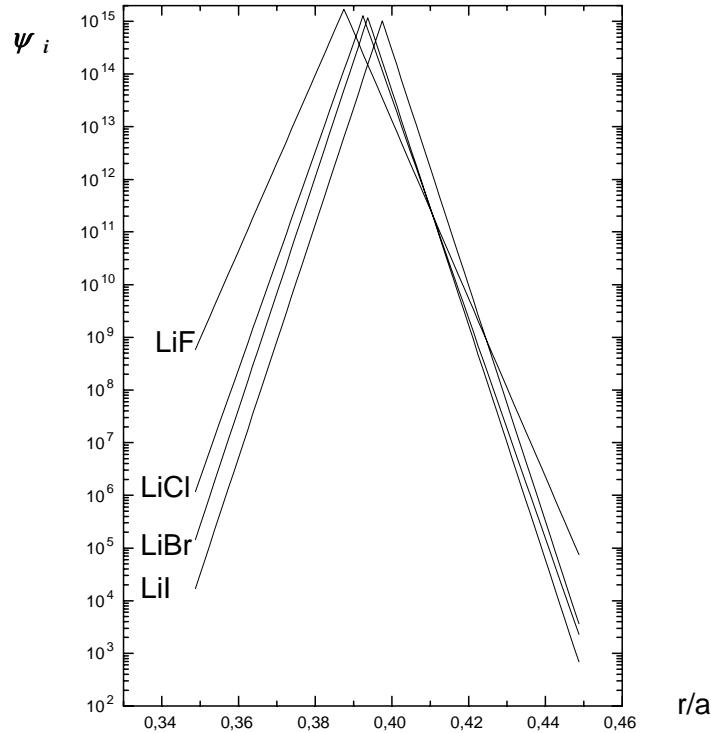
Fig.4. Normalized wavefunctions of lithium ion in LiF, LiCl, LiBr and LiI molecules.

Also from (14) we have

$$E(100) \approx -\int \psi_i^*(r+a)\left\{U_k\left(\frac{a}{2}\right)-U_i\left(\frac{a}{2}\right)\right\}\psi_i(r)dr \qquad (24)$$

Inserting the ground state wavefunction into (30) one can calculate the exchange integral $E(100)$ and then the effective mass of lithium ion from (15). Finally, the temperature of Bose-condensation (T_b) can be estimated [6] from

$$T_b = \frac{2\pi\hbar^2}{m^* k_B}\left(\frac{N}{2.612\times V}\right)^{\frac{2}{3}} = \frac{2\pi\hbar^2}{m^* k_B}\left(\frac{0.5}{2.612\times\left(\frac{a}{2}\right)^3}\right)^{\frac{2}{3}} \qquad (25)$$

where k_B is Boltsmann constant, N/V is boson number density. Calculated results are presented in Table 2.

Table 2. Estimated Bose-condensation temperature for Li^6 ions in halogenide crystals

Crystal	$U_k(a/2)$ (eV)	$U_i(a/2)$ (eV)	$\dfrac{m}{m_e}$	T_b (K)
Li^{6}F	10,525	7,13	0,13 10^{39}	0,35 10^{-33}
Li^{6}Cl	8,64	5,8	0,1 10^{46}	0,25 10^{-40}
Li^{6}Br	8,24	5,5	0,27 10^{48}	0,8 10^{-43}
Li^{6}I	7,72	5	0,85 10^{46}	0,24 10^{-41}

It should be noted that for these heavy lithium ion's effective masses at any real temperatures all ionic crystals are dielectrics. Indeed, if we assume that in a defect-free ideal crystal the dominant scattering mechanism for Li-ions is scattering by acoustical phonons and take into account that ion's concentration in ionic crystal and electron's concentration in a metal are of the same order of magnitude, and denote the electron effective mass in a metal by m_e, we can estimate the specific resistivity of ionic crystal ρ_c in comparison with that of metal ρ_m as

$$\rho_c = \rho_m\left(\frac{m^*}{m_e}\right)^{\frac{5}{2}} \qquad (26)$$

where $\rho_m = 10^5$ Ohm•cm is a typical metal resistivity. Experimental observation of wave-like ionic conductivity is thus highly problematical since real ionic conductivity in available crystals is completely dominated by defects and is many orders of magnitude higher.

Heterostructures

If, however, the ionic crystal is compressed so that Li wavefunction overlap becomes significant, than Bose-condensation temperature for Li^6 ions can be increased significantly. Denoting by a_s the lattice constant of compressed crystal we can write

$$E(100) \approx -\int \psi_i^*(r+a_s)\left\{U_k\left(\frac{a}{2}\right)-U_i\left(\frac{a}{2}\right)\right\}\psi_i(r)dr \qquad (27)$$

where $U_k\left(\dfrac{a}{2}\right)$ is experimental value of the ion binding energy in a crystal.

Substituting the ground-state wavefunction into (27) one can calculate the exchange integral and estimate the new values for effective mass of Li^6 ions, m^*, and Bose-condensation temperature, T_b,

$$m^* = \frac{\hbar^2}{2E(100)a_s^2} \tag{28}$$

$$T_b = \frac{2\pi\hbar^2}{m^* k_B}\left(\frac{0.5}{2.612\times\left(\dfrac{a_s}{2}\right)^3}\right)^{\frac{2}{3}} \tag{29}$$

The results of these calculations are presented in Fig.5 and Fig.6.
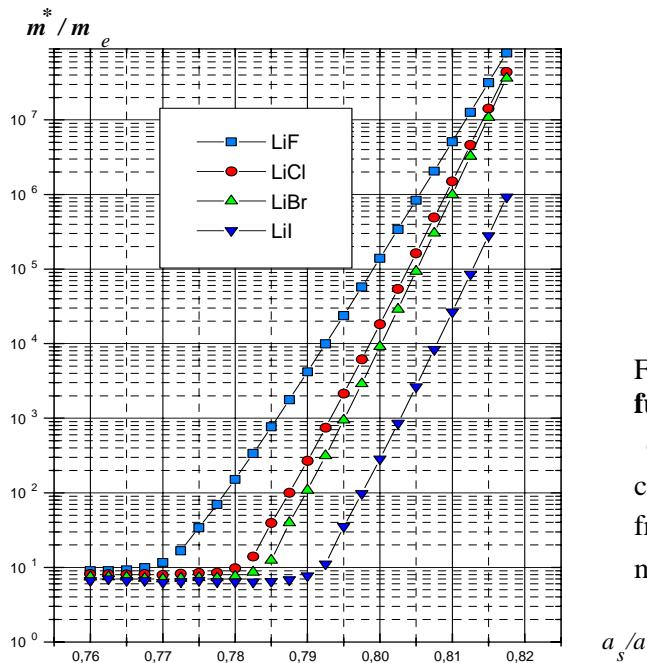
Fig.5. **Effective mass of Li^6 ions as a function of crystal compression.** a_s is the lattice constant of compressed crystal, a is lattice constant of strain-free ionic crystal, m_e is free electron mass.

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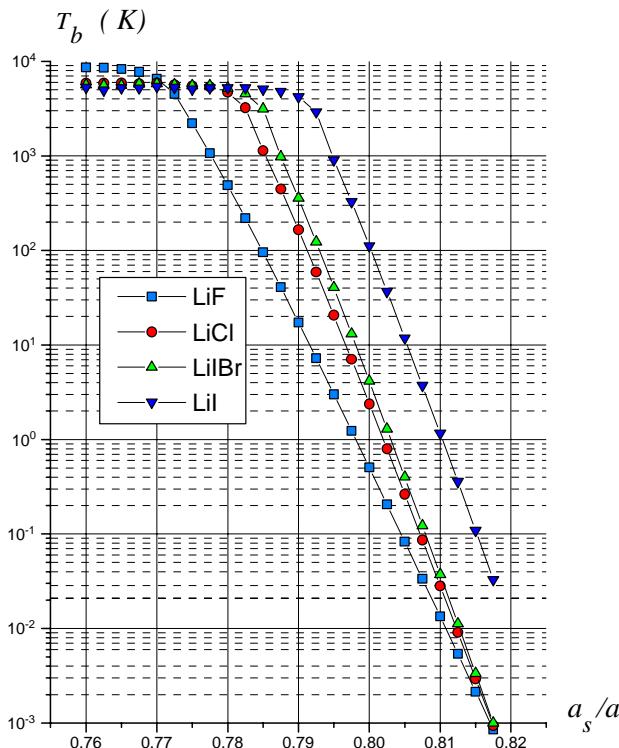
Fig.6. Bose-condensation temperature as a function of crystal compression

Our calculations have shown that in order to make Bose condensation temperature greater than 300K one should compress LiF by 22%, LiCl by 21,3%, LiBr by 21%, LiI by 20,3%. Since exact results are presently unavailable it is difficult to estimate the errors involved due to approximations used in the calculations. However, even if the calculated effective mass of lithium ions is increased by a factor of 25, the Bose condensation temperature of Li ions in crystals compressed by 21-22% is greater than 300K.
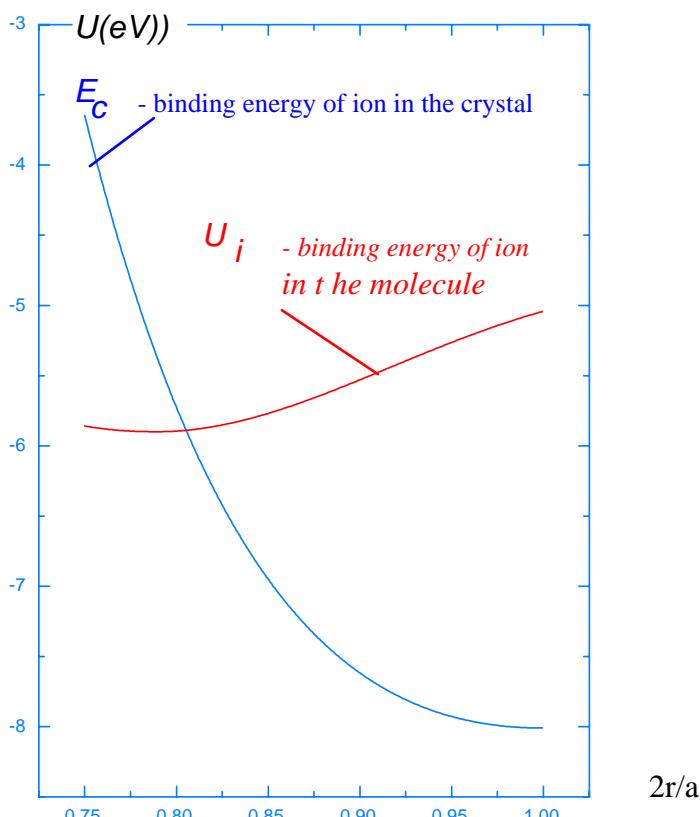
$$U_i(r) = -\frac{q^2}{4\pi\varepsilon_0(r - \Delta r)} + \lambda\exp(-\frac{r - \Delta r}{\rho}\} + C$$

$E_c = -\alpha q^2/4\pi\varepsilon_o r \ (1-(r\rho/r_o^2)\ exp((r_o-r)/\rho))$
$\alpha = 1.748 -$ Madelung constant, $r_o = a/2$.

Fig.6a. Binding energy as a function of distance between Li and Br ions.

These results can be interpreted qualitatively if one notes that in undeformed crystals the binding energy of ion in the crystal is larger than corresponding binding energy of ion in a molecule. Consequently, lithium ions occupy lattice sites. In compressed crystals already at $a_s/a\sim0,8$ the binding energy of ion in the crystal become equal to that in a molecule. Due to absence of potential barrier lithium ions can move through the crystal (see Fig.6a).

It has been amply demonstrated in semiconductor technology that during epitaxial growth of one semiconductor (e.g., Ge) on the substrate of another semiconductor (e.g., Si) the pseudomorphic film can be obtained [7] if the grown film thickness is less than the so called critical thickness (which is about several monolayers for the Ge/Si heterosystem with a lattice mismatch ~ 4%). Often a mixed alloy (Si_xGe_{1-x}) buffer layer is provided on Si substrate in order to reduce the dislocation density [7]. The similar legitimacies are watched at epitaxial cultivation of ionic materials [9].
Epitaxy is greatly assisted by similar structure and chemical bonding in the substrate and overlayer materials. In our case it means that desired compression can be accomplished if the ionic crystal with larger lattice constant is grown pseudomorphically on the substrate from another ionic crystal with smaller lattice period. In fact, a thin working layer can be overgown by a thick layer of substrate material forming thus a double heterostructure (see Fig.7(a)) or even a multi-quantum well structure (Fig.7(b)).

Thin layer (for example, Li^6Cl or $Li^6Cl_y F_{1-y}$) with larger lattice constant

Thick overgrown layer from substrate material		Thick layer from substrate material
		Thick layer from substrate material
		Thick layer from substrate material
Substrate from ionic crystal with smaller lattice constant (e,g, LiF or LiF_xCl_{1-x})		Substrate from ionic crystal with smaller lattice constant (e,g, LiF or LiF_xCl_{1-x})

a)   b)

Fig.7. Possible heterostructures with a thin compressed Li^6-containing ionic layers

In fact, a thin layer of the crystal to be compressed could be patterned (Fig. 8) and overgrown by a thick layer of substrate material. In that case it will be compressed along all three axes. It seems, however, that a thickness of the layer and a pattern pitch (h) should by of the order of several lattice constants.
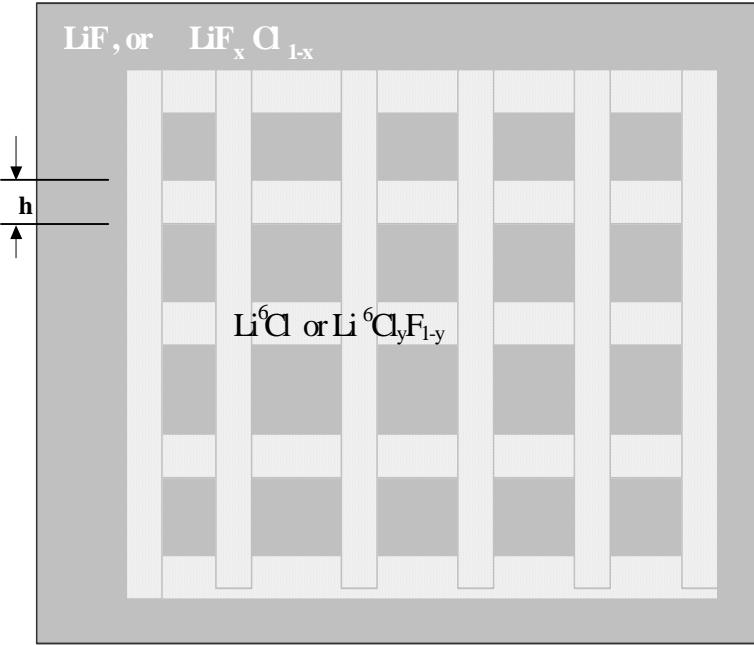
Fig.8. Network of highly compressed patterned Li^6Cl epilayer.

An epitaxial route to highly compressed ionic crystals seems to be worthy to attempt at using, for example, the molecular beam epitaxy. Evidently, very thin layers (in the 2-3 monolayer range) are desirable since compression of thick layers to the targeted 20% is practically impossible. Assuming lattice constant of the compressed crystal is equal to that of the substrate we estimated through (28)-(29) the effective mass of lithium ion and Bose condensation temperature for some combinations. Results are shown in Table 3.

Table 3. Calculated Bose-condensation temperature for epitaxially- compressed ionic crystals

Substrate and thick overlayer material	Thin layer material	Li^6 ion effective mass (m^*/m_e)	Bose-condensation temperature for Li^6 ions	Lattice compression a_s/a
LiF ($a_s/2$=2,014 Å)	Li^6Cl	24	1870	0,784
LiF ($a_s/2$=2,014 Å)	Li^6Br	7,9	5700	0,732
LiF ($a_s/2$=2,014 Å)	Li^6I	8,2	5460	0,671
NaF ($a_s/2$=2,317 Å)	Li^6I	6,5	5250	0,772
LiH ($a_s/2$=2,04 Å)	Li^6Cl	1270	34,5	0,793
LiH ($a_s/2$=2,04 Å)	Li^6Br	8,14	5400	0,741
LiH ($a_s/2$=2,04 Å)	Li^6I	6	5780	0,68

Inspecting Tables 2 and 3 one can state that an attempt to observe the superconductive state in ionic crystals containing Li^6 is completely useless since temperatures involved are less than 10^{-40}K. For compressed crystals, however, the story is different. In layered pseudomorphic structures it is possible to fix the ionic superconductivity at room temperature and even higher (on the premise, of cause, that assumptions involved are valid).

In order to reduce the dislocation density in epilayers it is better to use the solid solutions of ionic crystals. For example, on LiF substrate the layer of $(Li^6Cl)_{1-x}(Li^6F)_x$ could be formed. As to the ionic density, the alloy

$(Li^6Cl)_{1-x}(Li^6F)_x$ film is more and more like LiF with increasing x. And less compression is needed to obtain the targeted overlap of neighboring lithium ions. For $x < 0,5$ the electronic properties of the alloy will not, probably, differ substantially from that of pure Li^6Cl in a sense of wave function overlap between

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neighboring lithium ions. In any case some regions should exist in the compressed film where ionic superconductivity can be observed.

In the crystal lattice each lithium ion is surrounded by 6 halogen ions. To achieve the desired goals it is sufficient to increase the overlap of only two (from 6) molecular wavefunctions and if one is able to produce the ordered solid alloys the composition x can be increased up to 1-1/3=0.67. Presently the experimenters are unable to make such things.

In order to reduce the layer/substrate lattice mismatch the overlayer can be made from solid alloys. As an illustration let us take the following example. In the Li^6I / NaF system the lattice mismatch is about 22,8% ($a_s/a=0,772$). Admixing Li^6F we get the solid solution $(Li^6I)_{1-x}(Li^6F)_x$. For $x < 0,5$ the electronic properties of the alloy will not, probably, differ substantially from that of pure Li^6I in a sense of wave function overlap between neighboring lithium ions. But the average distance between nearest- neighbor ions (a_c) in the $(Li^6I)_{1-x}(Li^6F)_x$ could be made much closer to that of the NaF substrate (a_s). As a result the dislocation density in epilayer could be reduced. Due to Vegard's law $a_c = (a(1-x) +xb)$, where b is the lattice constant of admixed Li^6F, a is the lattice constant of Li^6I. For $x=0,3$ we have $a_c=2,7042$ ($Å$), $a_s/a_c=0,9014$. Under condition of equality of the lattice parameters of the compressed $(Li^6I)_{1-x}(Li^6F)_x$ film and substrate, compressing $(Li^6I)_{0,7}(Li^6F)_{0,3}$ by only 9%, we will compress the Li^6I by 22,8%.!

Thin layer (for example, $(Li^6I)_{1-x}(Li^6F)_x$ or $(Li^6I)_{1-x}(Na F)_x$ with larger lattice constant

Thick overgrown layer from substrate material	Thick layer from substrate material
	Thick layer from substrate material
	Thick layer from substrate material
Substrate from ionic crystal with smaller lattice constant (e,g, NaF or $(NaF)_{1-y}(LiCl)_y$	Substrate from ionic crystal with smaller lattice constant (e,g, NaF or $(NaF)_{1-y}(LiCl)_y$
a)	b)

Note also that ionic crystals can be compressed much more easily than semiconductors since their bulk moduli (B) are smaller (for example, $B_{Si}/B_{LiI} \approx 5,8$ and $B_{Ge}/B_{LiI} \approx 4,4$). The implementation of a compression of ionic materials in heterostructures ~ 20 % not seems completely unreal, as to an example for a compression LiI on 18 %, the same value of pressure as to a compression Ge on 4 % is required;.

. From other calculations follows, that the necessary value of pressure for LiI is equal ~ 50 Gpa . Since pressures of the order of 50 GPa are achievable in practice the experimenters have an opportunity to check if the Li^6I crystals are ionic superconductors at high pressure. The outcomes of calculations are reduced below.

$p=-1/6r^2 \ dE/dr$.
$E = -\alpha q^2/4\pi\varepsilon_o r \ (1-r\rho/r_o^2) \ exp((r_o-r)/\rho))$. $\alpha =1.748$, α is Madelung's constant, $r_o=a/2$. E - ion binding energy in the crystal
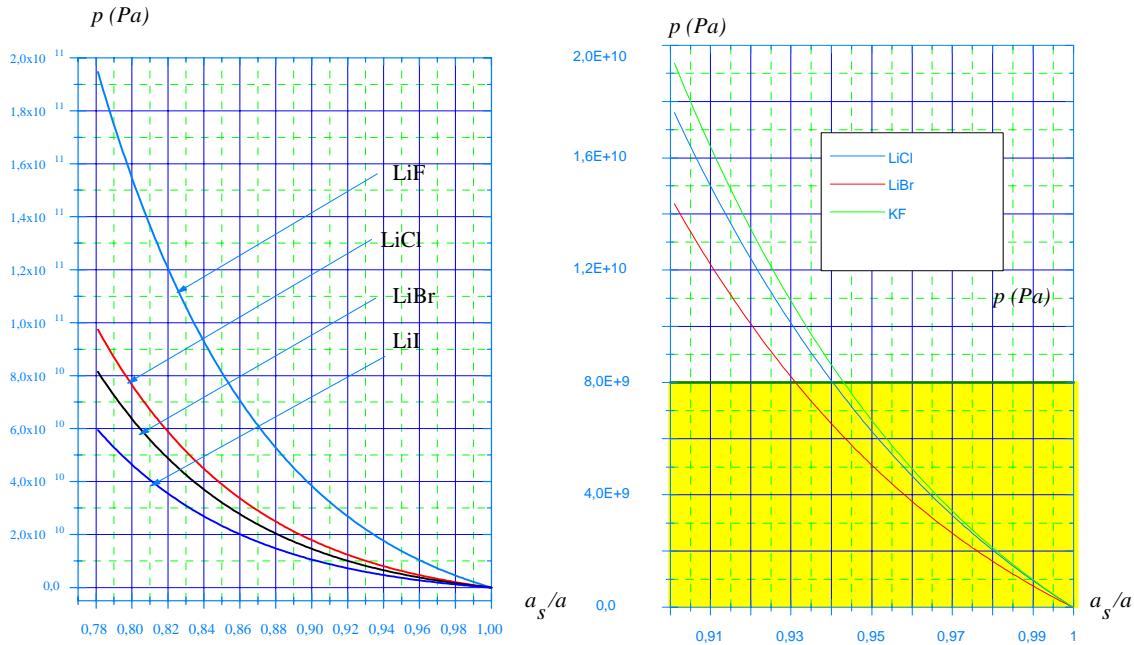
.Fig.9 Dependence of a constant crystal lattice on the value of pressure.

That is the minimum pressure are realized in structure containing a lamina, formed from $(Li^6I)_{1-x}$ $(Li^6F)_x$ or $(Li^6I)_{1-x}$ $(NaF)_x$ and substrate fulfilled from NaF or $(NaF)_{1-y}$ $(LiCl)_y$

Thin layer (for example, Li^6I or $(Li^6I)_y$ $(Li^6Br)_{1-y}$) with larger lattice constant

a)   b)
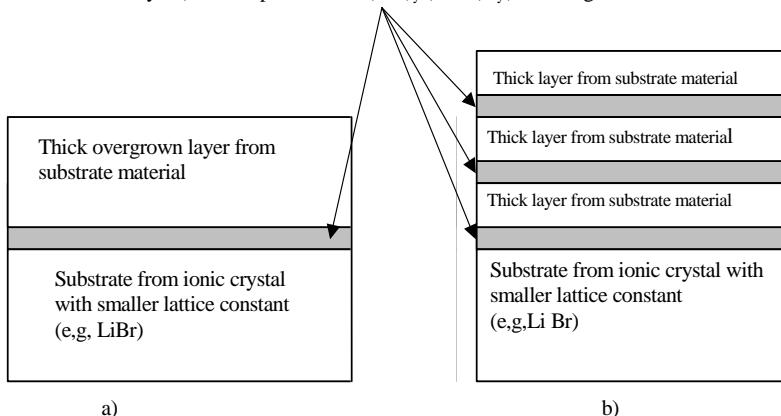
Other calculations have shown that in order to get superconductivity in LiI the necessary pressure should be about 50-70 GPa. It is, however, possible to reduce the magnitude of this pressure significantly by using epitaxially strained for example LiI/LiBr or LiBr/LiCl heterostructures and subjecting them to additional hydrostatic pressure.

Heterostructures with a small mismatch of lattices.

Substrate and thick overlayer material	Thin layer material	Lattice compression a_s / a
LiCl ($a_s/2$=2,570 Å)	Li^6I	0,857
NaF ($a_s/2$=2,317 Å)	Li^6Br	0,842
KF ($a_s/2$=2,674 Å)	Li^6I	0,891
LiBr($a_s/2$=2,751 Å)	Li^6I	0,917
RbF ($a_s/2$=2,815 Å)	Li^6I	0,938
NaCl ($a_s/2$=2,820 Å)	Li^6I	0,940
LiCl ($a_s/2$=2,570 Å)	Li^6Br	0,934

If on what or to the reasons Meissner effect in ionic superconductors does not become apparent, that is possible for idea's check it is necessary to pass current through an ionic superconductor,supplied with contacts from Li[6], or to carry out measurement of a capacity of ionic superconductors with usual contacts.

Current technology allows to obtain hydrostatic pressures in the range 8-100 GPa only in very small volumes ($\sim$0.01 mm^3) using diamond anvils. Therefore, it is reasonable first to fabricate the Li^{6}I/LiCl or (Li^{6}I)$_{1-x}$ (NaF)$_x$/LiCl or (Li^{6}I)$_{1-x}$ (Li^{6}F)$_x$/LiCl or (Li^{6}I)$_{1-x}$ (Li^{6}Cl)$_x$/LiCl. heterostructure and then to subject it to hydrostatic compression with P<8 GPa.

5. Conclusion

It is far from being clear to what extent the band-structure theory can be applied to the ions in ionic crystals. As to electrons, the theory already has a multiple experimental confirmations. But the author is unaware as to mathematical substantiation of the band theory for electrons. Unfortunately, for ions there is presently no experimental facts supporting or denying its applicability, simply because it is impossible to study magnetic properties of any substance at 10^{-40} K. Apparently, it is also valid that nobody never has compressed ionic crystals by 20% of their initial (1 atm) volume measuring simultaneously their electrical properties, since only recently this possibility has been demonstrated for extremely thin epilayers. Due to electron exchange interaction there are some peculiarities in Fermi-ion interactions. The behavior of fermionic ions should, perhaps, be similar to that of electrons in completely filled valence band even in compressed lattice. Ideally, one must be able to solve a many-particle problem with all interactions of valence electrons and ion's-core included. But such a solution, and especially its reduction to the form sufficiently simple for extracting the experimentally measured values, remains a dream. Therefore, only experiment is able to definitively answer the question about the adequacy of our calculations to reality.

The author hopes that some of the readers may be instrumental in fabrication of heterostructures described above.

Acknowledgments

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Appendix

For approximate calculation of exchange integral the following expression has been used

$$E(100) \approx -\int \psi_i^*(r + a_s)\left\{U_k\left(\frac{a}{2}\right) - U_i\left(\frac{a}{2}\right)\right\}\psi_i(r)dr$$

More correct expression will be obtained, if *a/2* is replaced by *a$_s$/2* and the dependence of ion binding energy in the crystal on pressure is taken into account.

Since the volume of one molecule in the crystal is 2r^3 the ion binding energy in the crystal under pressure is given by

$$U_k = -\frac{\alpha q^2}{4\pi\varepsilon_0 r}[1 - (r\rho/r_0^2)\exp((r_0 - r)/\rho)] + 2P(r^3 - r_0^3)$$

where P is pressure, $\alpha = 1.748$ is Madelung constant and $r_o = a/2$.

The connection between pressure (P) and inter-ion distance ($r = a_s/2$) in NaCl lattice is given by $dU_k/dr = 0$.

For ion binding energy in the molecule we have

$$U_i(r) = -\frac{q^2}{4\pi\varepsilon_0(r - \Delta r)} + \lambda\exp(-\frac{r - \Delta r}{\rho}) + C$$

It follows from the calculations described below that when $a_s/a \sim 0,8$ the magnitude of exchange integral become smaller by a factor of 2,5 in comparison with earlier approximation. By the same factor the effective mass of lithium ion is decreased and Bose condensation temperature is raised correspondingly.
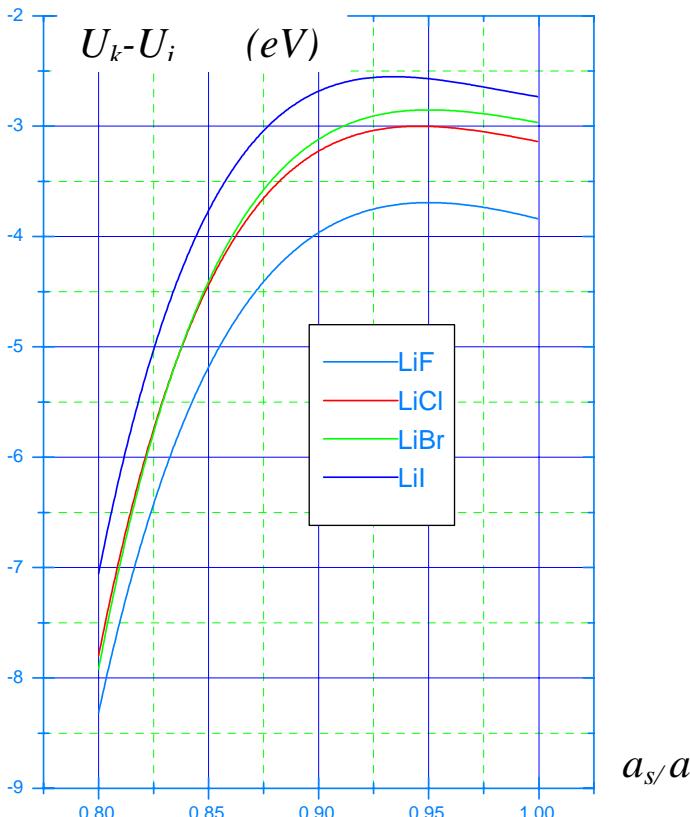
Why ionic crystals with lithium isotope were considered specifically?

There are several reasons for that choice:

1.   The rock-salt structure provides the minimum distance between oppositely charged ions in ionic crystals as compared with the crystals with CsCl-type structure.

2.   High compressibility of ionic crystals is of importance. Especially, LiI posses almost record-high compressibility.

3.   A wide choice of different crystals with lattice mismatch from several percent to several tens of percent is possible.

4.   As far as I know there is no phase transitions in single-charged ionic crystals up to the pressures of several tens of GPa, which could lead to electronic component of conductivity.

Achievement of ionic superconductivity through the use of other bosonic ions is less probable. The list of bosonic ions also includes the singly-charged deuterium ion and some doubly-charged ions that are formed in chemical compounds.

The compressibility of LiD as well as compressibility of the crystals composed from doubly-charged ions is significantly less than that for LiBr and LiI. It means that very high pressures will be needed (more than 100 GPa) in order to achieve the necessary compression. Under the term "necessary compression" I mean the compression of such a

magnitude that molecular wavefunctions of neighbor ions overlap, i.e. the distance between oppositely charged ions in compressed crystal must be equal to or less than that in a corresponding molecule. The achievement of these high hydrostatic pressures seems unreal presently. Under these high pressures the density of dislocations rises significantly, the allowed bands for electrons widen and transition to metallic state become possible. Besides, if electronic component of the current is present in compressed crystal, the spin and charge of the ions is changed and one can not define correctly the fermionic or bosonic nature of a given ion, since the question as to which ion (positive or negative) donate electron to the conduction band can not be answered unambiguously. As a consequence, the assumption about purely ionic interaction between bosonic ions, which is described by periodic potential becomes invalid. For the case considered there is practically no choice of materials which can be effectively used as compressing layers.

Acids (DCl, DI, DBr, DF) do not form NaCl-type crystals upon freezing. Since inter-ion distances in the acids are very small there are no substrates, which can be used to compress them.

Discussion

Below I am going to enlist some objections to my work that have been received in discussions and correspondence with different specialists adding short comments as to why the arguments appear not very convincing for the author.

1. *It can be argued that in ionic crystals there are no such things as positive or negative ions. The notion of ions is merely a simplification with unclear applicability range.* However, the measured conductivity of ionic crystals at room temperature is determined by ion movement through crystal vacancies and is of the order of 10^{-7}-10^{-6} (Ohm cm)$^{-1}$ at RT.

2. *Some doubts are cast upon the possibility to make the effective mass of the ion many orders of magnitude smaller than its gravitational mass since in metals the electron effective mass is of the order of m_e.*

Similar doubts would probably come also to my mind before the work was started if I did not know that in several semiconductors the effective electron mass is much smaller than m_e (a factor of 20 in GaAs and a factor of 70 in InSb).

3. *Objection consists in that the relevance of tight-binding approximation is called in question.*

In the situation when exact solution is impossible the appropriateness of any approximation could be tested only by experiment. It is known, however, that tight-binding approximation gives qualitatively correct results in the calculations of electronic band structure for both metals and semiconductors. This approximation does not lead to errors in the order of magnitude of calculated values for electron and hole effective masses. And the smaller the magnitude of the overlap integral is, the better (more exact) the calculated results are. In considering the ionic crystals we have exactly the case of small overlap integrals when the size of compressed lattice constant is larger than $2r_m$ (r_m is the distance between ions in a molecule). However, even if the calculated effective mass of lithium ions is increased by a factor of 30-40, the Bose condensation temperature of Li ions in the crystals compressed by 21-22% is greater than 300K.

For more exact solution of the problem it is necessary to find a periodic potential. Inserting this potential into Schrodinger equation and using plane wave method one can obtain the secular equation for exact dispersion E(k) in single-ion approximation. To find the lithium ion periodic potential in compressed crystal it seems to be necessary to solve self-consistently the quantum mechanical problem for the crystal containing sufficiently large number of molecules (greater than 100x100x100). As a preliminary, a complete system of lithium ion molecular wave functions must be constructed and a method similar to that of Hartree-Fock is to be used. In contrast to HF, however, the solution must be represented not as the Slater determinant, but as a sum of the products for different permutations of the lithium ion molecular wave functions. The problem at hand is far from being simple and even if somebody will be able to get a solution it is unlikely to enjoy more confidence than estimates obtained in the present work.

4. *For some readers it seems that in order to get the useful result the pressures required should provide the sufficient overlap of lithium nuclei wave functions. These pressures are orders of magnitude higher than those presented in my work.*

The argument is relevant if we compress pure Li[6]. But for compression of ionic crystals the situation is different. In a molecule composed from lithium and halogen the wave function of lithium ion have a maximum near the surface of the sphere with radius r_m. Beyond this distance the wave function is sharply diminished. Consequently, upon crystal compression the surfaces of neighboring spheres come close together and overlap integral steeply increases during compression as long as the distance between oppositely charges ions in crystal lattice is grater than corresponding distance in a molecule (r_m). When the distances mentioned above become equal the spheres are in touch and further compression does not lead to substantial increase of the overlap integral. Numerical results for the lithium ion effective mass (which is inversely proportional to the overlap integral) confirm this conclusion. These results can be interpreted

qualitatively if one notes that in undeformed crystals the binding energy of ion in the crystal is lower than corresponding binding energy of ion in a molecule. Consequently, lithium ions occupy lattice sites. But already in crystals compressed by 18-20% the binding energy of ion in the crystal becomes greater than that in a molecule. Due to disappearance of potential barrier the lithium ions can now move through the crystal.[1]

5. *For some people it seems that reasonable results could be obtained only if correlational interaction between lithium ions is taken into account. Their argument goes as follows. Since lithium ion is firmly sitting in the lattice site of ionic crystal and do not allow to occupy this site by other lithium ions then correlational effects must be accounted for.*

In my opinion it is not necessary. The fact that lithium ions arrange themselves over crystal lattice sites is already accounted for by the potential used in the calculations. The potential is specifically constructed to agree with observed lattice parameter, elastic properties, dissociation energy and molecular size. The fact that ion occupy the lattice site means only the high probability to find it in that place. The notion of lattice site for Li^6 ions in compressed crystals can become meaningless. The binding energy of Li ion at the site can be easily calculated. As long as this energy is lower than binding energy of the ion in a molecule the ions can be thought of as occupying lattice sites. In opposite case, which is realized already at 18-20% compression, the potential reach a minimum value not at a point but, most probably, on the surface similar to spherical surface in a molecule.

At present it is difficult to state with any certainty about the technical possibility for the fabrication of the proposed heterostructures since the author is unaware of any experiments on epitaxial growth of very thin lithium halogenides films on ionic crystals substrates. Published experiments with other ionic materials [9] have shown that pseudomorphic films (several monolayers thick) can be produced for layer/substrate mismatch up to 10%.It is hoped that using solid alloys between LiI (or LiBr) and other ionic compounds in order to reduce their misfit with corresponding substrates can lead to success especially if one takes into account a very high compressibility (almost record-high among binary chemical compounds) of LiI. It is quite possible that for the fabrication of materials with high temperature ionic superconductivity a combination of epitaxy and hydrostatic compression will be required.

As can be seen from Figure 9 very high pressures (> 50 GPa) are required in order to compress bulk crystals. Since for this pressure range the compression is never purely hydrostatic one may suspect that crystalline lattice will be greatly distorted due to dislocation generation and multiplication. Heterostructures could be a remedy in that respect. To obtain the necessary compression in a heterostructure (for example in LiI/LiBr with ~9% misfit) the pressures required are several times lower than 50 GPa, which must be applied for bulk LiI. The use of perfect substrates and growth of dislocation –free pseudomorphic layers can be regarded as additional factors for preservation of crystalline order upon subsequent compression.

Let us assume that ionic superconductor is created. The question then is what can be done with that. Ionic superconductivity has its own peculiarities. The discussion of the full range of differences between ionic and electronic superconductivity must be postponed until experimental validation. Some points, however, can be mentioned. The usage of ionic superconductors in direct current electrical circuits seems to be problematical, because one must be able to compensate the loss of ions at the one end of ionic superconductor and fight with their excess at the other end. This peculiarity can be used in advantage for the fabrication of capacitors. The metal-ionic superconductor- metal structure forms the capacitance. Obviously, the magnitude of the capacitance will be large since electric field is concentrated in thin near-contact regions (electrons from the metal can not penetrate into ionic superconductor, whereas ions from the former are unable to diffuse into metal).

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[1] It has been reported in [B. Srinivasa Rao and S. P. Sanyal , **Structural and elastic properties of sodium halides at high pressure,** PHYSICAL REVIEW VOLUME 42, NUMBER 3 1990-11,p.1810-1816   ] that in Na halides the type of crystal structure changes from NaCl to CsCl in the pressure range of 20-30 GPa. If similar structural changes do occur in Li halides ion movements in crystals is possible at least in the conditions of structural transformation and ionic superconductivity should probably be looked for at these conditions. [1]

The author does not see any obstacles for the application of ionic superconductors in alternating current circuits. Low frequency alternating current can be transmitted practically lossless through transformer coupling or through the system composed from ionic superconductor with ohmic contacts, which can be fabricated from a saturated water solution of some electrolyte (e.g. LiI) involving Li^6 ions. Ohmic contacts can also b made from ionic superconductor could probably replace the bulky windings of electric generators and motors. A cavity inside ionic superconductor will be an ideal lossless cavity for ultra-high frequency applications. When ionic Bose condensate is placed in the magnetic field the current is generated which opposes the penetration of the field deep into superconductor material and which persist after the field is switched off. It is thus possible to generate the ultra-high magnetic fields on the premise that Meissner effect exists in ionic superconductors.

In this connection I recollected a funny idea that came into my mind some 15-20 years ago (at that time no one from my friends wished to check it). An idea can be described as follows. If a spinning ring made from superconductor is stopped the charge carriers responsible for superconductivity keep on spinning and generate magnetic field. In case of Bose particles remaining at rest during spinning the source of the magnetic field will be a rotating superconductor. In its turn the Meissner effect will make some amendments. For usual superconductors the topic can be developed in many directions – one can, for example, to spin the superconductor above critical temperature, next cool it down and only then to stop in order to see what magnetic field will be produced. All this is somewhat unusual but for the generation of ultra-high magnetic fields using ionic superconductors the idea has an added bonus because the ion number density in ionic superconductors is many orders of magnitude higher than that of Cooper's pairs in traditional superconductors. Moreover, the magnetic field will, probably, be generated even if the Meissner effect is absent in ionic superconductors.