The effect of pressure on the optical gap of high-temperature superconductors

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(Submitted 24 January 1994)
Zh. Eksp. Teor. Fiz. **105**, 1759–1766 (June 1994)

Using the method of exact diagonalization of the Hamiltonian matrix within the framework of the Emery model, we numerically investigate the effect of pressure on the density of states and optical gap of high-temperature superconductors. We show that for the two-dimensional cluster Cu_4O_8 the optical gap can either increase or decrease with increasing pressure. The results of our calculations are in good agreement with experimental data, and allow us to predict the value of the derivative of the optical gap with respect to pressure for a number of compounds.

The effect of pressure on the properties of high-temperature superconductors has been the subject of a considerable number of papers.[1–5] In these papers attention is focused primarily on the dependence of the critical temperature T_c on the pressure P. In the majority of high-temperature superconductors with hole doping, the critical temperature increases[1,2] with increasing P, while for the case of electron doping the value of T_c decreases as a rule.[3] However, this rule is not universal:[4] for thallium-based superconductors a nonmonotonic dependence of $T_c(P)$ can even occur.[5]

In Ref. 6 we were successful in describing these features of the behavior of the critical temperature by starting from the fact that T_c is proportional to the binding energy Δ of the carriers, which was calculated for the cluster Cu_4O_8. In this case we predicted that positive value of the derivative dT_c/dP of the critical temperature with respect to pressure are possible in electronic high-temperature superconductors, as had earlier been observed experimentally for the compound $Sr_{0.84}Nd_{0.16}CuO_2$ (see Wooten *et al.*[7]). We modeled the effect of pressure by varying the value of the hopping matrix element between copper and oxygen atoms.

Along with the function $T_c(P)$, there is also considerable interest in the effect of pressure on the optical gap (the "charge-transfer" gap Δ_{ct}) in the density of electronic states. In Ref. 8 Tokura *et al.* studied experimentally the influence of pressure on the value of the optical gap for insulating structural analogues of high-temperature superconductors. For these compounds a layered structure is typical, with the fundamental structural unit a CuO_2 plane. These authors investigated high-temperature superconductor analogues that differed in the way oxygen atoms were arranged spatially around a copper atom. In the compound La_2CuO_4 (the T phase), six oxygen atoms form an octahedron around a copper atom; in $LaTbCuO_4$, five oxygen atoms form a square pyramid with its base in the CuO_2 plane (the T^* phase); and in $EuCuO_4$ (the T' phase) four oxygen atoms surround a copper atom in the CuO_2 plane.[9,10] For the corresponding doping, the following compounds of this class become superconducting: $La_{2-x}Si_xCuO_4$ (T phase, with $T_c\sim 40$ K), $(La,Gd)_{2-x}Si_xCuO_4$ (T^* phase, with $T_c\sim 35$ K), and $Nd_{2-x}Si_xCuO_4$ (T' phase, electron doping, with $T_c\sim 25$ K).[9] The optical gap, measured based on the absorption and reflection spectrum, increases with increasing pressure for La_2CuO_4 and decreases for $LaTbCuO_4$ and $EuCuO_4$ (see Ref. 8). This dependence of Δ_{ct} on P is interpreted in Ref. 8 in accordance with a postulated dependence of the value of the optical gap on the Madelung potential and electron hopping energy t. It is the view of these authors that the contributions from the Madelung potential and energy t to the value of Δ_{ct} have different signs, causing the gap to either increase or decrease, respectively.

In this paper we calculate the optical gap and density of states as a function of the hopping matrix element for copper-oxygen (which is determined by the interatomic spacing, and, consequently, the applied pressure). We show that, depending on the model parameters (the Coulomb repulsion at the copper and oxygen atoms, the charge-transfer energy from d orbitals of the copper to p orbitals of the oxygen), the optical gap can either increase or decrease with increasing applied pressure. The data from the experiments in Ref. 8 are in good agreement with our results within the framework of this model.

In the calculations of this paper we use the two-dimensional Emery model,[11] which describes the system of correlated charge carriers in the CuO_2 plane:

$$H=-t\sum_{\langle ik\rangle,\sigma}(d_{i\sigma}^{+}p_{k\sigma}+\text{H.c.})+\varepsilon\sum_{k,\sigma}n_{k\sigma}+U_d\sum_i n_{i\uparrow}n_{i\downarrow}$$

$$+U_p\sum_k n_{k\uparrow}n_{k\downarrow}+V\sum_{\langle ik\rangle,\sigma,\sigma'}n_{i\sigma}n_{k\sigma'},$$

where the notation is the same as that used in Refs. 6, 11. In calculating the electronic characteristics by the method of exact diagonalization we used the 12-node cluster Cu_4O_8 (see Ref. 6) with periodic boundary conditions. We studied the undoped state (the number of holes $N=4$, i.e., one hole is present per copper atom), which corresponds to the insulating phase. The temperature T is assumed to equal zero. In this case, in order to compute the single-particle density of states $N(\omega)$ and the value of the optical gap Δ_{ct} we can use the methods analogous to those set forth in Refs. 12, 13.

 1063-7761/94/060951-05$10.00

The density of states $N(\omega)$ is conveniently defined in the following way:

$$N(\omega)=\sum_i \sum_\sigma [g_{i\sigma}^+(-\omega)+g_{i\sigma}^-(\omega)],$$

where

$$g_{i\sigma}^+(\omega)=\sum_n |\langle\psi_n(N+1)|c_{i\sigma}^+|\psi_0(N)\rangle|^2\delta \times[\omega-E_n(N+1)+E_0(N)],$$

$$g_{i\sigma}^-(\omega)=\sum_n |\langle\psi_n(N-1)|c_{i\sigma}|\psi_0(N)\rangle|^2\delta \times[\omega-E_n(N-1)+E_0(N)].$$

Here $c_{i\sigma}$ [where $c_{i\sigma}=p_{i\sigma}(d_{i\sigma})$] is the annihilation operator for holes at the oxygen (copper) sites; $E_n(N)$ is the energy of the nth excited state of a system consisting of N holes, with $\psi_n(N)$ the corresponding wave function; $E_0(N)$ is the ground-state energy of a system consisting of N holes, and $\psi_0(N)$ is the ground-state wave vector; and $g_{i\sigma}^+(-\omega)$ is the partial contribution from site i. Note that $g_{i\sigma}^+(-\omega)$ describes states occupied by electrons with spin σ, while $g_{i\sigma}^-(\omega)$ describes states occupied by holes.

In order to calculate the density of states we make use of the Lanczos algorithm.[6,12,13] These calculations were carried out in three stages. In the first stage the energy and ground-state vectors were calculated for a system of N holes. Then the vectors $c_{i\sigma}^+|\psi_0(N)\rangle$ and $c_{i\sigma}|\psi_0(N)\rangle$ [where $c_{i\sigma}=p_{i\sigma}(d_{i\sigma})$] were calculated. After this, the eigenvalues of the Hamiltonian operator H were determined for a system of $N+1(N-1)$ holes, along with the corresponding matrix elements $\langle\psi_n(N+1)|c_{i\sigma}^+|\psi_0(N)\rangle$ and $\langle\psi_n(N-1)|c_{i\sigma}|\psi_0(N)\rangle$. The delta functions in the expressions for the density of states were approximated by Lorentzian peaks.

The primary assumption of the model of Ref. 6, namely that the pressure influences only the hopping matrix element t, was adopted here as well. This parameter is the most sensitive to applied pressure, since increasing P decreases the interatomic distance, which leads to a further overlap of the electron orbitals and, consequently, to an increase in t. The Coulomb repulsion energy V for carriers between the copper and oxygen sites, based on estimates of Ref. 14, is small compared to other parameters of the Emery model and in our calculations we set it equal to zero. The Coulomb repulsion energies for carriers on lattice sites U_d, U_p are assumed to be pressure-independent.[6]

Starting from the strong exponential dependence of the electron hopping energy t on the distance a between copper and oxygen atoms in the CuO_2 plane,[6,15] we will assume that the Madelung potential, which determines the charge-

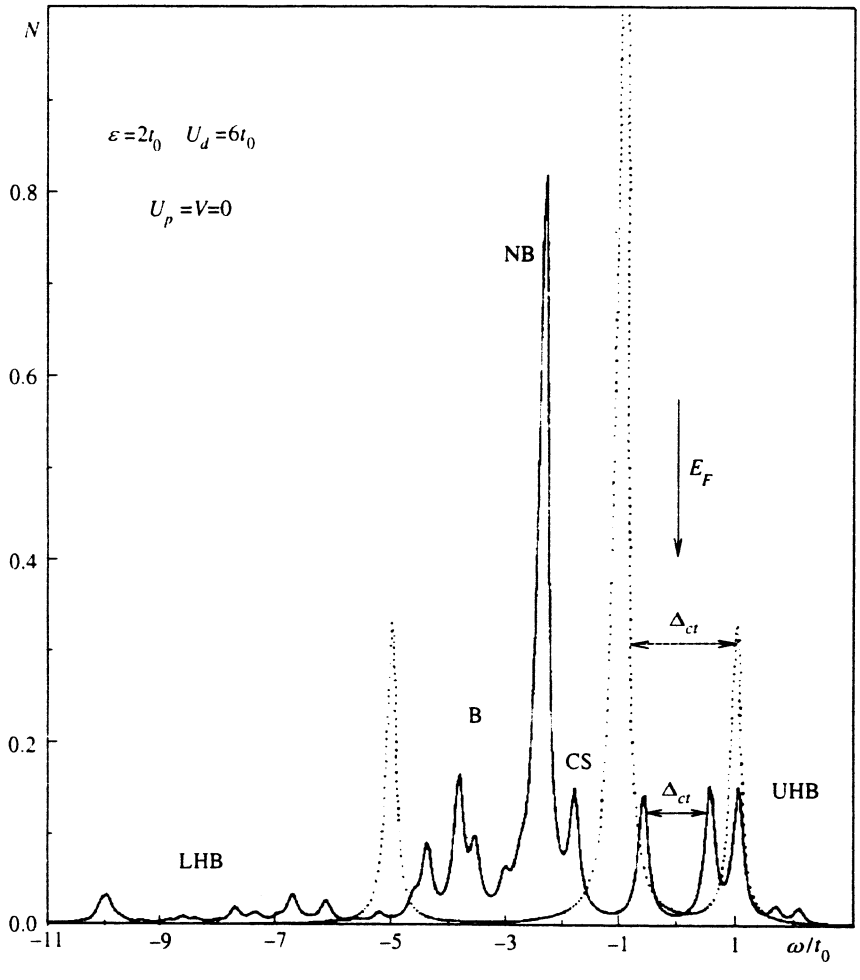

FIG. 1. One-particle density of states $N(\omega)$ of the cluster Cu_4O_8 for $t=t_0$ (solid curve) and $t=0.05t_0$ (dashed curve).

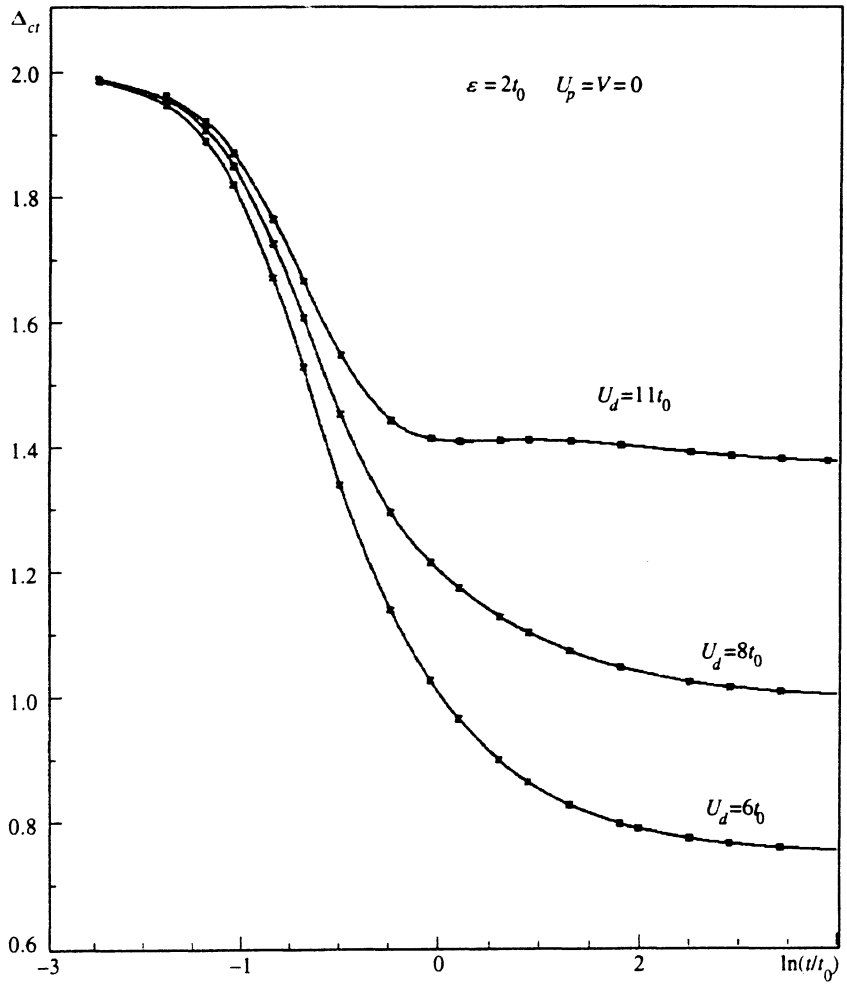

FIG. 2. Dependence of the optical gap Δ_{ct} (in units of t_0) on the logarithm of t for various values of U_d.

transfer energy ε from a d orbital of copper to a p orbital of oxygen, varies much more slowly than the quantity t as the interatomic distance decreases (as a power law; see Ref. 10). Thus, we will use the assumption that only the single parameter (t) depends on pressure, in contrast to the authors of Ref. 8, who explained the behavior of $\Delta_{ct}(P)$ by assuming the Madelung potential was a function of pressure. In this case, in agreement with the results of Ref. 9, we assume that the Madelung potential affects the original value of the optical gap (at normal pressure P_0).

The calculated density of states for the cluster Cu_4O_8, in the Emery model, is shown in Fig. 1 for various values of t and the following model parameters: $\varepsilon = 2t_0$, $U_d = 6t_0$, $U_p = V = 0$, where t_0 is the value of the parameter t for normal pressure. This choice is derived from estimates of these parameters obtained in Ref. 14 for the class of compounds under discussion. We have also used the widely accepted notation for the bands from Ref. 12. A narrow purely-oxygenic band is clearly evident, which has received the designation "nonbinding." To the left of it is located a binding band, which both copper and oxygen subsystems contribute to. The upper and lower Hubbard bands are a consequence of the strong Coulomb repulsion and correspond to the transitions $d^9 \to d^{10}$ and $d^9 \to d^8$ between atomic states of copper (see Ref. 12). For electron doping the Fermi level lies in the upper Hubbard band, while for hole doping it is in the region of correlated states. The optical gap Δ_{ct} separates the upper Hubbard band from the nonbinding band or the region of correlated states when strong Coulomb correlations are present in the system. For the undoped state we are considering here, the Fermi level lies at the center of the gap. As we should expect, for small values of t the bands degenerate into δ-function peaks. Increasing t causes broadening of all the bands except the nonbinding band. The small width of this band is caused by the two-dimensional nature of the CuO_2 structure, and does not depend on the model parameters; however, its position relative to the Fermi level and the density of states within it change (see Fig. 1). We also observe a shift in the other bands, which probably is caused by virtual hopping (the energy for which has a value of order t^2/U; see Ref. 16). The simultaneous broadening and shifting of the bands can give rise either to an increase or to a decrease in the optical gap with increasing pressure.

In order to compare the results of numerical calculations with the experimental data, we will construct a plot of the dependence of Δ_{ct} on $\ln t$, because the exponential coupling of the parameter t to the interatomic distance a (see Ref. 15) and the proportionality of a to the external pressure imply the following relation between the quantities P and t: $P = P_0 + \beta \ln(t/t_0)$, where β is a constant.

In Figs. 2 and 3 we show the dependence of the optical gap on the logarithm of t for various values of ε and U_d. For $t \ll t_0$, only ε has an effect on Δ_{ct} (for $t = 0$ we have

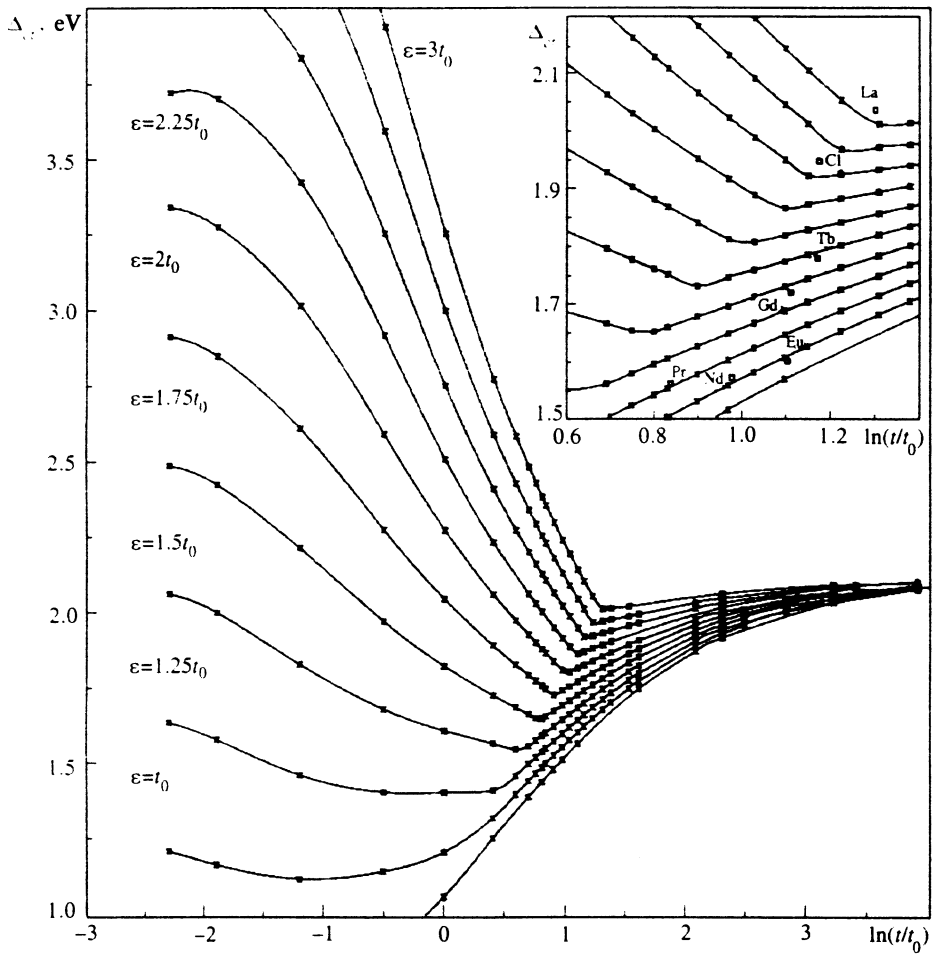

FIG. 3. Dependence of the optical gap Δ_{ct} (in eV) on the logarithm of t for $U_d=8t_0$, $U_p=4t_0$, and various values of ε: La–La_2CuO_4, Tb–$LaTbCuO_4$, Eu–Eu_2CuO_4, Nd–Nd_2CuO_4, Pr–Pr_2CuO_4, Gd–$(LaGd)CuO_4$, Cl–$CaCuO_2Cl_2$.

$\Delta_{ct}=\varepsilon$). In the other limiting case ($t\gg t_0,U_d,U_p$) Δ_{ct} does not depend on t and is determined by the parameter U_d and, to a lesser degree, by U_p (Fig. 2). This behavior of Δ_{ct} for large values of t probably implies the absence of a Mott transition at zero temperature in the Emery model. This result is consistent with the assertion that there is no Mott transition for the two-dimensional single-band Hubbard model in the weak-binding regime ($U\ll t$); see Ref. 17. It should be noted, however, that hydrostatic compression of a crystal can change the interatomic distances by several per cent, which corresponds to changing t by an amount of order t_0.

Let us consider the dependence of the optical gap on $\ln t$ for various ε. As is clear from Fig. 3, there exist regions of both positive and negative values of the derivative $d\Delta_{ct}/d\ln t$. In Fig. 3 we also compare our results with experimental data from Refs. 8, 9, where the experimental values of the optical gap for insulating analogues of the high-temperature superconductors were plotted under the assumption that the parameter ε depended on the oxygen environment of the copper atoms. The range of variation of the quantity t for each specific compound depends on the interatomic distance in these compounds for normal pressure. Since the Madelung potential, which is determined by the parameter ε, is directly proportional to the number of oxygen atoms around a copper atom, we assume that $\varepsilon(La_2CuO_4)>\varepsilon(LaTbCuO_4)>\varepsilon(Eu_2CuO_4)$ (corresponding to six, five, and four oxygen atoms). In this case, the results of the calculations (see Fig. 3) imply that $d\Delta_{ct}/d\ln t<0$ for La_2CuO_4 (T phase), while $d\Delta_{ct}/d\ln t>0$ for $LaTbCuO_4$ (T' phase) and Eu_2CuO_4 (T^* phase). In this case the values of the derivatives also are in quantitative agreement with the experimental data of Ref. 8 (see Table I). Using these three values as "references" we can predict the value of $d\Delta_{ct}/d\ln t$ for other members of this class of compounds. Here, we estimate the absolute values of these derivatives by normalizing the results in the same way for all the compounds with respect to the known value of $d\Delta_{ct}/dP$ in La_2CuO_4 (see column 6 of Table I). To get the best estimate of the derivatives we have also normalized the "reference" values relative to the compounds in the T, T', and T^* phases (see column 7 of Table I). Thus, for Nd_2CuO_4 we have $d\ln\Delta_{ct}/dP\simeq 9.2\cdot 10^{-3}$ GPa^{-1}, for Pr_2CuO_4 $d\ln\Delta_{ct}/dP\simeq 9.5\cdot 10^{-3}$ GPa^{-1}, for $(LaGd)CuO_4$ $d\ln\Delta_{ct}/dP\simeq 5.7\cdot 10^{-3}$ GPa^{-1}, and for $CaCuO_2Cl_2$ $d\ln\Delta_{ct}/dP\simeq 1.5\cdot 10^{-3}$ GPa^{-1}.

In conclusion, we emphasize that the approach we have used here provides a framework for the successful description not only of many features of the behavior of $T_c(P)$ (see Ref. 6), but also for calculations of the function $\Delta_{ct}(P)$, as well as predictions of the results of potential future experiments involving the influence of pressure on the optical gap of high-temperature superconductors.

TABLE I.

Compound	Δ_{ct}, eV	a, Å	$\frac{d\ln\Delta_{ct}}{dP}$, 10^{-3}/GPa Experiment	$\frac{d\ln\Delta_{ct}}{d\ln t}$	$\frac{d\ln\Delta_{ct}}{dP}$, 10^{-3}/GPa	$\frac{d\ln\Delta_{ct}}{dP}$, 10^{-3}/GPa
1	2	3	4	5	6	7
			T- Phase			
La_2CuO_4	2.04	1.90	−1.5	−0.04	−1.5	−1.5
$CaCuO_2Cl_2$	1.95	1.93	—	0.04	1.5	1.5
			T′- Phase			
$LaTbCuO_4$	1.78	1.93	4.2	0.11	4.1	4.2
$(LaGd)CuO_4$	1.72	1.94	—	0.15	5.6	5.7
			T*- Phase			
$EuCuO_4$	1.61	1.94	9.0	0.20	7.5	9.0
Nd_2CuO_4	1.58	1.97	—	0.205	7.7	9.2
Pr_2CuO_4	1.56	1.98	—	0.21	7.9	9.5

This work was carried out as part of Project No. 90.413 of the State Program on "High-Temperature Superconductivity."

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Translated by Frank J. Crowne