

DOES HIGH TEMPERATURE IONIC SUPERCONDUCTIVITY EXISTS?

VALERY M. IOFFE

Institute of Semiconductor Physics, Novosibirsk, Russia
alkornsk@mail.ru

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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. Ionic crystals LiCl, LiF, LiBr and LiI were considered with lithium isotope Li⁶. Calculations show that Bose condensation temperature for lithium ions in these crystals is of the order of 10⁻³⁴–10⁻⁴³ K. If, however, the crystal is compressed so that the wave functions of neighboring lithium ions are sufficiently overlapped, then Bose-condensation temperature of Li⁶-ions can be increased significantly. Our estimates show that by compressing the crystals by 20–22% in all three directions, one can raise the Bose-condensation temperature in all crystals considered to *above room temperature*. To realize materials with room temperature superconductivity in practice, the use of molecular beam epitaxy is proposed for the formation of heterostructures from thin and thick layers of thoughtfully chosen composition.

Keywords: Superconductivity; ionic crystals; pressure; heterostructures.

1. Introduction

We consider ionic crystals LiF, LiCl, LiBr and LiI with NaCl crystal structure. The distribution of lithium ions in the crystal lattice is governed 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 $\psi(\mathbf{r})$

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

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

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

where \mathbf{n} is a translation vector

$$n - n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3. \quad (4)$$

Here, n_1, n_2, n_3 are positive or negative integers; $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are three independent lattice translations; 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 the potential energy of the ion in the crystal.

Equation (1) differs from the well-known equation for electrons in a periodic potential only by the mass of the particle considered (see, e.g., Ref. 1). As a consequence, from well-known analysis of this equation, one can conclude that ion energy in ionic crystals is a function of wave vector \mathbf{k} and solutions for real-valued ion eigenenergies exist only for specific energy intervals. Note that naturally occurring ionic crystals composed from single-charged ions are formed from fermions. The only exception is the ion of Li⁶ isotope, which consists of even number of fermions, i.e., 3 neutrons, 3 protons and 2 electrons.

Let us estimate the possible characteristics of ionic crystals LiF, LiCl, LiBr and LiI with Li⁶ isotope using tight-binding approximation (an analysis is quite similar to that for electrons). If $U_k(\mathbf{r}) - U_i(\mathbf{r})$ is the difference of the ion potential energy in the crystal and in the corresponding molecule (the molecule is composed of positive lithium ion and negative halogen ion) and E_i is the ground state energy of lithium ion in the molecule, then for the rock salt cubic structure, we obtain taking into account only nearest-neighbor interaction

$$E(\vec{k}) = E(k_1, k_2, k_3) = E_i - E(0) + 2E(100)(\cos ak_1 + \cos ak_2 + \cos ak_3) \quad (5)$$

$$E(0) = - \int \psi_i^*(\mathbf{r}) \{U_k(\mathbf{r}) - U_i(\mathbf{r})\} \psi_i(\mathbf{r}) d\mathbf{r} \quad (6)$$

$$E(100) = - \int \psi_i^*(\mathbf{r} + \mathbf{a}) \{U_k(\mathbf{r}) - U_i(\mathbf{r})\} \psi_i(\mathbf{r}) d\mathbf{r}. \quad (7)$$

Here, k_1, k_2, k_3 are wave vector projections on different crystallographic axes, a is lattice constant and ψ_i is normalized Li⁶ ion wavefunction.

For the calculation of Li⁶ ion effective mass in the crystal, we can use a well-known (in tight-binding approximation) expression for NaCl-type lattice

$$m^* = \frac{\hbar^2}{2E(100)a^2}. \quad (8)$$

The form of molecular potential used in the calculations is fitted to experimental molecular dissociation energies, as well as their size, and elastic properties and lattice constants of ionic crystals. We take it as

$$U_i(r) = - \frac{q^2}{4\pi\epsilon_0(r - \Delta r)} + \lambda \exp\left(-\frac{r - \Delta r}{\rho}\right) + C \quad (9)$$

where fitting parameters are given by

$$C = \begin{cases} 0 & \text{if } r > r_c \\ \Delta U = E_d - E_{\min} & \text{if } r < r_m \\ 0.5\Delta U \{1 + \cos[\pi(r - r_m)/(r_c - r_m)]\} & \text{if } r_c > r > r_m \end{cases} \quad (10)$$

$$\Delta r = \begin{cases} 0 & \text{if } r > r_c \\ r_m - r_r & \text{if } r < r_m \\ 0.5(r_m - r_r)\{1 + \cos[\pi(r - r_m)/(r_c - r_m)]\} & \text{if } r_c > r > r_m . \end{cases} \quad (11)$$

In (10) and (11), r_m is the equilibrium inter-nuclear distance in the molecule, r_c is half of the ionic crystal lattice constant ($a/2$); E_d is dissociation energy of the molecule into ions, which can be calculated from experimentally measured dissociation energy of the molecule into atoms (E_{da}) and the difference between halogen electron affinity and lithium ionization potential (ΔE); E_{\min} and r_r are, respectively, the depth of the minimum on the potential energy curve and its location calculated from Eq. (9) with $C = \Delta r = 0$. Lattice constants and parameters λ and ρ were taken from Ref. 1, r_m and E_{da} from Ref. 2, and electron affinities and ionization potential can be found in Ref. 3. Numerical values of all relevant parameters are collected in Table 1.

Table 1. Parameters used for the calculation of potential energy curve.

Material	r_c (Å)	r_m (Å)	E_{da} (eV)	ΔE (eV)	λ (eV)	ρ (Å)	E_d (eV)	r_r (Å)	E_{\min} (eV)
LiF	2.014	1.564	6.0	-1.9	308.3	0.291	-7.9	1.480	-7.814
LiCl	2.570	2.021	4.8	-1.6	510.4	0.330	-6.4	2.002	-6.003
LiBr	2.751	2.170	4.4	-1.9	615.6	0.340	-5.9	2.168	-5.589
LiI	3.000	2.392	3.6	-2.2	624.0	0.366	-5.8	2.390	-5.109

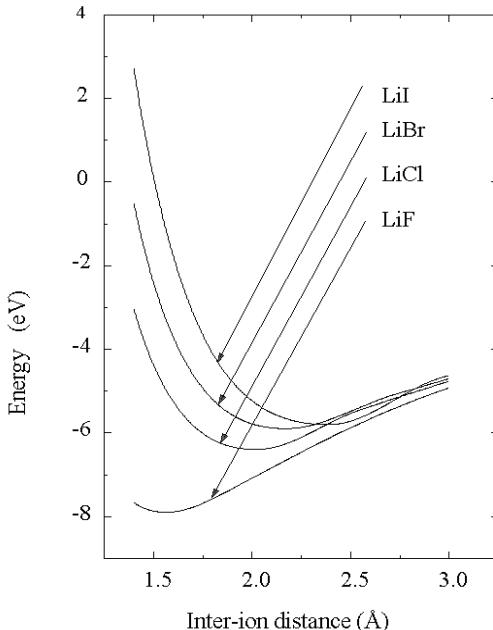


Fig. 1. Potential energy curves for molecules.

The calculated potential energy curves for Li-containing ionic molecules are shown in Fig. 1.

2. Bose Condensation of Li⁶ Ions in Unperturbed and Compressed Crystals

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

$$\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r} \frac{\partial \psi}{\partial r} + (E - U_i(r))\psi = 0 \quad (12)$$

with $U_i(r)$ given by Eq. (9).

The influence of halogen anion mass (M_h) on the calculated values is taken into account by replacing m on $mM_h/(m + M_h)$ in Eq. (12).

For numerical solution, we used the following conditions

$$\psi(r) = 1 \text{ when } r = r_m \quad (13)$$

$$\psi(r) = 0 \text{ when } r = 0 \quad (14)$$

$$\psi(r) = 0 \text{ when } r = a = 2r_c \quad (15)$$

$$E = E_d. \quad (16)$$

The normalized wavefunctions can be expressed as

$$\psi_i = \psi / \sqrt{\int 4\pi r^2 \psi^2(r) dr} \quad (17)$$

and are shown in Fig. 2.

Also from Eq. (7) we have

$$E(100) \approx - \int \psi_i^*(r + a) \left\{ U_k \left(\frac{a}{2} \right) - U_i \left(\frac{a}{2} \right) \right\} \psi_i(r) dr. \quad (18)$$

Inserting the ground state wavefunction into (18), one can calculate the overlap integral $E(100)$ and then the effective mass of lithium ion from Eq. (8). Finally, the temperature of Bose-condensation (T_b) can be estimated⁴ from

$$T_b = \frac{2\pi\hbar^2}{m^*k_B} \left(\frac{N}{2.612 \times v} \right)^{\frac{2}{3}} = \frac{2\pi\hbar^2}{m^*k_B} \left(\frac{0.5}{2.612 \times \left(\frac{a}{2} \right)^3} \right)^{\frac{2}{3}} \quad (19)$$

where k_B is Boltzmann's constant and N/V is boson number density. The calculated results are presented in Table 2, where m_e is a free electron mass.

Due to a huge value of lithium ion effective mass, all ionic crystals are dielectrics at any real temperature. Indeed, if we assume that in a defect-free crystal the dominant scattering mechanism for Li ions is scattering by acoustical phonons, we

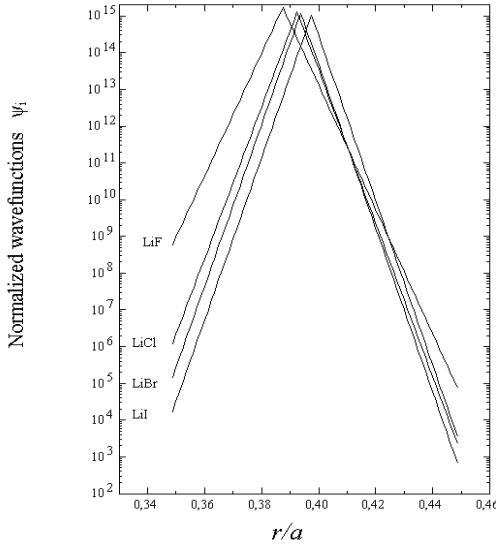


Fig. 2. Normalized wavefunctions of lithium ion in LiF, LiCl, LiBr and LiI molecules.

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

Crystal	$U_k(a/2)^a$ (eV)	$U_i(a/2)$ (eV)	$\frac{m^*}{m_e}$	T_b (K)
Li^6F	10.53	7.1	$0.13 \cdot 10^{39}$	$0.35 \cdot 10^{-33}$
Li^6Cl	8.64	5.8	$0.10 \cdot 10^{46}$	$0.25 \cdot 10^{-40}$
Li^6Br	8.24	5.5	$0.27 \cdot 10^{48}$	$0.80 \cdot 10^{-43}$
Li^6I	7.72	5.0	$0.85 \cdot 10^{46}$	$0.24 \cdot 10^{-41}$

^aExperimentally observed ion binding energies in the crystals were taken from Ref. 1.

can estimate the specific resistivity of ionic crystal ρ_c in comparison with that of metal ρ_m as

$$\rho_c = \rho_m \left(\frac{m^*}{m_e} \right)^{\frac{5}{2}} \quad (20)$$

where $\rho_m = 10^{-5}$ Ohm cm is a typical metal resistivity. No contradiction with experiment is obtained since real ionic conductivity in available crystals is completely dominated by defects, and is many orders of magnitude higher. If, however, the ionic crystal is compressed so that Li wavefunction overlap becomes significant, then Bose-condensation temperature for Li^6 ions can be increased significantly. In earlier work,⁵ the following expression has been used for overlap integral

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

where a_s is lattice constant of compressed crystal. A more consisting approach

would be to use

$$E(100) \approx - \int \psi_i^*(r + a_s) \left\{ U_k \left(\frac{a_s}{2} \right) - U_i \left(\frac{a_s}{2} \right) \right\} \psi_i(r) dr. \quad (22)$$

In this case, the periodic potential is replaced by its minimal value and pressure-induced modification is properly 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

$$U_k = -\frac{\alpha q^2}{4\pi\epsilon_0 r} (1 - r\rho/r_0^2) \exp[(r - r_0)/\rho] + 2P(r^3 - r_0^3) \quad (23)$$

where P is pressure, $\alpha = 1.748$ is Madelung's 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 $dU_k/dr = 0$. The calculated pressure dependence of lattice constant is shown in Fig. 3.

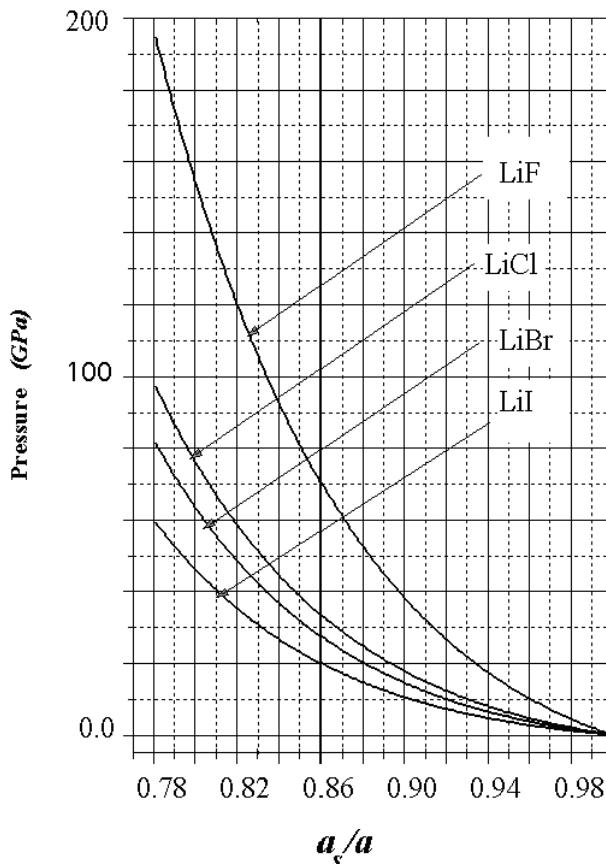


Fig. 3. The pressure required to decrease lattice constant from a to a_s .

(22)

Inserting the ground state wavefunction into (18), one can calculate the overlap integral $E(100)$ and then obtain the effective mass of lithium ion and the temperature of Bose-condensation (T_b) from

$$m^* = \frac{\hbar^2}{2E(100)a_s^2} \quad (24)$$

$$T_b = \frac{2\pi\hbar^2}{m^*k_B} \left(\frac{0.5}{2.612 \times \left(\frac{a_s}{2}\right)^3} \right)^{\frac{2}{3}}. \quad (25)$$

The results are shown in Figs. 4 and 5.

Our calculations have shown that in order to make Bose-condensation temperature greater than 300 K, one should compress LiF by 22%, LiCl by 21.3%, LiBr by 21%, LiI by 20.3%. The pressures required to achieve these compressions are 200, 100, 70 and 50 GPa for LiF, LiCl, LiBr and LiI, respectively.

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

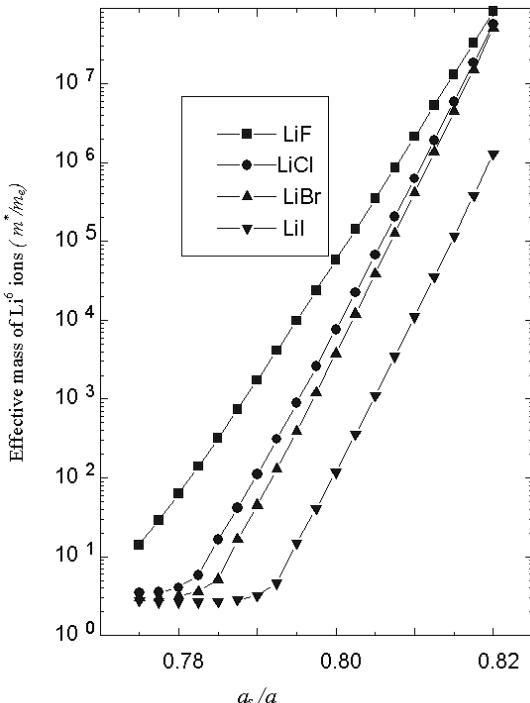


Fig. 4. Effective mass of Li^6 ions m^* as a function of crystal compression; a_s is the lattice constant of compressed crystal; a is lattice constant of strain-free ionic crystal; m_e is free electron mass.

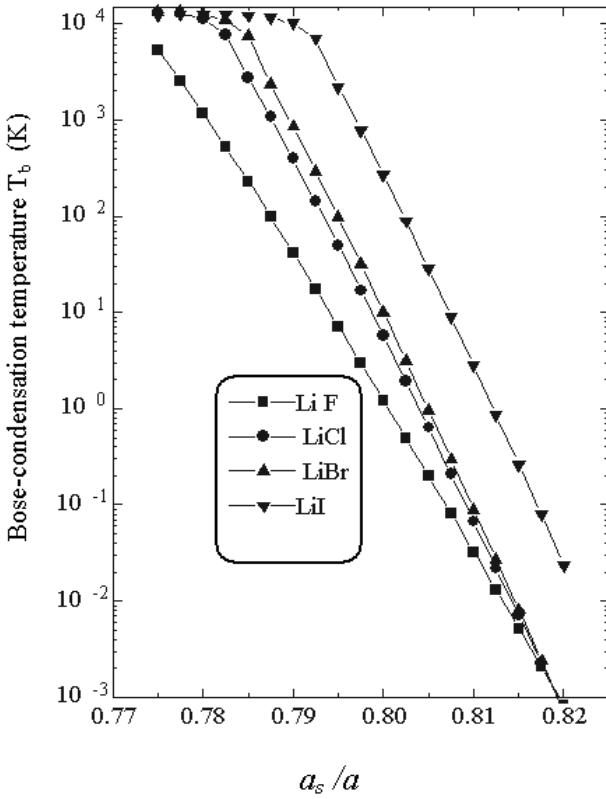


Fig. 5. Bose-condensation temperature for Li^6 ions as a function of crystal compression.

calculated effective mass of lithium ions is increased by a factor of 30, the Bose-condensation temperature of Li ions in crystals compressed by 21–22% is greater than 300 K. And the tight-binding approximation, when applied to electrons, does not lead to errors in the order of magnitude of the calculated effective mass.

As can be seen from Fig. 5, the compressions greater than 18% are of interest for performing practical measurements. For these large compressions, the notion of lattice site as a point where lithium ion energy is at minimum becomes meaningless. The lithium ion binding energy in the crystal (E_c) can be easily calculated from

$$E_c = -\frac{\alpha q^2}{4\pi\epsilon_0 r}(1 - r\rho/r_0^2) \exp[(r - r_0)/\rho] \quad (26)$$

where $\alpha = 1.748$ is Madelung's constant, $r_o = a/2$, $r = a_s/2$.

As long as this energy is less than the binding energy of the ion in a molecule, the ions occupy lattice sites. In the opposite case, which is realized already at 18–20% compression, the potential reaches a minimum value not at a point but on the surface similar to spherical surface in a molecule. The problem then becomes quite similar to that of electron in the solid and application of tight-binding approxima-

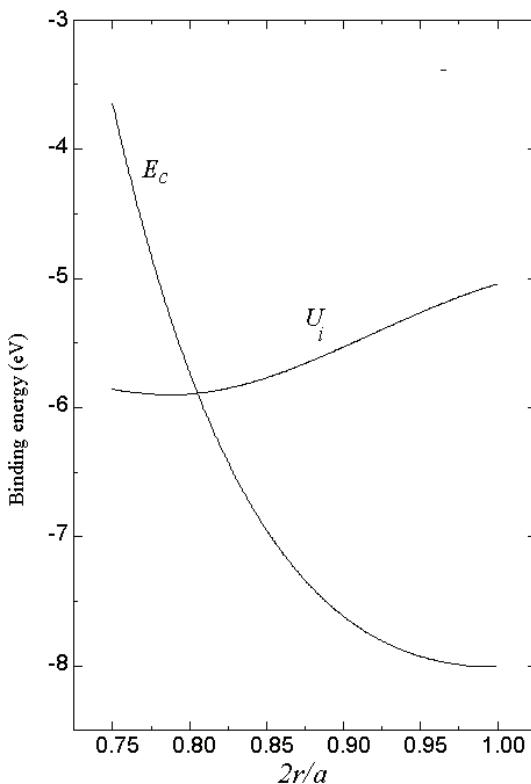


Fig. 6. Binding energy as a function of distance between Li and Br ions in the crystal (E_c) and in the molecule (U_i).

tion would appear more appropriate. See Fig. 6, which exemplifies the dependence of ion binding energy on the distance between Li and Br ions in the crystal and in the molecule.

3. Epitaxial Heterostructures

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 obtained⁶ if the grown film thickness is less than the so-called critical thickness (which is about several monolayers (ML) 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. Similar behavior is observed in epitaxial growth of ionic materials.⁷

Epitaxy is greatly assisted by similarity of the 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

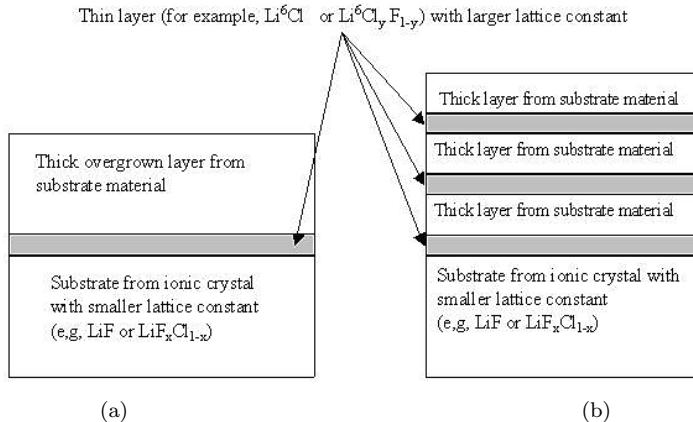


Fig. 7. Possible heterostructures involving thin compressed Li^6 -containing ionic layers.

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 (K)	Lattice compression a_s/a
LiF ($a_s/2 = 2.014 \text{ \AA}$)	Li^6Cl	9.7	4700	0.784
LiF ($a_s/2 = 2.014 \text{ \AA}$)	Li^6Br	3.1	14200	0.732
LiF ($a_s/2 = 2.014 \text{ \AA}$)	Li^6I	3.3	13600	0.671
NaF ($a_s/2 = 2.317 \text{ \AA}$)	Li^6I	2.7	13100	0.772
LiH ($a_s/2 = 2.04 \text{ \AA}$)	Li^6Cl	510	86	0.793
LiH ($a_s/2 = 2.04 \text{ \AA}$)	Li^6Br	3.3	14500	0.741
LiH ($a_s/2 = 2.04 \text{ \AA}$)	Li^6I	2.4	13000	0.680

lattice period. In fact, a thin (1–3 ML) working layer can be overgrown by a thick (10–100 ML) layer of substrate material forming thus a double heterostructure [see Fig. 7(a)] or even a multi-quantum well structure [Fig. 7(b)].

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 that the lattice constant of the compressed crystal is equal to that of the substrate, we estimated through Eqs. (24)–(25) the effective mass of lithium ion and Bose condensation temperature for some combinations. The results are shown in Table 3.

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 be of the order of several lattice constants.

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 tem-

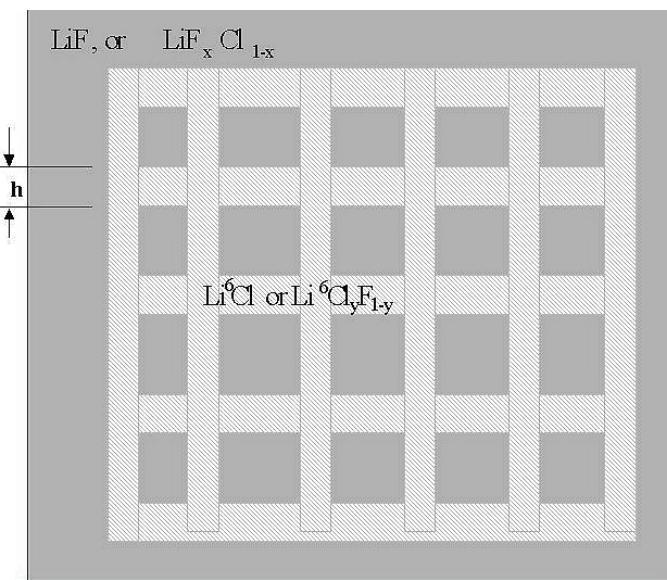


Fig. 8. Network of highly compressed patterned Li^6Cl epilayer.

peratures 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 course, that assumptions involved are valid).

In order to reduce the harmful effect of lattice misfit on epitaxial growth and minimize dislocation density in epilayers, it is better to use the solid solutions of ionic crystals as epilayers to be compressed. For example, on LiF substrate, the layer of $(\text{Li}^6\text{Cl})_{1-x}(\text{Li}^6\text{F})_x$ could be formed. As to the ionic density, the alloy $(\text{Li}^6\text{Cl})_{1-x}(\text{Li}^6\text{F})_x$ 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 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 even further, both members of heteroepitaxial composition can be made from solid alloys. As an illustration, let us take the following example. In the $\text{Li}^6\text{I}/\text{NaF}$ system, the lattice mismatch is about 22.8% ($a_s/a = 0.772$). Admixing Li^6F , we get the solid solution

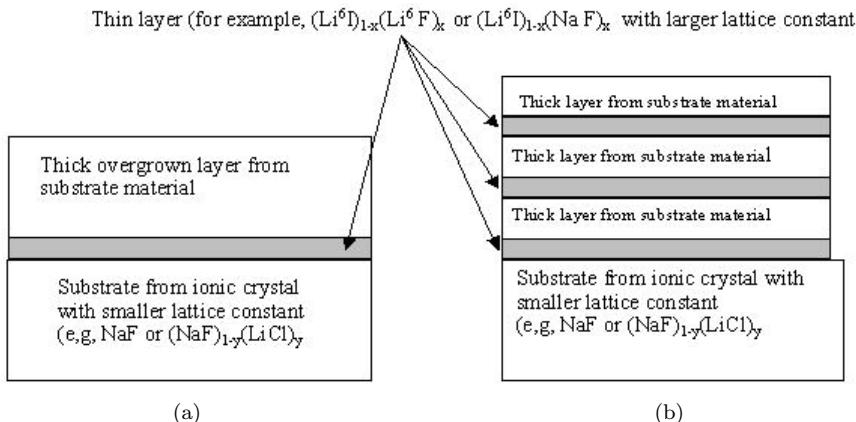


Fig. 9. Heterostructures formed from solid solutions.

$(\text{Li}^6\text{I})_{1-x}(\text{Li}^6\text{F})_x$. For $x < 0,5$, the electronic properties of the alloy will not, probably, differ substantially from that of pure 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 $(\text{Li}^6\text{I})_{1-x}(\text{Li}^6\text{F})_x$ 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 Li^6F and a is the lattice constant of Li^6I . For $x = 0,3$, we have $a_c = 2,7042 \text{ \AA}$, $a_s/a_c = 0,9014$. Under condition of equality of the lattice parameters in 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 Li^6I by 22,8%. Since this compression is excessively high (20% is sufficient), the substrate and thick compressing overlayers can also be made from solid solution, e.g., from $(\text{NaF})_{1-y}(\text{LiCl})_y$. as shown in Fig. 9.

Note also that ionic crystals can be compressed much more easily than semiconductors since their bulk moduli (B) are smaller ($B_{\text{LiI}} = 18.83$, $B_{\text{LiBr}} = 25.66$, $B_{\text{LiCl}} = 31.53$, $B_{\text{LiF}} = 69.8$ GPa⁸ and for example, $B_{\text{Ge}}/B_{\text{LiI}} \approx 4.4$). It means that in order to compress Li by 18%, the same pressure is required as for compression of Ge by 4%. In any case, the pressures to be applied are in excess of 50 GPa. It is, however, possible to reduce the magnitude of this pressure a few times. To this end, it is sufficient to fabricate the heterostructures with less than 10% lattice mismatch, which are more easily realizable in practice, and subject them to additional hydrostatic pressure. As an example, one can consider a thin layer of LiI on LiBr substrate or thin layer of LiBr on LiCl substrate. Other possible heteropairs are listed in Table 4.

It is possible to use $(\text{Li}^6\text{I})_x(\text{Li}^6\text{Br})_{1-x}$ instead of Li^6I and $(\text{Li}^6\text{Br})_x(\text{Li}^6\text{Cl})_{1-x}$ instead of Li^6Br .

Current technology allows us to obtain hydrostatic pressures in the range 8–100 GPa only in very small volumes using diamond anvils. For pressures less than

Table 4. Heterostructures with less than 20% misfit.

Substrate and thick overlayer material	Thin layer material	Lattice compression a_s/a
LiCl ($a_s/2 = 2.570 \text{ \AA}$)	Li^6I	0.857
NaF ($a_s/2 = 2.317 \text{ \AA}$)	Li^6Br	0.842
KF ($a_s/2 = 2.674 \text{ \AA}$)	Li^6I	0.891
LiBr ($a_s/2 = 2.751 \text{ \AA}$)	Li^6I	0.917
RbF ($a_s/2 = 2.815 \text{ \AA}$)	Li^6I	0.938
NaCl ($a_s/2 = 2.820 \text{ \AA}$)	Li^6I	0.940
LiCl ($a_s/2 = 2.570 \text{ \AA}$)	Li^6Br	0.934

8 GPa, the volume of the working chamber is almost unlimited. Therefore, it is reasonable to first try to fabricate the $\text{Li}^6\text{I}/\text{LiCl}$ or $(\text{Li}^6\text{I})_{1-x}\text{LiCl}_x/\text{LiCl}$ heterostructure (LiCl is a substrate) and then to subject it to hydrostatic compression with $P < 8 \text{ GPa}$.

4. 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 $10^{-7}\text{--}10^{-6} (\text{Ohm cm})^{-1}$ 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 also come 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, 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 the 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 300 K.

For more exact solution of the problem, it is necessary to find a periodic potential. Inserting this potential into the Schrödinger 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 $100 \times 100 \times 100$). As a preliminary, a complete system of lithium ion molecular wave functions must be constructed, and a method similar to that of Hartree–Fock has 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 of lithium and halogen, the wave function of lithium ion has 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 the overlap integral steeply increases during compression as long as the distance between oppositely charged ions in the crystal lattice is greater than the 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 the ion in the crystal is lower than the 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 the 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.^a

(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*

^aIt has been calculated in Ref. 9, for example, 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, the ion movements in crystals are possible at least in the conditions of structural transformation, and it will be interesting to look for ionic superconductivity under these conditions.

goes as follows. Since lithium ion is firmly sitting in the lattice site of ionic crystal and does not allow occupation of 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 the observed lattice parameter, elastic properties, dissociation energy and molecular size. The fact that the ion occupies the lattice site only means that the probability to find it in that place is high. The notion of the lattice site for Li⁶ 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 the binding energy of the ion in a molecule, the ions can be thought of as occupying lattice sites. In the opposite case, which is realized already at 18–20% compression, the potential reaches a minimum value not at a point but on the surface similar to the spherical surface in a molecule.

At present, it is difficult to state with any certainty 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 crystal substrates. Published experiments with other ionic materials⁷ have shown that pseudomorphic films (several monolayers thick) can be produced for layer/substrate mismatch up to 10%. It is hoped that the use of 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 Fig. 3, very high pressures (>50 GPa) are required in order to compress bulk crystals. In real experiments, it is always observed that disordering of crystalline structure of solids under high pressure is significantly increased. Then one may suspect that due to growth of irregularities in crystal lattice, the periodic ensemble of the latter will be greatly distorted. 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 an 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 one end of the ionic superconductor and fight with their excess at the other end. This peculiarity can be used to 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 the electric field is concentrated in thin near-contact regions (electrons from the metal cannot penetrate into the ionic superconductor, whereas ions from the former are unable to diffuse into the metal).

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^+ ions. Ohmic contacts can also be made from pure Li^+ metal, since in that case the Li^+ ions could probably tunnel from the metal into the ionic superconductor and vice versa. A closed frame made from ionic superconductor could probably replace the bulky windings of electric generators and motors. A cavity inside the 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 persists 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 recollect 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). The idea can be described as follows. If a spinning ring made from a superconductor is stopped, the charge carriers responsible for superconductivity keep on spinning and generate a magnetic field. In the 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, spin the superconductor above critical temperature, next cool it down and only then 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.

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 multiple experimental confirmations. However, the author is unaware as to the 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 and electrical properties of any substance at 10^{-40} K. It also seems that nobody has ever compressed ionic crystals with lithium isotope by 20% and more. 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 will be (super)conductive in doing experiments and discovering ionic superconductivity. Some additional information concerning ionic superconductivity can be found on the site www.v-ioffe.ru.

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