Charge gap and ferroelastic lattice distortion in high-temperature superconductors

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(Dated: November 7, 2008)

Abstract

It is shown that a ferroelastic lattice distortion is associated with the superconducting transition both in low- and high-temperature superconductors. A low-temperature ferroelastic transition in crystalline solids produces also a maximum in the temperature dependence of their thermal conductivity. In layered tetragonal superconductors with a sufficiently high transition temperature, a ferroelastic distortion is improper and is caused by an out-of-plane charge ordering. The relation between the out-of-plane charge gap and the maximum superconducting transition temperature for these superconductors is obtained.

PACS numbers: 74.20.-z, 63.70.+h, 66.70.+f
A ferroelastic transition in a crystalline solid produces a spontaneous temperature-dependent lattice distortion below the transition temperature $T_f$ [1]. A ferroelastic lattice distortion is normally improper and is associated with phase transitions of various types in crystalline solids such as ferroelectric and antiferroelectric transitions [2], ferromagnetic (magnetostriction) and antiferromagnetic transitions [2,3], and metal-insulator transitions. In the last case, a ferroelastic lattice distortion is a secondary effect of charge ordering (e.g., metal-insulator transitions in $BiFeO_3$ [4], $Fe_3O_4$ [5], $BaVS_3$ [6], $Ca_2RuO_4$ [7], $LiRh_2O_4$ [8], $LaMnO_3$ [9]). Here we show that the superconducting transition both in low- and high-temperature superconductors is also associated with a ferroelastic lattice distortion. In anisotropic (layered) high-temperature superconductors (cuprate [10] and pnictide [11] superconductors) with a sufficiently high transition temperature $T_c$, this ferroelastic lattice distortion is improper and is due to an out-of-plane charge ordering. The relation between the out-of-plane charge gap $\Delta_{ch}$ and the maximum superconducting transition temperature $T_c$ for cuprate and pnictide superconductors can be inferred from a general criterion of phase transitions in crystalline solids based on a concept of the critical number density of elementary excitations [12]. We show also that there is a proper low-temperature ferroelastic transition in crystalline solids which produces a maximum in the temperature dependence of their thermal conductivity. Low-temperature ferroelastic transitions in crystalline solids are consequences of a general trend of lowering crystal symmetry with decreasing temperature [13].

Recently, it was shown [12,14] that, for phase transitions in crystalline solids, there is a general relation between the energy $E_0$ of an elementary excitation and the transition temperature $T_c$ of the form

$$E_0 = \alpha T_c,$$  \hspace{1cm} (1)

where $\alpha \approx 18$ is a quantum constant. Here the Boltzmann constant $k_B$ is included in the definition of the temperature $T$.

The energy $E_f$ of an elementary ferroelastic excitation for a proper ferroelastic transition is equal to the energy $\hbar \omega$ of the optical phonon corresponding to the ferroelastic lattice distortion. The last energy has an order of the Debye temperature $\Theta_D$, so that

$$E_f \approx \Theta_D.$$  \hspace{1cm} (2)
Now the equation (1) gives the ferroelastic transition temperature $T_f$ for a proper ferroelastic transition in the form

$$T_f \cong \Theta_D / \alpha.$$ (3)

There is a low-temperature maximum in the temperature dependence of the thermal conductivity $k(T)$ for crystalline solids, both metals and insulators [2]. The location of this maximum $T_m$ is close to the transition temperature $T_f$ of the low-temperature ferroelastic transition as given by the equation (3), so that

$$T_m \approx T_f \cong \Theta_D / \alpha.$$ (4)

For example, in diamond, the Debye temperature is $\Theta_D = 1860K$ and the temperature of the thermal conductivity maximum is $T_m \approx 100K$ [2], in accordance with the relation (4). In copper (Cu), the Debye temperature is $\Theta_D = 310K$ and the maximum of the thermal conductivity is located at $T_m \approx 17K$ [2]. In gallium arsenide (GaAs), the Debye temperature is $\Theta_D = 355K$ and the maximum of the thermal conductivity occurs at $T_m \approx 20K$ [15].

The lattice thermal conductivity $k$ of a crystalline solid is proportional to the heat capacity $c_V$ per unit volume, the mean speed of sound $v_s$, and the mean free path $l_{ph}$ of a phonon, as given by the equation [2]

$$k = (1/3) c_V v_s l_{ph}.$$ (5)

Below the temperature of the thermal conductivity maximum $T_m \approx T_f$, the scattering of phonons is produced by ferroelastic domain boundaries, so that the mean free path of a phonon is approximately constant, $l_{ph} \cong const$, and the temperature dependence of the thermal conductivity $k(T)$ is determined by the temperature dependence of the heat capacity $c_V$,

$$c_V = (12/5) \pi^4 n k_B (T/\Theta_D)^3,$$ (6)

where $n$ is the number density of atoms. Thus, $k(T) \propto T^3$ in this temperature range, except for the region of very low temperatures where the electron thermal conductivity dominates in the case of metals.
In copper (Cu), the mean speed of sound (in the Debye model) is $v_s = 2.6\, \text{km/s}$ and the maximum value of the thermal conductivity $k_m = 50\, \text{W/cmK}$ (at $T_m \approx \Theta_D/\alpha$) gives an estimation of the mean free path of a phonon below $T_m$ at the level of $l_{ph} \approx 0.1\, \text{mm}$. Cu has an fcc crystal structure. The ferroelastic lattice distortion in Cu below the temperature of the thermal conductivity maximum $T_m \approx T_f$ is presumably rhombohedral (many metals, such as Co, Ti, Zr, rare earth metals, have a low-temperature hcp phase and high-temperature fcc and bcc phases). Note that, due to the Wiedemann-Franz law, the low-temperature maximum in the thermal conductivity of metals cannot be attributed to the electron thermal conductivity, since there is no maximum in the electrical conductivity of metals at these temperatures.

The temperature-dependent ferroelastic lattice distortion $\delta = \Delta a/a$ (where $a$ is a lattice parameter), which is increasing with the decreasing temperature, gives a negative contribution to the thermal expansion coefficient $\alpha_L = (1/L) dL/dT$ (where $L$ is a linear size of a crystal sample), similarly to magnetostriction in ferromagnetic alloys, and can produce an overall negative thermal expansion. Such is the case in gallium arsenide (GaAs) below 55 K [15] and in silicon (Si) at low temperatures. Since the linear thermal expansion coefficient $\alpha_L$ has an order of $10^{-6}\, \text{K}^{-1}$ in GaAs and Si at low temperatures, the maximum lattice distortion is rather small, $\delta < 10^{-4}$.

A negative thermal expansion is also observed in some superconductors (MgB$_2$, Ta) below the superconducting transition temperature $T_c$ [16] and is indicative of a temperature-dependent ferroelastic lattice distortion associated with the superconducting phase transition.

There is a close relation between superconductivity and low-temperature ferroelastic transitions, since the superconducting state is produced by the interaction between the electrons and lattice excitations. In the case of a proper ferroelastic lattice distortion associated with the superconducting transition, the energy $E_s$ of an elementary superconducting excitation is close to the energy $E_f$ of an elementary ferroelastic excitation, so that

$$E_s = \alpha T_c \approx E_f \approx \Theta_D.$$  \hspace{1cm} (7)

The equation (7) gives the relation between the maximum superconducting transition temperature $T_c$ and the Debye temperature in the form

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\[ T_c \cong \Theta_D / \alpha. \] (8)

In cuprate and pnictide superconductors, the superconducting transition temperature depends on the doping level and on deviations from the stoichiometric composition. The equation (8) corresponds in these cases to the maximum transition temperature which is achieved at the optimal doping level.

The relation (8) is valid for many superconductors, both low- and high-temperature ones, such as \( MgB_2 \) \( (T_c = 39 K, \Theta_D = 800\pm80 K) \) [12], \( Pr_2Ba_4Cu_7O_{15-\delta} \) \( (T_c = 16 K, \Theta_D = 340 K) \) [17], \( Pb \) \( (T_c = 7.2 K, \Theta_D = 90 K) \), \( Hg \) \( (T_c = 4.15 K, \Theta_D = 96 K) \), and many other elemental superconductors (see data on the maximum transition temperature achievable in elemental superconductors under pressure in Ref. 18).

The relation (8) seems to be valid in electron-doped cuprate superconductors [17]. However, in hole-doped cuprate superconductors [19] and in recently discovered pnictide superconductors [11], the maximum transition temperature \( T_c \) normally exceeds the value given by the equation (8). For example, in \( Ba_{0.5}K_{0.5}Fe_2As_2 \), the Debye temperature is \( \Theta_D = 246 K \), whereas the transition temperature is \( T_c = 38 K \) [11].

The properties of pnictide superconductors are similar to those of previously known high-temperature superconductors. For example, the temperature dependence of heat capacity \( c(T) \) in \( Ba_{0.5}K_{0.5}Fe_2As_2 \) [11] exhibits a broad maximum at the temperature \( T_{AFM}^* = \alpha_P T_c \approx 14 K \), where \( \alpha_P \approx 3/8 \) is the atomic relaxation constant [12]. This maximum in the temperature dependence of the heat capacity is caused by the contribution from antiferromagnetic fluctuations in the superconducting phase [12]. There is a similar maximum in the \( c(T) \) dependence below \( T_c \) in \( MgB_2 \) [16].

The value of the atomic relaxation constant \( \alpha_P \approx 3/8 \) is characteristic for high-temperature superconductors and can be attributed to their anisotropic layered crystal structure. In isotropic low-temperature superconductors, the value of the atomic relaxation constant is \( \alpha_P \approx 3/16 \) [12]. The in-plane penetration depth \( \lambda_{ab} \) in pnictide superconductors [20] has an order of the size of a crystalline domain \( d_c \), \( \lambda_{ab} \cong d_c \approx 180 nm \) [12], as is the case in other high-temperature superconductors.

In layered high-temperature superconductors with \( T_c > \Theta_D / \alpha \), a ferroelastic lattice distortion is improper and is caused by an out-of-plane charge ordering. In this case, the energy \( E_f \) of an elementary ferroelastic excitation is close to the magnitude of the out-of-
plane charge gap $\Delta_{ch}$, so that

$$E_s = \alpha T_c \approx E_f \approx \Delta_{ch},$$

and the maximum superconducting transition temperature $T_c$ is determined by the relation

$$T_c \approx \Delta_{ch}/\alpha.$$ 

The out-of-plane charge gap has been directly observed in the scanning tunnelling microscopy measurements performed on single crystals of a hole-doped cuprate superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$ in the direction perpendicular to the $CuO_2$ planes [10]. There is a modulation in the measured gap due to the lattice modulation with a period of $2.6\text{nm}$ along the orthorhombic a-axis (atoms are displaced in the c-axis direction). There is also a disorder in the gap maxima which occurs in association with the non-stoichiometric dopant oxygen atom locations, with gap values strongly increased in their vicinity. If the maximum transition temperature is $T_c \approx 80K \approx 7\text{meV}$ for these samples, then the energy $E_s$ of an elementary superconducting excitation is $E_s = \alpha T_c \approx 0.125\text{eV}$ and is close to the maximum measured mean charge gap $\Delta_{ch} = 0.114\text{eV}$. The last value does not include the disorder in the charge gap maxima ranging up to $0.140\text{eV}$.

The out-of-plane charge gap $\Delta_{ch}$ seems to be related to the out-of-plane Coulomb gap studied theoretically in Ref. 21.

With the enhancement of the distance between the $CuO_2$ planes in hole-doped cuprate superconductors, the out-of-plane charge gap $\Delta_{ch}$ tends to increase, and so does the maximum transition temperature $T_c$, in accordance with the relation (10). The record transition temperatures were achieved in multi-layered $Hg$-based cuprate oxides [18].

To summarize, we show that, due to the lowering of crystal symmetry with decreasing temperature, a low-temperature ferroelastic transition in crystalline solids occurs producing a maximum in the temperature dependence of their thermal conductivity. Superconductivity is closely related to low-temperature ferroelastic transitions in crystalline solids, the maximum superconducting transition temperature being close to the corresponding ferroelastic transition temperature. This ferroelastic transition is proper in the case of low-temperature superconductors and some high-temperature superconductors such as magnesium diboride. For most of high-temperature superconductors, the corresponding ferroelastic transition is
improper and is caused by an out-of-plane charge ordering. There is a direct experimental evidence for this out-of-plane charge gap in hole-doped cuprate superconductors.

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