Energy pseudogaps and structural transitions in metals

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Abstract

It is shown that a structural transition in a metal is associated with the opening of the energy pseudogap in the electronic spectrum in a low-temperature phase below the transition temperature. A relation between the magnitude of the energy pseudogap in the d-band of transition metals (at zero temperature) and the structural transition temperature is similar to a relation between the magnitude of the superconducting gap and the superconducting transition temperature in low-temperature and high-temperature superconductors. A relation between the magnitude of the energy pseudogap and the structural transition temperature in sp-metals is similar to a relation between the bandgap width (at zero temperature) and the metal-insulator transition temperature in semiconductors.

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The superconducting transition is associated with the opening of the energy gap in the electronic spectrum at the Fermi level [1]. The magnitude of the superconducting gap $2\Delta_{sc}(0)$ at zero temperature ($T = 0K$) is proportional to the superconducting transition temperature $T_c$, the proportionality coefficient for high-temperature superconductors being twice with respect to those for low-temperature superconductors [2]. Here we show that a similar relation with the same coefficients exists between the magnitude $\Delta(0)$ of the energy pseudogap in the d-band of transition metals and the structural transition temperature $T_s$.

For sp-metals, a relation between the magnitude of the energy pseudogap (corresponding to a relative shift of the s- and p-bands with respect to each other) and the structural transition temperature is different and similar to a relation between the bangap width at zero temperature and the metal-insulator transition temperature in semiconductors. The bandgap width in the undoped insulating phase of high-temperature superconductors is close to the magnitude of the energy pseudogap in metals which form charge-ordered layers in these superconductors [3,4].

The magnitude $2\Delta_{sc}(0)$ of the superconducting gap at zero temperature ($T = 0K$) is related to the superconducting transition temperature $T_c$ by the equation [2]

$$2\Delta_{sc}(0) = \alpha_P \alpha k_B T_c,$$

where $\alpha_P$ is the atomic relaxation constant, $\alpha_P = 3/16$ for low-temperature superconductors and $\alpha_P = 3/8$ for high-temperature superconductors, $\alpha = 18$ is a constant, and $k_B$ is the Boltzmann constant.

The difference of the free energies of the normal state and the superconducting state, respectively, at zero temperature is given by the formula

$$F_n - F_s = \frac{1}{2} N(E_F) \Delta_{sc}^2(0) - E_{fe},$$

where $N(E_F)$ is the density of states at the Fermi level, and $E_{fe}$ is an increase in the energy of electrons caused by a general contraction of the conduction band produced by a ferroelastic distortion associated with the superconducting transition (the ferroelastic energy) [3]. The first term on the right side of the equation (2) is the condensation energy $E_0$ [1].

The density of states at the Fermi level $N(E_F)$ can be determined from the electronic specific heat coefficient $\gamma$ [5],

\[ \text{[Equation]} \]
\[ \gamma = \frac{2\pi^2}{3} N(E_F) k_B^2, \]  

so that the equation (2) takes a form

\[ F_n - F_s = \frac{3}{16\pi^2} (\alpha P alpha)^2 \gamma T_c^2 - E_{fe}. \]  

(4)

For type I superconductors, the difference of the free energies of the normal state and the superconducting state is related to the critical field \( H_c(0) \) at zero temperature by a thermodynamic formula [1]

\[ F_n - F_s = \frac{H_c^2(0)}{8\pi} V_m, \]  

(5)

where \( V_m \) is the molar volume.

A comparison of the equations (4) and (5) with experimental data for the electronic specific heat coefficient \( \gamma \) and the critical field \( H_c(0) \) at zero temperature for type I superconductors shows that the ferroelastic energy \( E_{fe} \) is normally small in low-temperature superconductors with a sufficiently high \( T_c \). For example, the \( E_{fe}/E_0 \) ratio is about 0.06 for Ru and Cd, so that the equation (4) gives for low-temperature superconductors with the atomic relaxation constant \( \alpha_P = 3/16 \)

\[ F_n - F_s \approx 0.216 \gamma T_c^2. \]  

(6)

If the ferroelastic energy \( E_{fe} \) exceeds the condensation energy \( E_0 \), then the superconducting transition does not occur [3].

The magnitude of the superconducting gap can be determined by means of scanning tunneling spectroscopy. The tunneling spectra of Fe(Se,Te) [6] show that there are two superconducting phases in this compound. The surface phase corresponds to a low-temperature superconductivity with the superconducting transition temperature \( T_{c1} = 11K \), the superconducting gap \( 2\Delta_1(0) = 3.4meV \), and the atomic relaxation constant \( \alpha_P = 3/16 \). The bulk phase corresponds to a high-temperature superconductivity with the superconducting transition temperature \( T_{c2} = 14.5K \), the superconducting gap \( 2\Delta_2(0) = 8.4meV \), and the atomic relaxation constant \( \alpha_P = 3/8 \). The surface phase has presumably a tetragonal crystal structure, and the bulk phase has a monoclinic structure [7]. The lattice constant of the surface phase \( a = 0.38nm \) corresponds to the tetragonal phase.
The d-band in transition metals is normally split into subbands due to structural transitions or ferroelastic distortions associated with ferromagnetic or antiferromagnetic ordering [3]. If the full magnitude \( \Delta (0) \) of the energy pseudogap is related to the structural transition temperature \( T_s \) by the equation

\[
\Delta (0) = \alpha_P \alpha k_B T_s,
\]

then the difference \( E_2 - E_1 \) of the energies of a high-temperature phase and a low-temperature phase, respectively, can be estimated from the formula similar to the equation (4),

\[
E_2 - E_1 \simeq \frac{3}{16\pi^2} (\alpha_P \alpha)^2 \gamma T_s^2.
\]

The difference of the energies of a high-temperature phase and a low-temperature phase at the structural transition temperature \( T_s \) is equal to the latent heat of the transition, \( \Delta H \),

\[
E_2 - E_1 = \Delta H.
\]

A comparison of the equations (8) and (9) with experimental data for electronic specific heat coefficient \( \gamma \) and the latent heat of the structural transition \( \Delta H \) in transition metals [8] shows that the atomic relaxation constant is \( \alpha_P = 3/8 \) for the hcp-bcc transition in Ti, Zr, and Hf, and also for the fcc-bcc transition in Ca and for the hcp-bcc transition in Sr. For most of structural transformations in transition metals, the atomic relaxation constant is \( \alpha_P = 3/16 \), for example, in the case of structural transitions in Mn, Fe, Co, and in rare earth metals.

The fcc-bcc transition in Ca and the hcp-bcc transition in Sr are d-band type transitions. A partial filling of the d-band in alkaline earth metals is supported by an enhanced paramagnetic susceptibility exceeding the Pauli paramagnetic susceptibility, contrary to the case of alkali metals.

In the case of the hcp-bcc transition in Ti at \( T = 1166K \), the electronic specific heat coefficient is \( \gamma = 3.45mJmol^{-1}K^{-2} \), and the equation (8) with the atomic relaxation constant \( \alpha_P = 3/8 \) gives \( E_2 - E_1 \simeq 4.2kJmol^{-1} \), whereas the latent heat of the transition is \( \Delta H = 4.0kJmol^{-1} \). In the case of the \( \alpha - \beta \) transition in Mn at \( T_s = 973K \), the electronic specific heat coefficient is \( \gamma = 10.6mJmol^{-1}K^{-2} \), and the equation (8) with the atomic relaxation constant \( \alpha_P = 3/16 \) gives \( E_2 - E_1 \simeq 2.18kJmol^{-1} \), whereas the latent heat of
the transition is $\Delta H = 2.23 kJ mol^{-1}$. The equation (7) gives the magnitude of the energy pseudogap $\Delta = 0.68 eV$ for the hcp-bcc transition in Ti, and $\Delta_1 = 0.28 eV$ for the $\alpha - \beta$ transition in Mn.

The hcp-bcc transition in Be is an sp-band type transition. In this case, the full magnitude $\Delta (0)$ of the energy pseudogap is determined by the equation

$$\Delta (0) = \alpha k_B T_s,$$

which is similar to a relation between the bandgap width $E_g (0)$ at zero temperature and the metal-insulator transition temperature $T_{MI}$ in semiconductors [3],

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

The difference $E_2 - E_1$ of the energies of a high-temperature phase and a low-temperature phase, respectively, for sp-band transitions is given by the equation

$$E_2 - E_1 \approx \frac{3}{16\pi^2} \alpha^2 \gamma T_s^2 \approx 6.1 \gamma T_s^2.$$  

In the case of the hcp-bcc transition in Be at $T_s = 1450 K$, the electronic specific heat coefficient is $\gamma = 0.22 mJ mol^{-1} K^{-2}$, and the equation (12) gives $E_2 - E_1 \approx 2.8 kJ mol^{-1}$, whereas the latent heat of the transition is $\Delta H = 2.1 kJ mol^{-1}$. The magnitude of the energy pseudogap in Be is $\Delta = 2.25 eV$, according to the equation (10). The sp-band transition in Be produces a low density of states at the Fermi level in the low-temperature hcp phase and, as a consequence, its diamagnetism.

The fcc-hcp transition in Sr is also an sp-band transition, however, the magnitude of the energy pseudogap in Sr is much smaller than in Be, $\Delta = 0.8 eV$. The fcc-hcp transition in Ce at $T_s = 115 K$ is an sp-band transition. Other structural transitions in Ce, the hcp-fcc transition and the fcc-bcc transition, belong to a d-band type with the atomic relaxation constant $\alpha_P = 3/16$.

Structural transitions of a d-band type in d-metals and f-metals invoke also a change in the structure of the sp-bands, so that the location of the Fermi level is different in a high-temperature phase and a low-temperature phase. The $\beta$ phase of Mn (of the Hume-Rothery type) is ‘nonmagnetic’ (the Mn atoms have no magnetic moments) [9], which corresponds to a fully filled 6-state d-subband and an empty 4-state d-subband. In the $\alpha$ phase of Mn (of
the Frank-Kasper type), the 6-state d-subband is split. \( \alpha - Mn \) exhibits antiferromagnetic ordering with the Neel temperature \( T_N = 95K. \)

The magnitude \( \Delta_{AFM} \) of the antiferromagnetic pseudogap is determined by the formula similar to the equation (10) [2],

\[
\Delta_{AFM} = \alpha k_B T_N. \tag{13}
\]

This equation gives for the \( \alpha \) phase of Mn \( \Delta_{AFM} = 0.148eV \), so that there is a relation

\[
2\Delta_{AFM} \cong \Delta_1, \tag{14}
\]

where \( \Delta_1 = 0.284eV \) is the energy pseudogap associated with the \( \alpha - \beta \) transition in Mn.

For antiferromagnetic fluctuations in the superconducting phase, there is a similar relation between the magnitude \( \Delta_{AFM}^* \) of the antiferromagnetic pseudogap and the magnitude \( 2\Delta_{sc}(0) \) of the superconducting gap [2],

\[
\Delta_{AFM}^* \cong 2\Delta_{sc}(0). \tag{15}
\]

In view of the equations (13) and (1), this relation gives the temperature \( T_{AFM}^* \) of the maximum of antiferromagnetic fluctuations in the superconducting phase in the form [2]

\[
T_{AFM}^* \approx \alpha_P T_c. \tag{16}
\]

At the temperature \( T_{AFM}^* \), there is a peak (a shoulder feature) in the temperature dependence of the specific heat, for example, in the low-temperature superconductor \( KFe_2As_2 \) [10] with the superconducting transition temperature \( T_c = 3.7K \) and the atomic relaxation constant \( \alpha_P = 3/16. \) A similar peak in the specific heat at the temperature \( T_{AFM}^* \) was observed in the high-temperature iron pnictide superconductor \( Ba_{1-x}K_xFe_2As_2 \) [11] with the superconducting transition temperature \( T_c = 38K \) and the atomic relaxation constant \( \alpha_P = 3/8. \)

The bandgap width \( E_g(0) \) in the undoped insulating phase of high-temperature superconductors is normally close to the magnitude of the energy pseudogap in metals which form charge-ordered layers in these superconductors. The bandgap width \( E_g(0) \) is determined by the equation (11). In \( YBa_2Cu_3O_y \) with the superconducting transition temperature \( T_c = 92K \), the metal-insulator transition temperature in the undoped phase is \( T_{MI} = 410K \).
[12], so that \( E_g(0) = 0.635 \text{eV} \). The magnitude \( \Delta \) of the energy pseudogap associated with the hcp-fcc transition in Y at \( T_s = 1753K \), according to the equation \[7\] with the atomic relaxation constant \( \alpha_P = 3/16 \), is \( \Delta = 0.51 \text{eV} \).

In \( La_2CuO_4+\delta \) with the superconducting transition temperature \( T_c = 45K \) [13], the metal-insulator transition temperature in the undoped phase is \( T_{MI} = 240K \), and \( E_g(0) = 0.37 \text{eV} \). The magnitude \( \Delta \) of the energy pseudogap associated with the fcc-bcc transition in La at \( T_s = 1133K \) is \( \Delta = 0.33 \text{eV} \) (the atomic relaxation constant is \( \alpha_P = 3/16 \)).

In the possible high-temperature superconductor \( Ca_2RuO_4+\delta \), the metal-insulator transition temperature in the undoped phase is \( T_{MI} = 357K \) [14], so that \( E_g(0) = 0.55 \text{eV} \). The magnitude \( \Delta \) of the energy pseudogap associated with the fcc-bcc transition in Ca at \( T_s = 716K \) is \( \Delta = 0.42 \text{eV} \) (the atomic relaxation constant is \( \alpha_P = 3/8 \)).

In the electron-doped iron pnictide superconductor \( Ba(Fe_{1-x}Co_x)_2As_2 \) with the superconducting transition temperature \( T_c = 23K \) [15], the metal-insulator transition temperature in the undoped phase is \( T_{MI} \approx 150K \) (an extrapolated value) [3, 16], and \( E_g(0) = 0.23 \text{eV} \). The magnitude \( \Delta \) of the energy pseudogap associated with the hcp-fcc transition in Co at \( T_s = 700K \) is \( \Delta = 0.20 \text{eV} \) (the atomic relaxation constant is \( \alpha_P = 3/16 \)).

To summarize, we show that structural transitions in metals are associated with changes in their electronic structure. We obtain a relation between the magnitude of the energy pseudogap in a low-temperature phase and the structural transition temperature for sp-band type and d-band type transitions. In the case of d-band type transitions, this relation is similar to a relation between the magnitude of the superconducting gap at zero temperature and the superconducting transition temperature in low-temperature and high-temperature superconductors. The sp-band type transitions in metals are similar to the metal-insulator transition. The energy pseudogaps in metals which form charge-ordered layers in high-temperature superconductors determine the bandgap width in the undoped insulating phase of these superconductors.

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