The metal-insulator transition and lattice distortion in semiconductors

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Abstract

A relation between the energy of an elementary ‘insulating’ excitation corresponding to the metal-insulator transition and the bandgap width in a semiconductor is obtained. An effect of atomic relaxation on the temperature and pressure dependence of the bandgap width is considered. It is shown that the metal-insulator transition in a semiconductor causes a weak rhombohedral or monoclinic distortion in the case of a diamond and zincblende structure and a weak tetragonal or orthorhombic distortion in the case of a rocksalt structure. A change in the bandgap associated with a ferroelectric (antiferroelectric) transition in a semiconductor is also obtained.

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Recent experiment on the detwinning of single crystals of iron pnictide superconductors by a weak uniaxial pressure [1] gives evidence for the metal-insulator transition in underdoped pnictide superconductors. Thus, iron pnictide superconductors are superconducting narrow bandgap semiconductors, similarly to the case of cuprate superconductors. Here we consider the metal-insulator transition in semiconductors, including superconducting semiconductors such as lead telluride, cuprates, ruthenates, and iron pnictides. In most of insulators and semiconductors, the energy $E_i(0)$ of an elementary ‘insulating’ excitation which determines the metal-insulator transition temperature is equal to the bandgap width $E_g(0)$ at zero temperature ($0 \, K$) [2]. Here we infer a more general relation between the energy of an elementary ‘insulating’ excitation and the bandgap width, which holds for such narrow bandgap semiconductors as lead chalcogenides and indium pnictides. We show that the temperature and pressure (in the high-pressure region) dependence of the bandgap in a semiconductor is caused by atomic relaxation associated with transverse optical modes. A change in the bandgap caused by structural transitions such as ferroelectric and antiferroelectric transitions is considered. The metal-insulator transition causes a weak lattice distortion of a ferroelastic type [3] in semiconductors with a diamond, zincblende, and rocksalt structure, which produces a decrease in the coordination number $z$. This weak ferroelastic distortion leads, for example, to a perfect cubic cleavage in single crystals of lead chalcogenides which depends on the temperature [4] and vanishes at the metal-insulator transition temperature $T_{MI}$.

According to a general criterion for phase transitions in crystalline solids [2], there is a general relation between the energy $E_i(0)$ of an elementary ‘insulating’ excitation at zero temperature ($0 \, K$) and the metal-insulator transition temperature $T_{MI}$ of the form

$$E_i(0) = \alpha k_B T_{MI},$$

(1)

where $k_B$ is the Boltzmann constant, and $\alpha = 18$.

An elementary insulating excitation is a collective many-particle excitation which invokes a local lattice distortion within a crystalline domain with a size of $d_c \approx 180 \, nm$ [2]. The energy $E_i(0)$ of an elementary insulating excitation is proportional to the bandgap width $E_g(0)$ at zero temperature ($0K$),

$$E_i(0) = k E_g(0).$$

(2)
In most of insulators and semiconductors, $k=1$. A hydrogen-like model with the (high-frequency) dielectric constant $\varepsilon$ accounting for many-body effects (the crystal structure and electron correlations) gives an estimation of the bandgap width $E_g$ in the form

$$E_g = \frac{Z^2}{\varepsilon^2}Ry,$$  \hspace{1cm} (3)

where $Z$ is the mean effective charge of ions (in the units of the electron charge $e$), and $Ry = 13.6eV$ is the Rydberg constant. A charge $Z$ is close to $Z = 3.5$ for diamond, silicon, and germanium, is close to $Z = 4.0$ for III-V semiconductors (GaAs, GaSb), and is close to $Z = 4.5$ for II-VI semiconductors (cadmium and zinc chalcogenides). In silica ($SiO_2$), the dielectric constant is $\varepsilon = 3.85$, and the bandgap width is $E_g (0) \approx 10eV$ [5], so that $Z \approx 3.5$, as in silicon. In $CaWO_4$ with a tetragonal crystal structure, the dielectric constant is $\varepsilon = 8$, and the bandgap width is $E_g (0) \approx 4.2eV$ [6], so that $Z \approx 4.5$, as in II-VI semiconductors. In cuprates and ruthenates, a charge $Z$ is close to $Z \approx 2$ ($La_2CuO_4$), or $Z \approx 2.5$ ($Ca_2RuO_4$) (see below).

In narrow bandgap semiconductors with a rocksalt and zincblende structure, the coefficient $k$ in the equation (2) is an integer number which is larger than 1. In lead chalcogenides, the value of the coefficient $k$ is close to the coordination number $z = 6$ in the rocksalt structure. In indium pnictides, InSb and InAs, the value of the coefficient $k$ is close to the coordination number $z = 3$ corresponding to a rhombohedral distortion of the zincblende structure.

In lead chalcogenides, the metal-insulator transition temperature $T_{MI}$ corresponds to a temperature at which their cubic cleavage vanishes [4]. The equation (1) gives the energy $E_i (0)$ of an elementary ‘insulating’ excitation, and the equation (2) gives the value of the coefficient $k$ for lead chalcogenides:

| Semiconductor | $E_g (0)$ (eV) | $T_{MI}$ (K) | $E_i (0)$ (eV) | $k$ |
|---------------|---------------|--------------|---------------|-----|
| PbS           | 0.29          | 935          | 1.45          | 5   |
| PbSe          | 0.165         | 640          | 0.99          | 6   |
| PbTe          | 0.19          | 610          | 0.95          | 5   |
The temperature dependence of the bandgap width \( E_g(T) \) and the high-frequency dielectric constant \( \varepsilon(T) \) in lead chalcogenides follows the relation (3) with \( Z=\text{const} \) [4].

The value of the photo-voltage in lead chalcogenide films (times the charge of an electron \( e \)) is determined by the energy \( E_i \) of an elementary insulating excitation and is much higher than the bandgap width \( E_g \) [4]. A non-radiative recombination in a semiconductor is connected with the creation of an elementary insulating excitation with a subsequent heating of the lattice in the process of the decay of this excitation. In the case of lead chalcogenides, the energy of an elementary insulating excitation is accumulated by the Auger recombination [4].

The energy \( E_i(T) \) of an elementary insulating excitation depends on the temperature \( T \) as follows [2]

\[
E_i(T) = E_i(0) - \beta k_B T. \tag{4}
\]

A dimensionless atomic relaxation constant \( \beta \) is normally close to 6. Its value is determined by the excitation of two transverse optical modes along the three crystallographic axes with a maximum value of the propagation vector \( q = q_{\text{max}} \). A decrease in the value of \( \beta \) to \( \beta = 5 \) in the case of cadmium chalcogenides is caused by the suppression of one of these atomic relaxation modes and can be attributed to a monoclinic lattice distortion associated with the metal-insulator transition. Similar is the case of silicon and germanium. In the case of zinc chalcogenides, the value of \( \beta \) is \( \beta = 6 \). This value corresponds to a rhombohedral or the c-axis distortion for a zincblende and hexagonal structure, respectively.

The equation (4) determines the temperature dependence \( E_g(T) \) of the bandgap width for most of semiconductors (with \( E_g = E_i \)). For indium antimonide InSb, \( k = 3 \), and the equations (2) and (4) give

\[
E_i = 3E_g = E_i(0) - \beta k_B T, \tag{5}
\]

so that the temperature dependence of the bandgap width in InSb is given by the equation

\[
E_g(T) = E_g(0) - \frac{1}{3} \beta k_B T \approx E_g(0) - 2k_B T, \tag{6}
\]
where \( \beta \approx 6 \).

The temperature dependence of the bandgap width in lead chalcogenides is anomalous and at low temperatures below \( T_0 \), where \( E_g(T) \) has a maximum, has the form

\[
E_g(T) = E_g(0) + \beta k_B T, \tag{7}
\]

where \( \beta \approx 5 \).

The temperature \( T_0 \) is determined by the equation

\[
E_i(T_0) = E_i(0) - \beta k_B T_0 = z_0 E_g(T_0) = 2 \left( E_g(0) + \beta k_B T_0 \right), \tag{8}
\]

where \( z_0 = 2 \) is a coordination number in an orthorhombically distorted rocksalt structure. Above \( T_0 \), the energy \( E_i(T) \) of an elementary insulating excitation in lead chalcogenides is proportional to the bandgap width \( E_g(T) \),

\[
E_i(T) = z_0 E_g(T) = 2 E_g(T). \tag{9}
\]

The \( E_i(T) \) dependence is given by the equation (8). The value of the temperature \( T_0 \) at which \( E_g(T) \) has a maximum is close to \( T_0 \approx 440K \) for PbTe, \( T_0 \approx 510K \) for PbSe, and \( T_0 \approx 680K \) for PbS [4].

An atomic relaxation constant \( \beta \) determines also a change in the bandgap width caused by a structural transition of a ferroelectric (antiferroelectric) type with the transition temperature (the Curie temperature) \( T_s \), in accordance with the equation

\[
E_g(0) - E_i(0) = \beta k_B T_s. \tag{10}
\]

Bismuth ferrite (\( BiFeO_3 \)) exhibits a metal-insulator transition at \( T_{MI} \approx 1200K \) and a ferroelectric transition at \( T_s \approx 1100K \) [7]. The equation (8) gives \( E_i(0) = 1.85eV \) (\( k = 1 \)) and the equation (10) with \( \beta \approx 6 \) gives \( E_g(0) \approx 2.4eV \). According to the equation (8) with \( \beta \approx 6 \), the bandgap width \( E_g(T_{MI}) \) just below the metal-insulator transition temperature \( T_{MI} \) is equal to \( E_g(T_{MI}) \approx 1.3eV \). Optical absorption measurements give the values \( E_g(0) \approx 2.5eV \) and \( E_g(T_{MI}) \approx 1.5eV \) [7].

Another perovskite compound, barium bismuthate (\( BaBiO_3 \)) undergoes a metal-insulator transition at \( T_{MI} = 893K \) and a structural transition of an antiferroelectric type at \( T_s = 425K \) [8]. The \( \alpha \) phase (below \( T_s \)) is monoclinic, the \( \beta \) phase (between \( T_s \) and \( T_{MI} \)) is
rhombohedral, and the $\gamma$ phase (above $T_{MI}$) is cubic. According to equations (1) and (10), $E_i (0) \approx 1.4eV$ and $E_g (0) \approx 1.6eV$.

Barium bismuthate doped with K, $Ba_{1-x}K_xBiO_3$, is a high-temperature superconductor of an improper (charge-ordered) type [1] with the maximum superconducting transition temperature $T_c = 30K$ at $x = 0.25$ [9]. Superconductivity in $Ba_{1-x}K_xBiO_3$ occurs only in a cubic metallic phase [9]. The corresponding charge gap in the superconducting phase is about $\Delta_{ch} \approx 0.05eV$ (see ref. 1). There are other superconducting semiconductors, such as $SrTiO_3$ (doped with Nb) [10] and $PbTe$ (doped with Tl) [11]. In the last case, the thallium doping seems to be equivalent to the doping with an additional non-stoichiometric Te, so that a composition $Pb_{1-x}Tl_xTe$ corresponds to a composition $PbTe_{1+x/2}$. The optimal doping level with a highest $T_c$ has not been achieved due to a low solubility limit of Tl ($x_0 = 0.015$). $PbTe_{1+\delta}$ should be a superconductor analogous to $FeSe_{1-\delta}$ [12].

Cuprates and ruthenates are also superconducting semiconductors. For example, $La_2CuO_4$ exhibits a metal-insulator transition (coinciding with an antiferromagnetic transition) at $T_{MI} = T_N = 240K$. The equation (1) gives the bandgap width of $E_g (0) = 0.37eV$. $La_2CuO_{4.093}$ is a high-temperature superconductor of an improper (charge-ordered) type with the superconducting transition temperature $T_c = 45K$ [13]. $Ca_2RuO_{4+\delta}$ undergoes a metal-insulator transition at $T_{MI} = 357K$ for $\delta = 0$ [14]. According to the equation (1), the bandgap width is $E_g (0) = 0.55eV$. The metal-insulator transition temperature $T_{MI}$ and the bandgap width $E_g (0)$ decrease with increasing $\delta$ [14] similarly to the case of cuprates. There should be the superconducting phase for sufficiently high $\delta$. Similar is the case of $Sr_2RuO_{4+\delta}$. Due to a larger atomic radius of Sr as compared with those of Ca, the non-stoichiometric oxygen is presumably present on interstitial sites in the superconducting $Sr_2RuO_4$. In $(Ca_{1-x}Sr_x)_2RuO_4$, the metal-insulator transition temperature $T_{MI} (x)$ goes to zero at $x_0 \approx 0.08$ [14]. There should be the superconducting phase in the region of doping $x \approx 0.01 - 0.02$. A decrease in the magnetic susceptibility $\chi (T)$ of $(Ca_{1-x}Sr_x)_2RuO_4$ at low temperatures in the doping range $x \approx 0.01 - 0.02$ is caused by the presence of the superconducting phase with $T_c \approx 10K$ for $x = 0.01$. Above $T_c$, the Curie law is valid [14],

$$\chi (T) \propto T^{-1}. \quad (11)$$

Recent experiment on the detwinning of single crystals of iron pnictide superconductors by a weak uniaxial pressure [1] shows that the samples have a multi-phase composition in the
underdoped region. The Co doping stabilizes the $Ba(Fe_{1-x}Co_x)_2As_2$ phases (products of the partial decomposition of $BaFe_2As_2$ should also be present). However, two phases coexist in the doping range between $x = 0.025$ and $x = 0.061$, an insulating antiferromagnetic phase with a low $x$, and a metallic superconducting phase with a high $x$. These two phases form an oriented quasi-two-dimensional epitaxial structure [15], which can explain the a-b anisotropy of the in-plane resistivity. The thickness of the monophase layers has an order of the radius of the atomic relaxation region, i.e. has an order of $8$ nm [16].

Both the metal-insulator transition temperature and the Neel temperature decrease with increasing doping level $x$, similarly to the case of $(Ca_{1-x}Sr_x)_2RuO_4$ [14]. Iron pnictide superconductors are superconducting semiconductors similarly to cuprate and ruthenate superconductors.

A weak uniaxial pressure in this experiment orients the quasi-two-dimensional epitaxial structure formed by the two phases of $Ba(Fe_{1-x}Co_x)_2As_2$ and changes relative volumes of the insulating and metallic phases (a partial superconducting transition for $x = 0.016$ and $x = 0.025$) [1].

The pressure dependence of the energy $E$ of an elementary excitation in the high-pressure region is given by the equation [16]

$$E(P) = E(0) - \alpha_P P / n_0,$$

where $n_0 \approx 1.1 \times 10^{22} cm^{-3}$ is a constant, $P$ is the pressure, and $\alpha_P$ is the atomic relaxation constant, $\alpha_P = 2$ for ferroelectric, antiferroelectric, and metal-insulator transitions.

This value of $\alpha_P$ is determined by the excitation of two transverse optical modes with $q = q_{max}$ along the polarization axis in the case of ferroelectric and antiferroelectric transitions and along the easy ferroelastic axis in the case of metal-insulator transitions (the axis along which a main lattice distortion associated with the metal-insulator transition is directed).

The value of the atomic relaxation constant $\alpha_P$ for ferromagnetic transitions is $\alpha_P = 4$ and corresponds to transverse optical modes with $q = q_{max}$ in the plane perpendicular to the magnetization vector.

The value of the atomic relaxation constant for the melting transition is $\alpha_P = 18$ and can be attributed to the excitation of three acoustical and three optical modes along the three crystallographic axes.
A weak ferroelastic distortion associated with the metal-insulator transition in semiconductors determines the shape of single crystals. Single crystals of diamond have an octahedral morphology due to a weak rhombohedral distortion associated with a high-temperature metal-insulator transition. Single crystals of lead chalcogenides have a simple cubic morphology due to a weak tetragonal (orthorhombic) distortion caused by the metal-insulator transition.

Similarly, a low-temperature ferroelastic transition with the transition temperature \( T_f \approx \theta_D/\alpha \), where \( \theta_D \) is the Debye temperature, \([17]\) produces a weak rhombohedral distortion in fcc metals, a weak tetragonal (or orthorhombic) distortion in bcc metals, and a weak c-axis distortion in hcp metals. In insulators, a low-temperature ferroelastic distortion corresponds to a relative expansion of the lattice at zero temperature and produces a negative thermal expansion below the ferroelastic transition temperature \( T_f \). For example, in \( MnF_2 \) a low-temperature ferroelastic transition occurs at \( T_f \approx 20K \) and is marked by a minimum in the temperature dependence of the unit cell volume \([18]\). The amplitude \( \delta = \Delta a/a \) (\( a \) is the lattice parameter) of a low-temperature ferroelastic distortion in \( MnF_2 \) is about \( \delta \approx 0.5 \times 10^{-4} \).

A relative expansion of the lattice in insulators with decreasing temperature below \( T_f \) is caused by interatomic repulsion at short interatomic distances (the Born-Mayer equation for the cohesive energy of ionic crystals \([19]\)).

In metals, a low-temperature ferroelastic distortion corresponds to a relative contraction of the lattice at zero temperature and produces a positive thermal expansion below \( T_f \). A ferroelastic distortion associated with the superconducting transition \([17]\) has an opposite sign and compensates this effect, so that an overall thermal expansion, for example, in \( MgB_2 \) is very small below the superconducting transition temperature \( T_c \) \([20]\).

To summarize, we show that there is a general relation between the energy of an elementary insulating excitation and the metal-insulator transition temperature which is valid for narrow bandgap semiconductors too. We give an estimation of the bandgap width in insulators and semiconductors. The temperature and pressure (in the high-pressure region) dependence of of the bandgap width is obtained. We show that there is a weak lattice distortion of a ferroelastic type associated with the metal-insulator transition in semiconductors.
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