Effect of charge ordering on superconductivity in high-temperature superconductors

Fedor V.Prigara

Institute of Physics and Technology, Russian Academy of Sciences,

21 Universitetskaya, Yaroslavl 150007, Russia[*]

(Dated: November 11, 2010)

Abstract

It is shown that charge ordering in layered crystalline metals causes an increase in the normal state energy of the conducting layers. If this increase in the energy exceeds the difference between the superconducting state energy and the normal state energy of the metal, then the superconducting transition occurs. A relation between the charge gap in the superconducting phase and the bandgap width in the undoped insulating phase of high-temperature superconductors is obtained.

PACS numbers: 74.20.-z, 71.30.+h, 71.45.Lr

Recently, it was shown [1] that charge ordering ('charge-density-wave') and superconductivity coexist in a layered pnictide superconductor $SrPt_2As_2$ related to the high-temperature iron pnictide superconductors, such as $Ba\left(Fe_{1-x}Co_x\right)_2 As_2$. Earlier, it was shown [2] that the charge gap is present in all high-temperature superconductors in which the maximum superconducting transition temperature T_c exceeds the transition temperature $T_f \approx \theta_D/\alpha$ of a low-temperature ferroelastic transition (here θ_D is the Debye temperature and $\alpha = 18$ is a constant). Here we consider an effect of charge ordering in layered crystalline metals on superconductivity with account for a ferroelastic distortion in the conducting layers induced by charge ordering in adjacent charge-ordered layers. Charge ordering is necessary for improper high-temperature superconductivity (with the transition temperature $T_c > T_f$), but it is not sufficient. All improper high-temperature superconductors (cuprates, iron pnictides, barium bismuthate doped with K, and possible high-temperature superconductors $Ca_2RuO_{4+\delta}$and $Sr_2RuO_{4+\delta}$) are superconducting semiconductors [3]. Here we obtain a relation between the charge gap in the superconducting phase and the bandgap width in the undoped insulating phase of improper high-temperature superconductors. We obtain also the value of the optimal doping level in hole-doped high-temperature superconductors and in electron-doped iron pnictide superconductors.

Charge ordering implies a local metal-insulator transition in some layers of a layered crystalline metal with an opening of the charge gap in the corresponding energy band. The energy bands associated with the conducting layers remain metallic. Charge ordering causes a ferroelastic lattice distortion in chrge-ordered layers corresponding to a relative expansion of the lattice at zero temperature (0 K) [3]. This ferroelastic distortion leads to a periodic lattice modulation due to a misfit between the lattice parameters of metallic layers and charge-ordered layers, respectively, below the charge ordering temperature T_s.

For a sinusoidal lattice modulation, the displacement u of atoms from their mean locations is given by the formula

$$u = u_0 sin\left(\frac{2\pi}{P}x\right), \tag{1}$$

where P is the period of the lattice modulation along the x-axis. The length l of a period of the sinusoid is given by the formula

$$l = P\left(1 + \frac{\pi^2 u_0^2}{P^2}\right). \tag{2}$$

Thus, the amplitude $\delta = (l - P)/P$ of a ferroelastic distortion along the x-axis is related to the amplitude u_0/P of the lattice modulation as follows

$$\delta = \frac{\pi^2 u_0^2}{P^2}. \tag{3}$$

The amplitude u_0 of the atomic displacement has an order of the Born-Mayer parameter $\rho = 0.036nm$ [4]. For example, in $Bi_2Sr_2CaCu_2O_{8+\delta}$, the amplitude of the atomic displacement is $u_0 = 0.04nm$ [5]. Since the period of the lattice modulation in $Bi_2Sr_2CaCu_2O_{8+\delta}$ along the a-axis (atoms are displaced from their mean locations in the c-axis direction) is $P = 2.6nm$, the relation (3) gives the amplitude of a ferroelastic a-axis distortion at a level of $\delta = 2.4 \times 10^{-3}$.

This value is close to $\delta_0 = a_0/d_c$, where $a_0 = 0.45nm$ has an order of the lattice parameter, and $d_c = 180nm$ is the size of a crystalline domain [2]. The amplitude of a ferroelastic distortion in $Bi_2Sr_2CaCu_2O_{8+\delta}$ has an order of the amplitude of ferroelastic fluctuations in the superconducting phase just below the transition temperature T_c [2].

In a layered tetragonal compound $LaAgSb_2$ which exhibits a charge-ordering ('charge-density-wave') transition at $T_s = 210K$ [6], the period P of the lattice modulation along the a-axis is $P = 16.6nm$. If the amplitude u_0 of the atomic displacement has an order of the Born-Mayer parameter $\rho = 0.036nm$, then the equation (3) gives the amplitude of the a-axis ferroelastic distortion at a level of $\delta \cong 0.5 \times 10^{-4}$ (or $\delta \cong \frac{1}{4}\rho/d_c$). Such is an order of the amplitude of a low-temperature ferroelastic distortion in metals and insulators [3, 7, 8].

A pnictide superconductor $SrPt_2As_2$ exhibits a charge-ordering ('charge-density-wave') transition at $T_s = 470K$ [1]. The amplitude δ of the orthorhombic distortion is

$$\delta = 2\frac{b - a}{b + a} \cong 0.011. \tag{4}$$

The period P of the lattice modulation along the a-axis is $P = 0.72nm$. The equation (3) gives an estimation of the amplitude u_0 of the atomic displacement in the form

$$u_0 \cong \frac{P}{\pi}\delta^{1/2} \cong 0.024nm, \tag{5}$$

or $u_0 \cong \frac{2}{3}\rho$, where ρ is the Born-Mayer parameter.

The energy pseudogap associated with a multi-band structure of the electronic spectrum (an analogue of the charge gap in layered compounds) can exist even in elemental metals. In *3d* transition metals, the *d*-band consists of two subbands [9], corresponding to e_g and t_{2g} states in the splitting by the crystal electric field picture [4]. The magnitude of the energy pseudogap in *3d* transition metals is about $0.5eV$. Magnetic ordering (in Cr, Mn, Fe, Co, and Ni) is associated with the filling of the upper subband. The 4-state subband (e_g states) stabilizes a bcc crystal structure, and the 6-state subband (t_{2g} states) stabilizes fcc and hcp crystal structures.

Absence of the superconducting transition down to zero temperature (T=*0 K*) in a metal means that the energy E_s of the superconducting state is higher than the energy E_n of the normal state due to the compensation of a low-temperature ferroelastic distortion in the superconducting phase [3]. (A low-temperature ferroelastic distortion causes a decrease in the value of the energy E_n of the normal state in metals).

The energy E of a layered crystalline metal is

$$E = E_1 + E_2 + E_{12}, \tag{6}$$

where E_1 is the energy of the charge-ordered layers, E_2 is the energy of the conducting layers, and E_{12} is the energy of interaction between these layers.

Charge ordering (a local metal-insulator transition in some layers) causes a decrease in the energy E_1 of the charge-ordered layers. However, the energy E_2 of the conducting layers increases due to a ferroelastic distortion in these layers induced by charge ordering in adjacent layers (the epitaxial strain effect), since a low-temperature ferroelastic distortion has opposite signs in metals and insulators [3]. If an increase ΔE_2 in the energy of the conducting layers exceeds the difference $E_{2s} - E_{2n}$ of the energies of the superconducting state and the normal state, respectively,

$$\Delta E_2 > E_{2s} - E_{2n}, \tag{7}$$

then the superconducting transition occurs.

A total energy E of a layered metal decreases (on cooling) both at the charge-ordering transition and at the superconducting transition.

A magnitude $\Delta_{ch}(0)$ of the charge gap at zero temperature $(0K)$ is related to the charge-ordering transition temperature T_s as follows [3]

$$\Delta_{ch}(0) = \alpha k_B T_s, \tag{8}$$

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

A ferroelastic distortion associated with the metal-insulator transition (and charge ordering) corresponds to a relative expansion of the lattice at zero temperature $(0K)$. In ZnO with a wurtzite crystal structure, the bandgap width $E_g(0)$ at zero temperature is $E_g(0) = 3.44eV$ [10], and the relation analogues to the equation (8) gives the metal-insulator transition temperature T_{MI} in the form $T_{MI} = E_g(0)/\alpha k_B = 2216K$. A ferroelastic distortion associated with this high-temperature metal-insulator transition in ZnO is a c-axis distortion. The c/a ratio increases with decreasing temperature ($c/a = 1.59$ at $T = 1500K$, and $c/a = 1.60$ at $T = 0K$). A ferroelastic distortion in the insulating phase produces a negative thermal expansion at low temperatures. A linear thermal expansion coefficient along the a-axis α_a is negative below $100K$, and a linear thermal expansion coefficient along the c-axis α_c is negative below $120K$ [10].

A relative expansion of the lattice at zero temperature $(0K)$ in insulators causes a decrease in the volume of the Brillouin zone. The valence band contracts, and the energy of a crystal decreases. Similar is the effect of a relative expansion of the lattice at zero temperature associated with the superconducting transition, due to the opening of the superconducting energy gap.

In metals, a relative contraction of the lattice at zero temperature causes an increase in the volume of the Brillouin zone, so that the conduction band expands on the energy scale, and the energy of the bottom of the conduction band decreases. As a result, the energy of a metal decreases due to a low-temperature ferroelastic distortion. A ferroelastic distortion associated with the superconducting transition compensates a low-temperature ferroelastic distortion in a meta [3], so that the energy E_s of the superconducting state can be both higher or lower than the energy E_n of the normal state.

A ferroelastic distortion associated with ferromagnetic or ferrimagnetic ordering normally corresponds to a relative expansion of the lattice at zero temperature, for example, in the nickel chromite spinel $NiCr_2O_4$ [11]. Antiferromagnetic ordering in insulators is normally associated with a relative contraction of the lattice at zero temperature, for example, in

manganese fluoride MnF_2 [7].

In optimally doped improper high-temperature superconductors, the superconducting transition coincides with the charge-ordering transition, so that a magnitude $\Delta_{ch}(0)$ of the charge gap at zero temperature is determined by the equation

$$\Delta_{ch}(0) = \alpha k_B T_c, \tag{9}$$

where T_c is the maximum superconducting transition temperature.

In narrow bandgap semiconductors, there is a relation between the energy $E_i(0)$ of an elementary insulating excitation, which determines the metal-insulator transition temperature T_{MI}, and the bandgap width $E_g(0)$ at zero temperature of the form [3]

$$E_i(0) = zE_g(0), \tag{10}$$

where z is the coordination number.

There is a similar relation between the bandgap width $E_g(0)$ in the undoped insulating phase and the charge gap $\Delta_{ch}(0)$ at zero temperature in the superconducting phase of improper high-temperature superconductors,

$$E_g(0) = z\Delta_{ch}(0). \tag{11}$$

The bandgap width $E_g(0)$ in the insulating phase (at zero temperature) is determined by the metal-insulator transition temperature T_{MI}, as given by the equation analogues to the equation (8),

$$E_g(0) = \alpha k_B T_{MI}. \tag{12}$$

For example, in $YBa_2Cu_3O_y$, the metal-insulator transition temperature is $T_{MI} = 410K$ at $y = 6.23$ [12], so that the bandgap width in the undoped insulating phase is $E_g(0) = 0.635eV$. The maximum superconducting transition temperature is $T_c = 92K$ at the optimal doping level of $p_m \cong 0.20$ (p is the number of holes per Cu atom), so that a magnitude of the charge gap in the superconducting phase is $\Delta_{ch}(0) = 0.14eV$. According to the equation (11), the coordination number is $z = 5$.

In $La_2CuO_{4+\delta}$, the metal-insulator transition temperature is $T_{MI} = 240K$ at $\delta = 0$, so that the bandgap width in the undoped insulating phase is $E_g(0) = 0.37eV$. The maximum

superconducting transition temperature is $T_c = 45K$ at the optimal doping level of $p_m \cong 0.20$ ($\delta = 0.093$) [13], so that a magnitude of the charge gap in the superconducting phase is $\Delta_{ch}(0) = 0.07eV$. The coordination number is $z = 5$.

In a hole-doped iron pnictide superconductor $Ba_{1-x}K_xFe_2As_2$, an extrapolated value of the metal-insulator transition temperature at $x = 0$ is $T_{MI} \cong 150K$ [3], so that $E_g(0) = 0.23eV$. The maximum superconducting transition temperature is $T_c = 38K$ at the optimal doping level of $p_m = 0.25$ [14], so that a magnitude of the charge gap in the superconducting phase is $\Delta_{ch}(0) = 0.06eV$. The coordination number, according to the equation (11), is $z = 4$.

In all these cases, a value p_m of the optimal doping level in a hole-doped improper high-temperature superconductor is related to the coordination number z as follows

$$p_m = 1/z. \tag{13}$$

According to the equation (11), this relation gives

$$\Delta_{ch}(0) = p_m E_g(0). \tag{14}$$

In $Ba(Fe_{1-x}Co_x)_2As_2$, the magnitude $\Delta_{ch}(0)$ of the charge gap was directly measured by means of scanning tunneling spectroscopy [15]. Experimental values of the charge gap are ranging from $24meV$ to $40meV$. Since the maximum superconducting transition temperature in this electron-doped iron pnictide high-temperature superconductor is $T_c = 23K$ [16], the equation (9) gives $\Delta_{ch}(0) = 36meV$. The magnitude $\Delta(0)$ of the superconducting gap is determined by the equation [17]

$$2\Delta(0) = \alpha_P \alpha k_B T_c, \tag{15}$$

where $\alpha_P = 3/8$ for layered high-temperature superconductors [2]. The equation (15) gives for $Ba(Fe_{1-x}Co_x)_2As_2$ $2\Delta(0) = 13meV$. This value agrees with experimental values of the superconducting gap [15].

The coordination number z for the transition metal atom in this compound is $z = 3$ [1]. Since the bandgap width $E_g(0)$in the undoped insulating phase is $E_g(0) = 0.23eV$ (see above), the charge gap $\Delta_{ch}(0)$in the superconducting phase is related to $E_g(0)$ in electron-doped iron pnictide superconductors as follows

$$E_g(0) = 2z\Delta_{ch}(0). \tag{16}$$

Due to a two-phase composition of the $Ba(Fe_{1-x}Co_x)_2As_2$ system even in the nearly optimally doped region [3,18], it is difficult to determine the optimal doping level in electron-doped iron pnictide superconductors. It seems that the mean optimal doping level $\bar{n}_m$ (n is the number of electrons per Fe atom) in these superconductors is given by the formula

$$\bar{n}_m = 1/(4z). \tag{17}$$

In $SrPt_2As_2$, only one of the two $PtAs$ layers within a unit cell is conducting and another $PtAs$ layer exhibits charge ordering [1]. If we assume that in the $Ba(Fe_{1-x}Co_x)_2As_2$ system only one of the two $FeAs$ layers within a unit cell is conducting and another $FeAs$ layer is charge-ordered, the a real optimal doping level n_m is

$$n_m = 2\bar{n}_m = 1/(2z). \tag{18}$$

In view of the equation (16), the last relation gives

$$\Delta_{ch}(0) = n_m E_g(0). \tag{19}$$

The equation (19) is analogues to the equation (14) for hole-doped high-temperature superconductors.

In a hole-doped iron pnictide superconductor $Ba_{1-x}K_xFe_2As_2$, the coordination number $z = 4$ can be attributed to the As atoms [1].

A pairing mechanism for high-temperature superconductivity as well as for low-temperature superconductivity is presumably the interaction of electrons with ferroelastic fluctuations. Ferroelastic fluctuations are always present in the superconducting phase of both low-temperature and high-temperature superconductors [2]. Antiferromagnetic fluctuations are also present in the superconducting phase [17], however, only in paramagnetic metals [2]. An improper high-temperature superconductor $Ba_{1-x}K_xBiO_3$ with $T_c = 30K$ [19] does not exhibit antiferromagnetic ordering in the undoped insulating phase.

To summerize, we show that charge ordering (a local metal-insulator transition) in some layers of layered high-temperature superconductors induces the superconducting transition

in adjacent conducting layers. The lattice modulation in layered high-temperature superconductors is produced by a misfit in the lattice parameters between the charge-ordered layers and the conducting layers.. There is a relation between the charge gap in the superconducting phase and the bandgap width in the undoped insulating phase of high-temperature superconductors. There is also a relation between the value of the optimal doping level and coordination number. In electron-doped iron pnictide superconductors, only one of the two $FeAs$ layers in a unit cell is conducting and another $FeAs$ layer is charge-ordered.

---

[1] K.Kudo, Y.Nishikubo, and M.Nohara, J.Phys. Soc. Jpn. (submitted), arXiv:1010.3950 (2010).

[2] F.V.Prigara, arXiv:1001.4152 (2010).

[3] F.V.Prigara, arXiv:1001.3061 (2010).

[4] V.S.Urusov, *Theoretical Crystal Chemistry* (Moscow University Press, Moscow, 1987).

[5] J.A.Slezak, J.Lee, M.Wang et al., Proc. Nat. Acad. Sci. USA **105**, 3203 (2008).

[6] S.L.Bud'ko, S.A.Law, P.C.Canfield, G.D.Samolyuk, M.S.Torikachvili, and G.M.Schmiedeshoff, J.Phys.: Condens. Matter **20**, 115210 (2008).

[7] R.Schleck, Y.Nahas, R.P.S.M.Lobo, J.Varignon, M.B.Lepetit, C.S.Nelson and R.L.Moreira, Phys. Rev. B **82**, 054412 (2010).

[8] D.T.Adroja, A.D.Hillier, P.P.Deen et al., Phys. Rev. B **82**, 104405 (2010).

[9] E.M.Sokolovskaya and L.S.Guzei, *Metal Chemistry* (Moscow University Press, Moscow, 1986).

[10] H.Morkoc and U.Ozgur, *Zinc Oxide: Fundamentals, Materials, and Device Technology* (Wiley-VCH, Berlin, 2009).

[11] H.Ishibashi and T.Yasumi, J.Magn. Magn. Mater. **310**, e610 (2007).

[12] Y.Wang and N.P.Ong, Proc. Nat. Acad. Sci. USA **98**, 11091 (2001).

[13] T.Hirayama, M.Nakagawa, and Y.Oda, Solid State Commun. **113**, 121 (1999).

[14] J.K.Dong, L.Ding, H.Wang, X.F.Wang, T.Wu, X.H.Chen, and S.Y.Li, New J.Phys. **10**, 123031 (2008).

[15] H.Zhang, J.Dai, Y.Zhang et al., Phys. Rev. B **81**, 104520 (2010).

[16] S.L.Bud'ko, N.Ni, and P.C.Canfield, Phys. Rev. B **79**, 220516(R) (2009).

[17] F.V.Prigara, arXiv:0708.1230 (2007).

[18] J.-H. Chu, J.G.Analytis, K.De Greve, P.L.McMahon, Z.Islam, Y.Yamamoto, and I.R.Fisher, arXiv:1002.3364 (2010).

[19] D.G.Hinks, B.Dabrowski, J.D.Jorgensen, A.W.Mitchell, D.R.Richards, S.Pei, and D.Shi, Nature **333**, 836 (1988).

---

* Electronic address: fprigara@recnti.uniyar.ac.ru