

# IS IT POSSIBLE TO MAKE MATERIALS WITH IONIC SUPERCONDUCTIVITY?

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**Abstract.** 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  $\text{Li}^6$  can be used for that purpose. The results show that Bose-condensation temperature for  $\text{Li}^6$ -ions is of the order of  $10^{-34} - 10^{-43}\text{K}$  in all crystals. If, however, the crystal is compressed by 20-22%, it can rise the Bose-condensation temperature in all crystals considered to *above room temperature*.

## 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  $\psi(\vec{r})$

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

$$\hat{H} = \frac{\hbar^2}{2m} \Delta + U(\vec{r}) \quad (2)$$

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

where  $\vec{n}$  is translation vector

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

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  $\Delta \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ ,  $\hbar$  is Planck's constant divided by  $2\pi$ ,  $m$  is the

mass of lithium ion, and  $U(\vec{r})$  is potential energy of the ion in the crystal.

Equation (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.

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  $\text{Li}^6$ , which consists of 3 neutrons, 3 protons and 2 electrons.

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

$$\hat{H}_i = \frac{\hbar^2}{2m} \Delta + U_i(\vec{r}) \quad (5)$$

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

$$\hat{H}_i \psi(\vec{r}) = E_i \psi(\vec{r}) \quad (6)$$

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

$$\psi(\vec{r}) = \sum_{\vec{l}} e^{2\pi i \vec{k} \cdot \vec{l}} \psi_i(\vec{r} - \vec{l}) \quad (7)$$

where  $\psi_i(\vec{r} - \vec{l})$  is an eigenfunction of  $\hat{H}_i$  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

$$E(\vec{k}) = E_i - \sum_{\vec{l}} E(\vec{l}) e^{2\pi i \vec{k} \cdot \vec{l}} \quad (8)$$

$$E(\vec{l}) = - \int \psi_i^*(\vec{r} + \vec{l}) \{U_k(\vec{r}) - U_i(\vec{r})\} \psi_i(\vec{r}) d\vec{r} \quad (9)$$

integration being performed over crystal volume.

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

$$E(\vec{k}) = E(k_1, k_2, k_3) = E_i - E(0) + 2E(100) \{ \cos ak_1 + \cos ak_2 + \cos ak_3 \} \quad (10)$$

$$E(0) = - \int \psi_i^*(\vec{r}) \{U_k(\vec{r}) - U_i(\vec{r})\} \psi_i(\vec{r}) d\vec{r} \quad (11)$$

$$E(100) = - \int \psi_i^*(\vec{r} + \vec{a}) \{U_k(\vec{r}) - U_i(\vec{r})\} \psi_i(\vec{r}) d\vec{r} \quad (12)$$

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  $\text{Li}^6$  ion effective mass we can use a well-known (in tight-binding approximation) expression

$$m^* = \frac{\hbar^2}{2E(100)a^2} \quad (13)$$

If we choose the molecular potential in the form

$$U_i(r) = -\frac{q^2}{4\pi\epsilon_0 r} + \lambda \exp\left(-\frac{r}{\rho}\right) \quad (14)$$

and calculate the  $\lambda$  and  $\rho$  parameters according to [1], then we obtain from (14) potential curves shown in Fig.1.

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

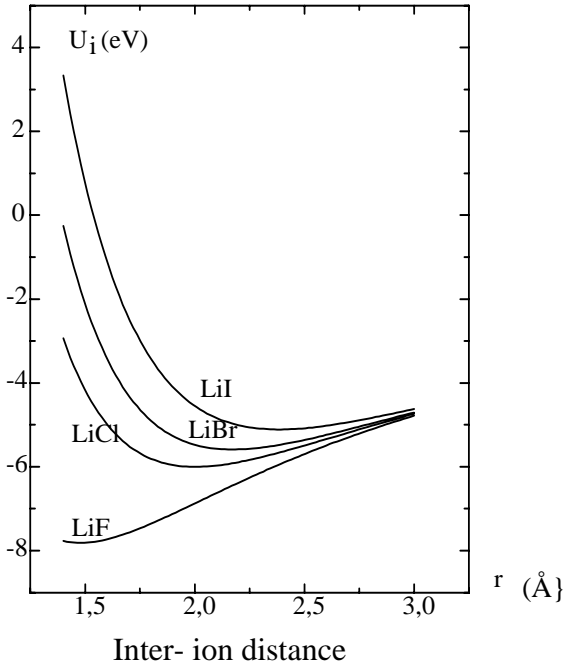


Fig.1. Potential curves for lithium ion in the molecules calculated from eq. (14)

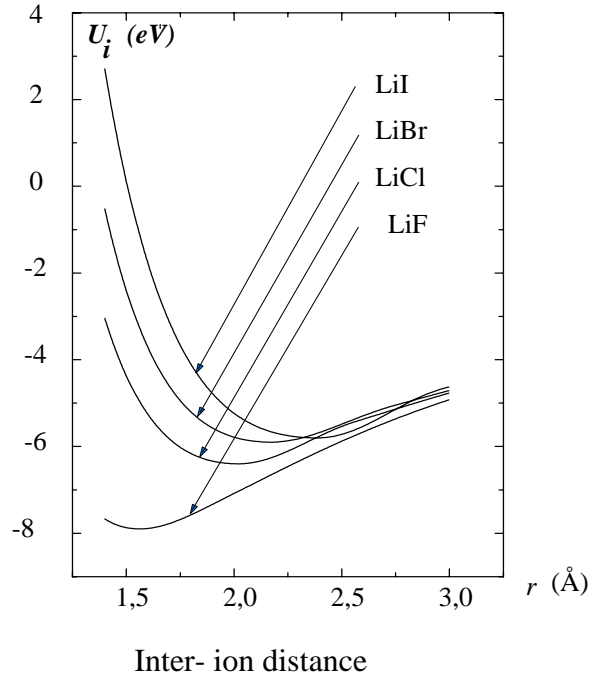


Fig.2. Refined potential for lithium ion in LiF, LiCl, LiBr and LiI molecules

$$U_i(r) = -\frac{q^2}{4\pi\epsilon_0(r-\Delta r)} + \lambda \exp\left(-\frac{r-\Delta r}{\rho}\right) + C \quad (15)$$

$C=0$  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  $\lambda$   $u$   $\rho$  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]. Results are presented in table 1.

Table 1. Parameters used for the calculation of molecular potential

material	$a/2$ lattice constant Å	$r_m$ molecu- lar size Å	$\Delta E$ Difference between halogen electron affinity and Li ionization potential, eV	$E_{da}$ Dissocia- tion energy of the molecule into atoms, eV	$\lambda$ eV	$E_d=E_{da}+\Delta E$ Dissocia-tion energy of the molecule into ions eV	$r_r$ Calculated inter-ion distance in the molecule according to (14), Å	$\rho$ 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

### 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

$$\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r} \frac{\partial \psi}{\partial r} + (E - U_i(r))\psi = 0 \quad (16)$$

For numerical solution we used the following conditions

$$\psi(r) = 1 \text{ when } r = r_m, \psi(r) = 0 \text{ when } r = 0 \text{ and } r = a = 2r_c, E = E_d \quad (17)$$

The normalized wavefunctions can be expressed as

$$\psi_i = \psi / \sqrt{\int 4\pi r^2 \psi^2(r) dr} \quad (18)$$

and are shown in Fig.3.

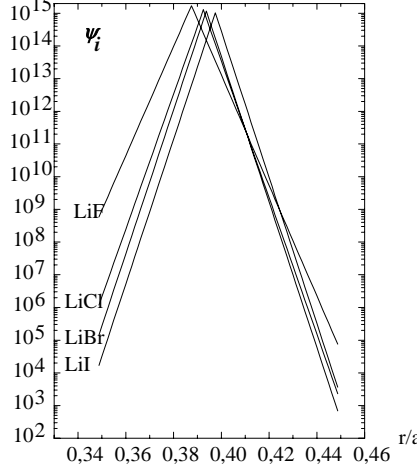


Fig.3. Normalized wavefunctions of lithium ion in LiF, LiCl, LiBr and LiI molecules.

$$E(100) \approx -\int \psi_i^*(r+a) \left\{ U_k \left( \frac{a}{2} \right) - U_i \left( \frac{a}{2} \right) \right\} \psi_i(r) dr \quad (19)$$

Inserting the ground state wave function into (18) one can calculate the exchange integral  $E(100)$  and then the effective mass of lithium ion from (13). Finally, the temperature of Bose-condensation ( $T_b$ ) can be estimated [6] from

$$T_b = \frac{2\pi\hbar^2}{m^*k_B} \left( \frac{N}{2.612 \times V} \right)^{\frac{2}{3}} = \frac{2\pi\hbar^2}{m^*k_B} \left( \frac{0.5}{2.612 \times \left( \frac{a}{2} \right)^3} \right)^{\frac{2}{3}} \quad (20)$$

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

Table 2. Estimated Bose-condensation temperature for  $\text{Li}^6$  ions in halogenide crystals

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

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  $\rho_c$  in comparison with that of metal  $\rho_m$  as  $\rho_c \sim \rho_m (m^*/m_e)^{5/2}$ .

Where  $\rho_m=10^5 \text{ Ohm}\cdot\text{cm}$  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  $\text{Li}^6$  ions can be increased significantly. Denoting by  $a_s$  the lattice constant of compressed crystal we can write

$$E(100) \approx -\int \psi_i^*(r+a_s) \left\{ U_k\left(\frac{a}{2}\right) - U_i\left(\frac{a}{2}\right) \right\} \psi_i(r) dr \quad (21)$$

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

Substituting the ground-state wavefunction into (21) one can calculate the exchange integral and estimate the new values for effective mass of  $\text{Li}^6$  ions,  $m^*$ , and Bose-condensation temperature,  $T_b$ ,

$$m^* = \frac{\hbar^2}{2E(100)a_s^2} ; \quad T_b = \frac{2\pi\hbar^2}{m^*k_B} \left( \frac{0.5}{2.612 \times \left(\frac{a_s}{2}\right)^3} \right)^{\frac{2}{3}} \quad (22)$$

The results of these calculations are presented in Fig.4 and Fig.5.

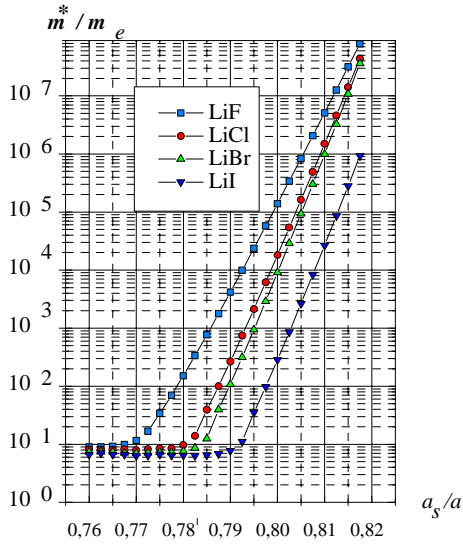


Fig.4. Effective mass of  $\text{Li}^6$  ions as a function of crystal compression.  $a_s$  is the lattice constant of compressed crystal,  $a$  is lattice constant of strain-free ionic crystal,  $m_e$  is free electron mass.

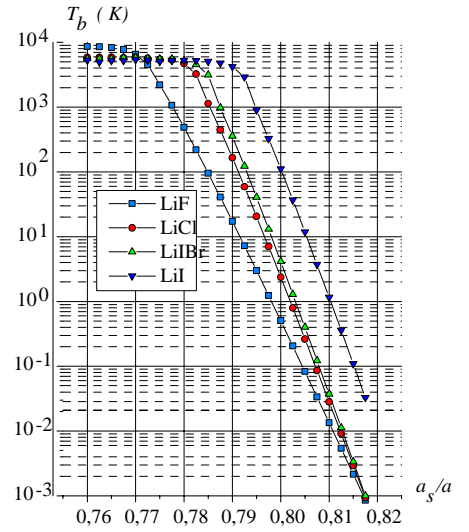


Fig.5. Bose-condensation temperature as a function of crystal compression

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  $\sim 4\%$ ). Often a mixed alloy ( $\text{Si}_x\text{Ge}_{1-x}$ ) 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 overgrown by a thick

layer of substrate material forming thus a double heterostructure (see Fig.6(a)) or even a multi-quantum well structure (Fig.6(b)).

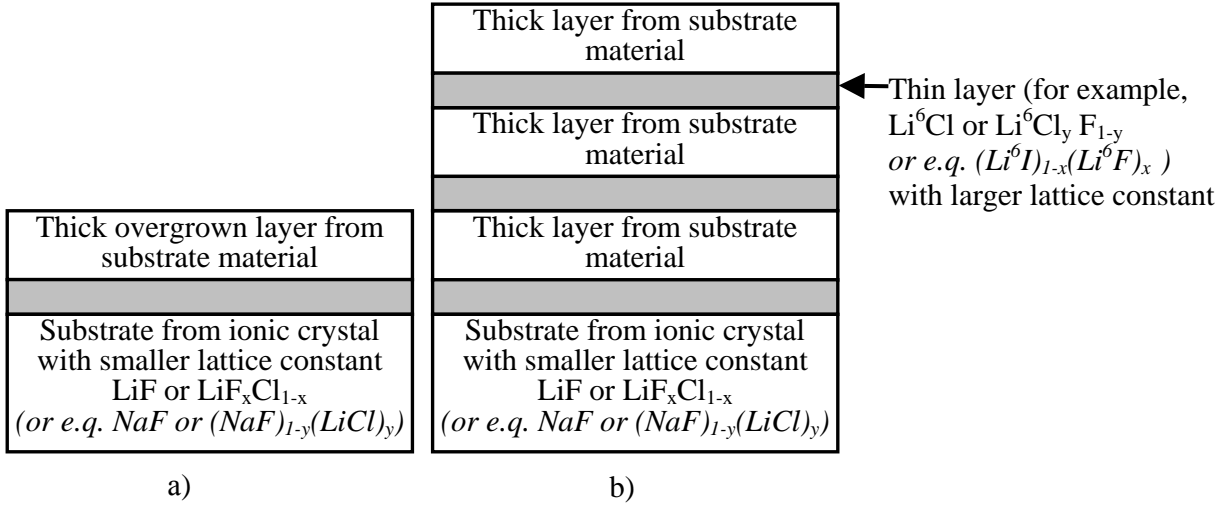


Fig.6. Possible heterostructures with a thin compressed Li<sup>6</sup>-containing ionic layers

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 (22) 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 <sup>6</sup> ion effective mass ( $m^* / m_e$ )	Bose-condensation temperature for Li <sup>6</sup> ions	Lattice compression $a_s / a$
LiF ( $a_s/2=2,014 \text{ \AA}$ )	Li <sup>6</sup> Cl	24	1870	0,784
LiF ( $a_s/2=2,014 \text{ \AA}$ )	Li <sup>6</sup> Br	7,9	5700	0,732
LiF ( $a_s/2=2,014 \text{ \AA}$ )	Li <sup>6</sup> I	8,2	5460	0,671
NaF ( $a_s/2=2,317 \text{ \AA}$ )	Li <sup>6</sup> I	6,5	5250	0,772
LiH ( $a_s/2=2,04 \text{ \AA}$ )	Li <sup>6</sup> Cl	1270	34,5	0,793
LiH ( $a_s/2=2,04 \text{ \AA}$ )	Li <sup>6</sup> Br	8,14	5400	0,741
LiH ( $a_s/2=2,04 \text{ \AA}$ )	Li <sup>6</sup> I	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<sup>6</sup> is completely useless since temperatures involved are less than 10<sup>-40</sup>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 course, 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<sup>6</sup>Cl)<sub>1-x</sub>(Li<sup>6</sup>F)<sub>x</sub> could be formed. As to the ionic density, the alloy (Li<sup>6</sup>Cl)<sub>1-x</sub>(Li<sup>6</sup>F)<sub>x</sub> 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<sup>6</sup>Cl in a sense of wave function overlap between 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<sup>6</sup>I - NaF system the lattice

mismatch is about 22,8% ( $a_s/a=0,772$ ). Admixing  $\text{Li}^6\text{F}$  we get the solid solution  $(\text{Li}^6\text{I})_{1-x}(\text{Li}^6\text{F})_x$ . For  $x < 0,5$  the electronic properties of the alloy will not, probably, differ substantially from that of pure  $\text{Li}^6\text{I}$  in a sense of wave function overlap between neighboring lithium ions. But the average distance between nearest- neighbor ions ( $a_c$ ) in the  $(\text{Li}^6\text{I})_{1-x}(\text{Li}^6\text{F})_x$  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  $\text{Li}^6\text{F}$ ,  $a$  is the lattice constant of  $\text{Li}^6\text{I}$ . 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  $(\text{Li}^6\text{I})_{1-x}(\text{Li}^6\text{F})_x$  film and substrate, compressing  $(\text{Li}^6\text{I})_{0,7}(\text{Li}^6\text{F})_{0,3}$  by only 9%, we will compress the  $\text{Li}^6\text{I}$  by 22,8%.!

Note also that ionic crystals can be compressed much more easily than semiconductors since their bulk moduli (B) are smaller (for example,  $B_{\text{Si}}/B_{\text{LiI}} \approx 5,8$  and  $B_{\text{Ge}}/B_{\text{LiI}} \approx 4,4$ ).

In order to compress the LiI crystal by 22% of its initial volume the pressure applied must be in the 2-3 GPa range. From other calculations follows, that the necessary value of pressure for LiI is equal  $\sim 50$  GPa. Since pressures of the order of 50 GPa are achievable in practice the experimenters have an opportunity to check if the  $\text{Li}^6\text{I}$  crystals are ionic superconductors at high pressure [8]. On an evocative site [8] there is also padding information concerning an ionic superconductivity.

### 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. 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. 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 interdispersed by relatively thick layers of thoughtfully-chosen solid alloys

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