Pressure dependence of T_c and the van Hove scenario of high-T_c superconductivity

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The critical temperature of high-T_c superconductors changes under the application of high pressure. We discuss, within the van Hove scenario of high-T_c superconductivity, the effect of pressure on T_c. In this scenario a maximum T_c is achieved when the Fermi energy coincides with the van Hove singularity in the density of states. The application of pressure is assumed to have two major effects: First it changes the interatomic distances and thus the transfer integrals, having an effect on the density of states. Second, pressure application causes a redistribution of charge carriers, thereby increasing the number of holes in the CuO planes, which causes a change of the Fermi energy. The latter effect turns out to be the most important in order to explain the existence of a maximum, while the former influences dT_c/dP at both sides of the maximum, leading to an asymmetric $T_c(P)$, as observed experimentally.

I. INTRODUCTION

The CuO planes undoubtedly play a crucial role in the behavior of the high-temperature superconductors, in both the superconductive and normal states. The charge carriers in the CuO planes are in the tight-binding limit, hopping from site to site, feeling a strong short-range repulsion. Noninteracting particles in two dimensions with merely nearest-neighbor hopping have a very simple dispersion,

$$\epsilon(\mathbf{k}) = -2t[\cos(k_x a_x) + \cos(k_y a_y)] ,$$

where t is the hopping integral and $a_{x,y}$ are the lattice constants. This dispersion has saddle points at the momenta $\mathbf{k}=(0,\pm\pi/a_y)$ and $\mathbf{k}=(\pm\pi/a_x,0)$, leading to a logarithmic van Hove singularity in the density of states $N(E)$. Hopping further than nearest neighbors and the presence of interactions do not remove the singularity, merely its shape and position are modified.

The existence of this singularity may be crucial for a proper description of the physics of the CuO planes. Indeed it has been shown[1] that a simple reformulation of BCS theory, with a van Hove singularity near the Fermi energy as the only new ingredient as compared to the standard formulation, leads to quantitatively different results. The critical temperature can be much higher than in the standard formulation, arriving at its maximum value when the Fermi energy coincides with the van Hove singularity, while the isotope effect for phonon superconductors under this condition is minimal and smaller than in the standard BCS theory. The dependence of T_c on the distance of the Fermi energy to the van Hove singularity possibly explains the doping dependence of T_c in the high-temperature superconductors. Recently it was confirmed by specific-heat measurements that the Fermi level is close to a van Hove singularity in $YBa_2Cu_3O_{7-y}$.[2] Also, a short coherence length, as observed in the high-T_c materials, is naturally obtained in the van Hove scenario.[3] Furthermore, with E_F close to the van Hove singularity, the lifetime from electron-electron interactions depends approximately linearly on the frequency and the temperature, rather than the quadratic dependences of Fermi-liquid theory with a parabolic dispersion.[4] Such a linear dependence is observed in the high-temperature superconductors, most prominently in the linear-in-temperature resistivity of the normal state up to several hundred degrees K.

It is well known that T_c of the high-temperature superconductors changes under the application of a high pressure.[5,7] Generally, it is observed that T_c has a maximum as a function of pressure. In many experiments, the initial increase of T_c is steeper than the decrease in the very high-pressure regime. We shall show that such a behavior can be obtained by the van Hove scenario with the assumption that pressure has two main effects: First, the application of pressure changes the distance between the atoms, and therefore the overlap integrals. Volume changes of the order of 25% have been observed. Second, due to a change in the electrostatics of the problem,[8] a redistribution of the charge carriers occurs, leading to an increase of the number of holes in the CuO planes, coming from the chains or other than CuO planes. These two effects lead, within the van Hove scenario, to a change of the critical temperature, as we shall discuss below.

II. PRESSURE DEPENDENCE OF T_c

In Fig. 1, some experimental data on $YBa_2Cu_4O_8$, obtained by the Amsterdam high-pressure group,[5] are shown. The critical temperature clearly has a maximum as a function of the applied pressure. For a number of compounds, especially $YBa_2Cu_4O_8$, one observes an initially positive dT_c/dP which subsequently becomes smaller or even negative, as in Fig. 1. In other materials also an always negative dT_c/dP is observed. Rather flat curves are often observed with samples that have a relatively high T_c. Often the reported data seem to lie on asymmetric curves, with $|dT_c/dP|$ smaller at the highest pressures. We concentrate mainly on the data on $YBa_2Cu_4O_8$ and shall show that such a behavior can be obtained within the van Hove scenario of superconductivity.

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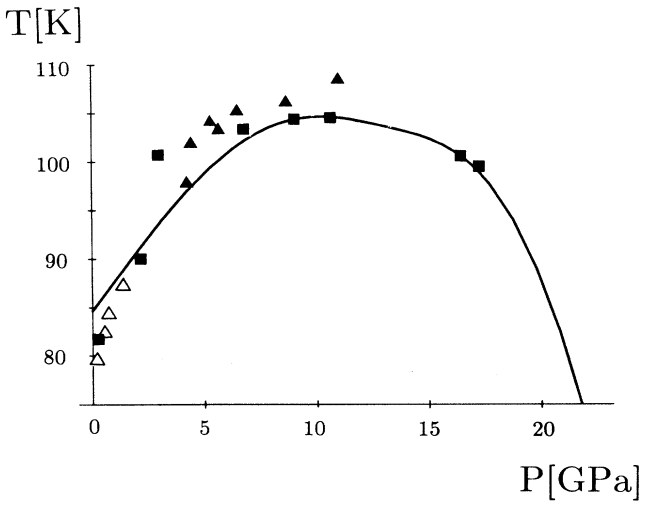

FIG. 1. Experimental data of T_c as a function of pressure up to 18 GPa. Taken from Ref. 5: squares, Scholtz *et al.*; solid triangles, van Eenige *et al.*; open triangles, Bucher *et al.* The curve follows from the van Hove scenario, explained in this paper.

In the calculation of the critical temperature, either by taking the zero gap limit of BCS theory, or by calculating the Cooper instability of the normal state, a usually innocent approximation is made. Namely, one can approximate $\epsilon(\mathbf{k})$ integrals over a density of states $N[\epsilon(\mathbf{k})]$, multiplied by some other expression that is peaked near E_F, by taking the density of states at E_F in front of the integral. When a peak in the density of states occurs near the Fermi energy, however, this approximation fails. By taking properly into account that the density of states is not structureless, one finds an approximate expression for T_c that differs from the standard BCS expression.[6]

$$T_c = 1.36D \exp\left\{-\left[\frac{2}{N_0 V}+\left[\ln\frac{D}{\omega_D}\right]^2 -1+\frac{\delta^2}{2}\left[\frac{1}{4k_B^2T_c^2}+\frac{1}{\omega_D^2}\right]\right]^{1/2}\right\}. \quad (1)$$

Here the parameter $\delta = E_F - E_{\mathrm{VHS}}$, E_{VHS} is the energy at which the van Hove singularity is located, $D = 16t\sqrt{1-(2t_2/t)}$, where t and t_2 are the nearest-neighbor and next-nearest-neighbor hopping integrals, with $2t_2/t < 1$, and V is a BCS interaction, cut off at a frequency ω_D. N_0 is a constant density of states (basically a normalization factor), and *not* $N(E_F)$, given by $N_0 = 8/(\pi^2 D)$. The maximum value of T_c achieved for $\delta = 0$. This maximum is higher than in standard BCS: For $\delta = 0$, and in the weak-coupling limit, the first term under the square root dominates. The argument of the exponential is proportional to $\sqrt{1/V}$ rather than $1/V$ favoring a larger T_c. Furthermore, whatever the boson responsible for the superconductivity is, the prefactor is of the order of the bandwidth rather than ω_D, which is effective in raising T_c compared to standard BCS in case ω_D is small. With ω_D absent as a prefactor in (1), the isotope effect for phonon superconductors is reduced.

Application of pressure has several effects: First, it changes the distances between the atoms in the sample. In the relevant pressure regime the relative distance change is proportional to the applied pressure, the proportionality constant being the linear compressibility. Estimates of the linear compressibilities in the a, b, and c directions of $YBa_2Cu_4O_8$ are 3.0×10^{-3}/GPa, 1.5×10^{-3}/GPa, and 4.0×10^{-3}/GPa, respectively.[7] Similar values apply to $YBa_2Cu_3O_{7-y}$. The closer the atoms come together, the larger the overlap integrals, so the larger the hopping elements t and t_2. The lattice parameters change relatively little under pressures up to 20 GPa, 6% in the a direction and 3% in the b direction. Despite the small changes of the lattice constants, the overlap integrals may change considerably for narrow band materials, with only a small overlap between the localized atomic orbitals. Generally, the smaller the distance between the sites, the smaller the relative change of the overlap as the distance changes. Therefore, t_2/t will become larger under application of pressure. This, however, cannot compete with the increase of t in the expression for D, $D = 16t\sqrt{1-(2t_2/t)^2}$, which will therefore increase. Since the change of the lattice constants is small (depending linearly on the applied pressure) we will assume a linear relation between D and P.

Thus, the prefactor in (1) increases, tending to raise T_c. The argument of the square root, however, increases too, tending to suppress T_c: the energy-independent density of states N_0 decreases due to an enlarged bandwidth, the logarithmic term increases due to the increase of D, and the value of δ increases: Since the bandwidth increases, the density of state decreases everywhere except at the van Hove singularity. It is easily seen (Fig. 2) that, with a constant number of carriers, the distance of the Fermi level to the van Hove singularity increases with increasing bandwidth, irrespective of whether E_F is above or below the singularity. The further E_F initially is away from the van Hove singularity, the larger the change of δ. This leads to a decrease of T_c, except when $\delta = 0$. This effect is amplified due to the presence of T_c in the prefactor of the δ^2 term.

Expression (1) has a maximum as a function of D. This maximum, however, occurs for a too small value of D to be of importance for the pressure experiments on the high-T_c superconductors: With $N_0V = 0.186$ and

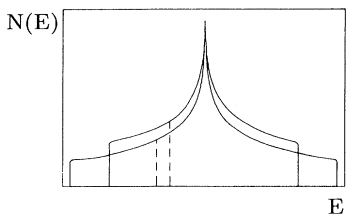

FIG. 2. The density of states and the Fermi energy for different bandwidths at a constant number of carriers. The dashed lines indicate the positions of the Fermi energy. Since the areas below the Fermi level should be equal, E_F is smaller for a larger bandwidth, i.e., at larger pressure.

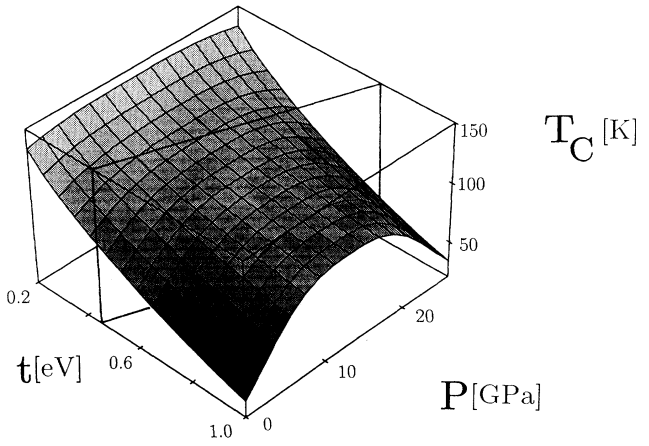

FIG. 3. T_c as a function of the transfer integral t (t_2/t was kept constant as a function of pressure) in eV and the pressure in GPa. The change of the transfer integral depends on the pressure, indicated by the vertical $t(P)$ surface. The dependence of T_c on the combination of both effects is given by the cut between the $t(P)$ surface and the T_c surface. Such a curve is shown in Fig. 1. We used the following values for the parameters: $\omega_D = 0.055$ eV, $t_2/t = 0.2$, and $N_0 V = 0.2$ at 1 atm and adjusted δ at 1 atm such that the maximum in Fig. 1 occurs at 10 GPa.

$\omega_D = 0.065$ eV, at 1 atm (values as used by Newns *et al.*),[1] we find that the maximum always lies at a value of D that is smaller than the 1-atm value of D. In the relevant regime T_c thus is a decreasing function of D.

A second effect of the applied pressure is a change of the electrostatics of the system which causes a charge redistribution to take place in such a way that the carrier concentration in the CuO planes increases. Such an effect has been observed in neutron studies on $YBa_2Cu_3O_{7-y}$.[7] Consequently E_F will change, and therefore, with the lattice constants fixed, the parameter δ in expression (1) will change. The change of δ as a function of P is given by

$$\frac{d\delta[n_h(P)]}{dP} = \frac{d\delta(n_h)}{dn_h}\frac{dn_h(P)}{dP} \propto N(E_F)^{-1}\frac{dn_h(P)}{dP} . \quad (2)$$

Here $n_h(P)$ is the number of holes as a function of pressure and dn_h/dP for $YBa_2Cu_4O_8$ is estimated to be 0.009/GPa per CuO_2 unit.[5] With 0.13 holes/CuO_2 at 1 atm this gives 0.31 holes/CuO_2 at 20 GPa. This large change of the number of carriers makes a "scan" of the density of states over a substantial energy range possible. Using this behavior of $\delta(P)$ in expression (1) yields the pressure dependence of T_c which, due to the factor $N(E_F)^{-1}$, is more flat near the top than the T_c versus carrier concentration curve, i.e., the boundary of the superconducting region in the T_c-doping phase diagram (see Fig. 3).

Both the discussed effects on T_c are combined in Fig. 3. The "pressure axis" contains only the effect of a change of δ due to a change of the carrier concentration, with a fixed D. In this direction the behavior of T_c is symmetric around a maximum and rather flat near this maximum. The "t axis" describes the effect of a change of the interatomic distances, with a fixed number of carriers. T_c is a decreasing function of t in this direction, the decrease being larger for a larger $|\delta|$. The latter behavior comes purely from the effect that is illustrated in Fig. 2. With t being a function of the pressure one finds the combined effect on T_c by cutting the gray surface with the vertical $t(P)$ surface (see Fig. 1). Obviously, $T_c(P)$ has a maximum. The curve is asymmetric due to the nonzero $|dT_c/dt|_\delta$ at constant number of carriers. T_c rises more steeply left of the maximum than it decreases at the right of the maximum. This is a very characteristic feature of the experimental data. At higher pressures T_c decreases quickly.

III. CONCLUSION

In conclusion, assuming the two main effects of pressure application on high-temperature superconductors being a change of the transfer integral and a redistribution of the carrier concentration, leading to an increase of the number of holes in the CuO planes, the van Hove scenario is able to give a good qualitative account of the experimentally observed variation of T_c as a function of pressure. The major effect certainly seems to be the increase of the carrier concentration in the CuO planes, since it is this effect that can cause a maximum of $T_c(P)$ in the relevant pressure regime. This reflects the doping dependence of T_c in the phase diagram. The details of T_c as a function of pressure, however, like the derivative dT_c/dP, depend on the change of the transfer integrals due to the change of the interatomic distances. Values of $|dT_c/dP|$ that are larger at the left side of the maximum than at the right side are in agreement with experiments. The relatively sharp drop of T_c at about 20 GPa might explain the difficulty of observing a resistive transition at these pressures. The Amsterdam group[9] had many unsuccessful tries to measure T_c above 18 GPa in $YBa_2Cu_4O_8$. A large $|dT_c/dP|$ in combination with a pressure gradient over the sample might explain this.

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