Vertex correction to the Eliashberg equation for the superconducting critical temperature

J. Cai, X. L. Lei, and L. M. Xie
Shanghai Institute of Metallurgy, Academia Sinica, Shanghai 200050, China
(Received 8 December 1988)

The effects of the electron-phonon vertex correction, including high-order correction, on the superconducting transition temperature T_c are discussed. For an Einstein spectrum, a self-consistent vertex solution is obtained which goes beyond the ladder approximation and satisfies the Ward identity. The numerical results show that the T_c change due to this vertex correction is significant at small coupling constant λ, but much smaller for large λ.

I. INTRODUCTION

The recent discovery of high-T_c superconductivity in oxide systems ($La_{2-x}Ba_xCuO_4$ and $YBa_2Cu_3O_7$, etc.) has spurred a remarkable surge of interest and research activity. A large number of models have been suggested for this superconductivity. The identification of the primary mechanism responsible for high T_c however is still an open problem. Although different mechanisms and models are based on completely different conceptions and interactions, many of them still invoke the T_c equation in conventional BCS or Eliashberg theory to give an estimation of superconducting transition temperature in phonon-, exciton-, and plasmon-mediated pairing models.[1-4] It is well known that the derivation of the Eliashberg equation[5] rests on the Migdal approximation,[6] which states that the contribution from electron-phonon vertex corrections to the electron self-energy are of order of $\alpha=\hbar\omega_D/\varepsilon_F$, where ω_D is the characteristic phonon frequency and ε_F is the Fermi energy. In conventional metallic superconductors, in which ε_F is of the order of 10^4 K and thus $\alpha\lesssim 1\%$, the linearized Eliashberg equation has been proven to be a good theoretic basis for the discussion of superconducting critical temperature.

The situation in high-T_c oxides however is quite different. Experiments showed that both $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_7$ are low-carrier density systems with $n\sim 10^{21}/\text{cm}^3$, much smaller than that in a conventional superconductor. Even making a conservative estimation $\hbar\omega_D\sim 0.04$ eV and $N(0)\lesssim 10^{22}$ eV/cm^3, we have $\alpha\gtrsim 0.2$. This shows that the linearized equation in its conventional form is not good enough for high-T_c oxides. In other boson (nonphonons) exchange mechanisms, the characteristic frequencies are generally much larger than ω_D, the applicability of the T_c equation with Migdal approximation is even more questionable.

The theoretical calculation of the superconducting critical temperature beyond the Migdal approximation is generally a formidable task, especially for high-T_c oxides which are strongly anisotropic. To estimate this effect, people usually discuss model three-dimensional systems, as addressed by Grabowski and Sham.[7] They discussed the lowest-order vertex for a model interaction but dropped all the higher-order contributions. The purpose of this paper is to discuss the effect of the vertex correction, including higher-order corrections within ladder and nonladder approximations, on superconducting transition temperature T_c for the same model system, hoping that the results obtained are qualitatively meaningful in the estimation of the superconducting critical temperature for oxide systems.

We confine our discussion to the case of an Einstein spectrum which has also been widely used in boson (nonphonon) exchange models in the estimation of T_c for oxide systems.[1-4] The Einstein spectrum not only simplifies the calculations but also makes it possible to obtain a self-consistent solution which goes beyond the ladder approximation and satisfies the Ward identity. Our results show that the T_c change due to vertex correction is significant at small and mediate λ, but much smaller for large λ.

II. VERTEX CORRECTION TO THE LINEAR ELIASHBERG EQUATION

A. Ladder approximation

We begin with the Hamiltonian of an electron-phonon system.[8] The self-energy of the superconducting condensed state is shown graphically in Fig. 1(a), and the corresponding linearized gap equation at $T\rightarrow T_c$ can be written as

$$\omega_n[1-Z(p)]=-\frac{1}{\beta}\sum_k \frac{\omega_m Z(k)}{\omega_m^2 Z(k)^2+\varepsilon(k)^2}\times V_{\text{eff}}(k-p)\Gamma(k,p)\,, \tag{1a}$$

$$X(p)=-\frac{1}{\beta}\sum_k \frac{\varepsilon(k)}{\omega_m^2 Z(k)^2+\varepsilon(k)^2}\times V_{\text{eff}}(k-p)\Gamma(k,p)\,, \tag{1b}$$

$$\Phi(p)=-\frac{1}{\beta}\sum_k \frac{\Phi(k)}{\omega_m^2 Z(k)^2+\varepsilon(k)^2}\times V_{\text{eff}}(k-p)\Gamma(k,p)\,, \tag{1c}$$

in which $k=(\mathbf{k},i\omega_m)$, $p=(\mathbf{p},i\omega_n)$; $\omega_m=(2m+1)\pi/\beta$, $\omega_n=(2n+1)\pi/\beta$; m and n are integers; $\mathbf{k}$ and $\mathbf{p}$ are momenta; $\Gamma(k,p)$ is the total vertex part $\varepsilon(p)=\varepsilon_{\mathbf{p}}+X(p)$; and $Z(p)$, $X(p)$, and $\Phi(p)$ are the components of the electron self-energy $\hat{\Sigma}(p)$ in the Nambu representation [here $\hat{I}$ is the 2×2 unit matrix and $\hat{\sigma}_i$ $(i=1,2,3)$ the Pauli

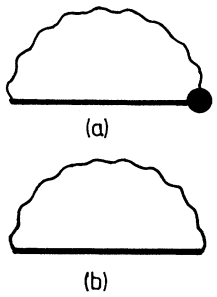

FIG. 1. Self-energy (a) with vertex correction and (b) without vertex correction. The wavy lines represent the effective interaction between electrons and the heavy solid lines represent the electron Green's function.

matrices]

$$\hat{\Sigma}(\mathbf{p},i\omega_n)=i\omega_n[1-Z(p)]\hat{I}+x(p)\hat{\sigma}_3+\Phi(p)\hat{\sigma}_1 . \quad (2)$$

Since we are interested in the vertex correction on T_c only, we can ignore the anomalous Green's function correction (or spin fluctuation). In Eq. (1) the effective interaction between electrons $V_{\rm eff}(q)$ is composed of two parts:

$$V_{\rm eff}(q)=V_{\rm SC}(\mathbf{q})+V_{e\text{-ph}}(q) , \quad (3)$$

where $V_{\rm SC}$ stands for the screened Coulomb potential, which is usually taken as (static approximation)

$$V_{\rm SC}(\mathbf{q})=\frac{V_c(\mathbf{q})}{\epsilon_e(\mathbf{q})}$$

with $\epsilon_e(\mathbf{q})$ being the static dielectric function of electrons. The fact that the effective electron-phonon (e-ph) interaction $V_{e\text{-ph}}$ is strongly frequency dependent but weakly momentum dependent, makes it possible to neglect the momentum dependence of the electron-phonon interaction by averaging out the momentum component of the electron-phonon spectrum on the Fermi surface, leading to

$$V_{e\text{-ph}}(\mathbf{q},i\omega_l)=2\int d\omega\frac{\omega\alpha^2F(\omega)}{\omega^2+\omega_l^2} , \quad (4)$$

where $\alpha^2F(\omega)$ is the Eliashberg function, in which the electron screening and polarization effects are included. For conventional metallic superconductors, a good approximation is to use the unit part in place of the vertex part as was done by Migdal, and Eqs. (1) reduce to the well-known linearized Eliashberg equation.

In the following, we are going to approximately determine the vertex part in Eqs. (1). First we discuss the vertex part within the ladder-graph approximation [shown in Fig. 2(a)]:

$$\Gamma(k,p)=1-\frac{1}{\beta}\sum_s V_{\rm eff}(s)\mathcal{G}(k+s)\mathcal{G}(p+s)\Gamma(k+s,p+s) \quad (5)$$

where $\mathcal{G}$ is the normal electron Green's function. The total vertex can be divided into an electron-electron part and an electron-phonon part:

$$\Gamma(k,P)=\Gamma_{e\text{-}e}(k,p)\Gamma_{e\text{-ph}}(k,p) , \quad (6)$$

with

$$\Gamma_{e\text{-}e}(k,p)=1-\frac{1}{\beta}\sum_s V_{\rm SC}(s)\mathcal{G}(k+s)\times\mathcal{G}(p+s)\Gamma_{e\text{-}e}(k+s,p+s) , \quad (7a)$$

and

$$\Gamma_{e\text{-ph}}(k,p)=1-\frac{1}{\beta}\sum_s [V_{e\text{-ph}}(s)\Gamma_{e\text{-}e}(k+s,p+s)]\times\mathcal{G}(k+s)\mathcal{G}(p+s)\times\Gamma_{e\text{-ph}}(k+s,p+s) . \quad (7b)$$

In deriving Eqs. (7a) and (7b) we have used the fact that the electron-phonon vertex part is mainly a function of variable $(k-p)$ and varies slowly with k and p. It is worth noting here that the electron vertex part can be combined into a modified Eliashberg spectrum and averaged on the Fermi surface as discussed before, but we still use $\alpha^2F(\omega)$ for it. The electron-phonon vertex correction has been studied thoroughly in the literature.[9,10] Obviously, for strong electron-phonon coupling or large phonon characteristic frequency the higher graphs (vertex correction) should not be discarded. Nevertheless, we can still simplify our calculation by considering that the dominant contribution to the integration comes from the frequency region ω_m, $\omega_n\sim kT_c\ll\omega_D$, and the momentum region $q\gg p_F\omega/\epsilon_F$.[6,11] It should be noted that in principle large $\alpha=\omega_D/\epsilon_F$ means a possible large momentum dependence of the vertex and gap functions, but as pointed out by Grabowski and Sham,[7] the numerical solution for the electron gas shows[12] that the node of the gap function Φ comes mainly from the variation in frequency, not in momentum. Thus, as did Grabowski and Sham, we treat the momentum-transfer dependence of the effective interaction and vertex function as unimportant compared with the frequency dependence in the determination of superconducting T_c. For quasi-one-dimensional systems of very strong momentum-dependent interaction, this may not be justified.[7] In the present paper we confine our discussion to the former case and simplify the integral equation

$$\Gamma_{e\text{-ph}}(k,p)=1+2\int d\omega\frac{\alpha^2F(\omega)}{\omega}\frac{1}{\beta}\sum_s\frac{\omega^2}{\omega^2+\omega_s^2}\mathcal{G}(k+s)\mathcal{G}(p+s)\Gamma_{e\text{-ph}}(k+s,p+s) \quad (8)$$

approximately into an algebraic equation

$$\Gamma_{e\text{-ph}}(i\omega_m,i\omega_n)=\left[1+2\int d\omega\frac{\alpha^2F(\omega)}{\omega}\lim_{q\to 0}C(\omega;q,\omega_m,\omega_n)\right]^{-1} , \quad (9)$$

in which

$$C(\omega;q,\omega_m,\omega_n)=-\frac{1}{\beta}\sum_s \frac{\omega^2}{\omega^2+(\omega_s-\omega_n)^2}\mathcal{G}(s,i\omega_s)\mathcal{G}(s+q,i\omega_m-i\omega_n+i\omega_s)\,. \tag{10}$$

Notice that the function C describes the electron-phonon correlation which has a maximum at $\omega=0$ and decreases to zero at large frequency. This can be seen directly from the expression (10). The C function, which is a smooth and monotonous function of variables ω_m and ω_n, behaves as $\Lambda_0\omega^2/[\omega^2+(\omega_m-\omega_n)^2]$ at low frequency (small ω_m and ω_n), and varies as $\Lambda_\infty/\omega_m^2$ or $\Lambda_\infty/\omega_n^2$ at high-frequency (large ω_m or ω_n) [here all the energies and frequencies ($\hbar=1$) are measured by the Fermi energy ε_F]. Thus, in analogy with Grabowski and Sham, it may be obtained by interpolating between zero-frequency and infinite-frequency limits,[7] resulting in

$$\Gamma_{e\text{-ph}}(i\omega_m,i\omega_n)=\left[1+2\int d\omega\frac{\omega\alpha^2F(\omega)}{\omega^2+(\omega_m-\omega_n)^2}\Lambda_0\frac{2(\Lambda_\infty/\Lambda_0)}{\omega_m^2+\omega_n^2+2(\Lambda_\infty/\Lambda_0)}\right]^{-1}, \tag{11}$$

where for three-dimensional systems

$$\Lambda_0(\omega)=\frac{0.293\omega}{\omega+0.667}\,, \tag{12a}$$

$$\frac{\Lambda_\infty(\omega)}{\Lambda_0(\omega)}=\frac{4\sqrt{2}}{3}\frac{0.667+\omega}{0.586}\gtrsim 2.14\,, \tag{12b}$$

and for two-dimensional dispersionless systems,

$$\Lambda_0(\omega)=\frac{\omega\pi/8}{1+\omega}\,, \tag{13a}$$

$$\frac{\Lambda_\infty(\omega)}{\Lambda_0(\omega)}=16(1+\omega)\gtrsim 16\,. \tag{13b}$$

Furthermore, if the upper cutoff frequency ω_c in the Eliashberg function is less than 1, the last factor in Eq. (11) may be replaced by 1 since the dominant contribution of ω_m and ω_n in the linearized gap Eq. (1) comes from the region of $\omega_m\sim\omega_n\sim kT_c\lesssim\omega_c$. Therefore we have the simplified expression for the electron-phonon vertex in the ladder approximation

$$\Gamma_{e\text{-ph}}(i\omega_m,i\omega_n)=\Gamma_{e\text{-ph}}(i\omega_m-i\omega_n)=\left[1+2\int d\omega\frac{\omega\alpha^2F(\omega)}{\omega^2+(\omega_m-\omega_n)^2}\Lambda_0(\omega)\right]^{-1}. \tag{14}$$

As to the electron-electron interaction part we will use the conventional pseudopotential μ^* approximation. Equation (1) is then reduced to

$$\begin{aligned}
\omega_n[1-Z(p)]&=-\frac{1}{\beta}\sum_k\frac{\omega_m Z(k)}{\omega_m^2Z(k)^2+\varepsilon(k)^2}V_{e\text{-ph}}(i\omega_m-i\omega_n)\,,\\
X(p)&=-\frac{1}{\beta}\sum_k\frac{\varepsilon(k)}{\omega_m^2Z(k)^2+\varepsilon(k)^2}V_{e\text{-ph}}(i\omega_m-i\omega_n)\,,\\
\Phi(p)&=-\frac{1}{\beta}\sum_k\frac{\Phi(k)}{\omega_m^2Z(k)^2+\varepsilon(k)^2}[\mu^*-V_{e\text{-ph}}(i\omega_m-i\omega_n)]\,.
\end{aligned} \tag{15}$$

Here Φ, Z, ε, and X now represent their respective phonon parts only. $V_{e\text{-ph}}(i\omega_m-i\omega_n)$ is the renormalized effective electron-phonon interaction including the vertex correction

$$V_{e\text{-ph}}(i\omega_m-i\omega_n)=2\int d\omega\frac{\omega\alpha^2F(\omega)}{\omega^2+(\omega_m-\omega_n)^2}(1+\mu^*\Lambda_0)\left[1+2\int d\omega\frac{\omega\alpha^2F(\omega)}{\omega^2+(\omega_m-\omega_n)^2}\Lambda_0\right]^{-1}. \tag{16}$$

In the case of an Einstein spectrum

$$\alpha^2F(\omega)=\frac{\lambda}{2}\omega_E\delta(\omega-\omega_E)\,, \tag{17}$$

the effective electron-phonon interaction without vertex correction is

$$V_{e\text{-ph}}(i\omega_n)=\lambda\frac{\omega_E^2}{\omega_n^2+\omega_E^2}\,. \tag{18}$$

The effect of the vertex correction is equivalent to a change of the interaction constant λ and the characteristic frequency

ω_E:

$$V_{e\text{-ph}}(i\omega_n) = \lambda_1 \frac{\omega_{E1}^2}{\omega_n^2 + \omega_{E1}^2}, \tag{19}$$

where

$$\lambda_1 = \frac{\lambda}{1+\lambda a\omega_E/(b+\omega_E)}, \qquad \omega_1 = \left[1+\lambda\frac{a\omega_E}{b+\omega_E}\right]^{1/2}\omega_E . \tag{20}$$

For this special case, $\lambda\omega_E^2$ is an invariant quantity. The vertex correction in the ladder approximation [Eqs. (14) and (20)] is an extension of that given in Ref. 7 and can be reduced to that of Migdal in the small ω_c limit.

B. Nonladder approximation

We can go beyond the ladder graphs by taking the proper vertex part determined by the self-consistent equation as depicted by Fig. 2(b). It is worth noting that if $\Gamma(p,k)$ is a function of $p-k$, the vertex part shown in Fig. 2(b) associated with the self-energy given in Fig. 1(a) satisfies the Ward identity. The Ward identity[13]

$$\Gamma(p,0) = \frac{\partial G^{-1}(p)}{\partial p_0} = 1 - \frac{\partial \Sigma(p)}{\partial p_0}, \tag{21}$$

and a "generalized" Ward identity[11]

$$q_0\Gamma(p,p+q) = \mathcal{G}^{-1}(p+q) - \mathcal{G}^{-1}(p) \tag{22}$$

(in the limit $\mathbf{p}\rightarrow 0$) are a consequence of charge and current conservation. It is an exact relationship between vertex functions and self-energies. The ladder graphs for Γ can satisfy Ward identity only with a self-energy given by Fig. 1(b), i.e., no vertex correction at all. To include the vertex correction in self-energy it is necessary to go beyond ladder graphs and the vertex equation becomes a nonlinear integral equation. Figure 2(b) is one of the simplest possibilities. To solve this nonlinear integral equation for an Einstein spectrum, we need only to iterate our ladder approximation expression Eq. (14) repeatedly. The final results are the fixed points of following equations:

$$\lambda_n = \frac{\lambda}{1+\lambda_{n-1}a\omega_{En-1}/(b+\omega_{En-1})}, \qquad \omega_{En-1} = [1+\lambda_{n-1}a\omega_{En-1}/(b+\omega_{En-1})]^{1/2}\omega_E , \tag{23}$$

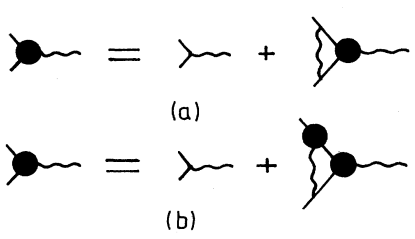

FIG. 2. The vertices of (a) the ladder approximation and (b) nonladder approximation.

i.e., solutions of a two-variable algebraic equations

$$\bar\lambda = \frac{\lambda}{1+\bar\lambda a\bar\omega_E/(b+\bar\omega_E)}, \qquad \bar\omega E = [1+\bar\lambda a\bar\omega_E/(b+\bar\omega E)]^{1/2}\omega_E . \tag{24}$$

Thus Eqs. (24) are self-consistent equations for the effective coupling constant and characteristic frequency, since they depend functionally on themselves.

III. T_c WITH VERTEX CORRECTION AND DISCUSSION

For an Einstein spectrum the vertex correction is to renormalize λ and ω_E into $\bar\lambda$ and $\bar\omega_E$. We plot (λ_1,ω_1) in the ladder approximation and $(\bar\lambda,\bar\omega)$ in the nonladder approximation in Figs. 3 and 4 as functions of the original interaction constant λ and characteristic frequency ω_E according to Eq. (20) and Eq. (24), respectively. The superconducting transition temperature T_c with vertex correction can be obtained from the original Eliashberg equation (without vertex correction) with the modified coupling constant $\bar\lambda$ and characteristic frequency $\bar\omega_E$. We can use the reasonably accurate T_c formula obtained from the conventional Eliashberg equation in Ref. 14. For an Einstein spectrum, in small and intermediate λ region,

$$T_c = \frac{2\gamma}{\pi}\omega_E \exp\left[-\frac{1+\lambda}{\lambda-\mu^*}\right], \tag{25}$$

while in large λ limit (for $\lambda > \Lambda = 2$)

$$T_c = 0.182(\lambda\omega_E^2)^{1/2}. \tag{26}$$

By combining Eqs. (24), (25), and (26), the transition temperature T_c with vertex correction is easily evaluated. As an example we show in Fig. 5 the calculated value of T_c for three-dimensional systems. Our results confirm

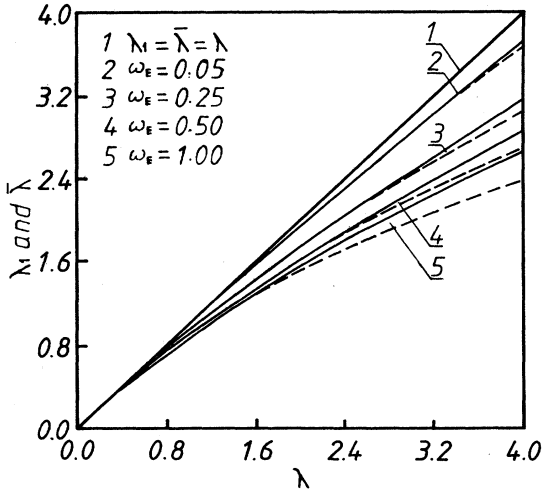

FIG. 3. The normalized electron-phonon interaction constants λ_1 in ladder approximation (dashed lines) and $\bar\lambda$ in nonladder approximation are plotted as functions of λ for various characteristic frequency ω_E. Line 1 stands for the case of $\lambda_1 = \bar\lambda = \lambda$.

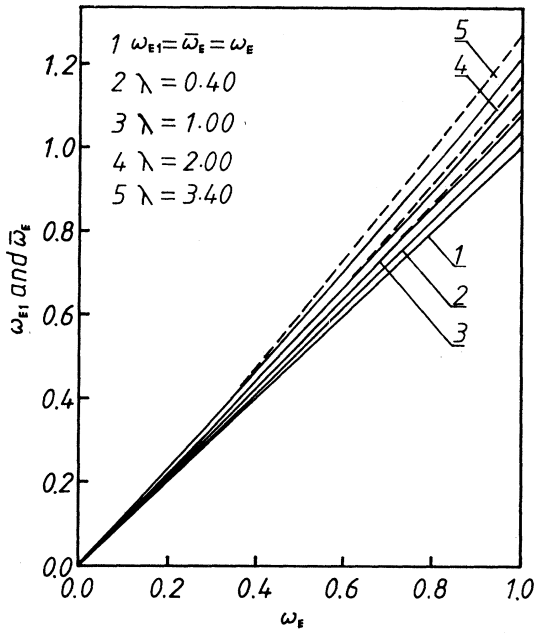

FIG. 4. The normalized characteristic frequencies ω_{E1} in ladder approximation (dashed lines) and $\bar{\omega}_E$ in nonladder approximation are plotted as functions of ω_E for various electron-phonon interaction constants λ. Line 1 represents the case of $\omega_{E1}=\bar{\omega}_E=\omega_E$.

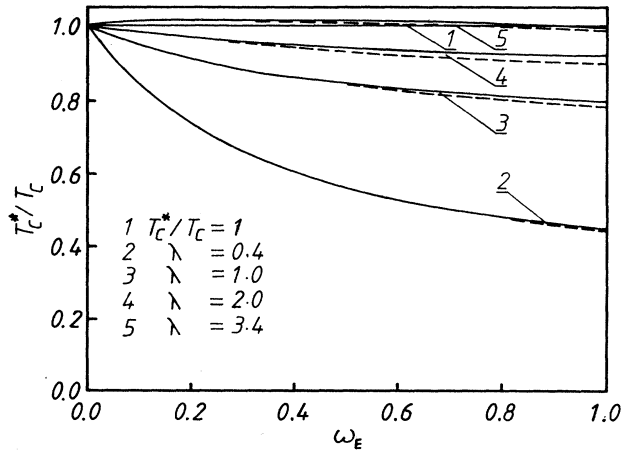

FIG. 5. The ratios of the superconducting critical temperature with vertex correction T_c^* to that without vertex correction T_c for a superconductor of Einstein spectrum, are plotted as functions of ω_E for various values of λ. Dashed lines are in ladder approximation and solid lines in nonladder approximation.

that if the phonon characteristic frequency is less than 1% that of the Fermi energy as in the metallic case, the vertex correction is negligible within a few percent, in agreement with that obtained by Migdal. In the case of a large phonon characteristic frequency, however, the vertex correction becomes important.

As is seen in Fig. 5 in the weak-coupling region, the change of T_c can be as large as 50%. In the large λ region, T_c changes are relatively small compared with the weak-coupling case. For λ value of 1–2, the calculated T_c involving vertex corrections will be about 80% of that of the original values.

It is worth noting that although $\lambda\omega_E^2$ is an invariant quantity, it does not imply zero vertex correction of T_c in large $\lambda\omega_E^2$ case. Expression (26) is applicable only in the case with vertex correction for large $\bar{\lambda}$. Therefore, the region for Eq. (26) to be valid is greatly reduced due to vertex correction. In the numerical calculation we have assumed that the electron pseudopotential μ^* is an invariant constant (we choose $\mu^*=0.2$). This assumption has been proven to be correct for metallic materials, in which the phonon Debye energy is less than 5% that of the Fermi energy, while μ^* is equal nearly to 0.1–0.3. These results may not be valid for nonmetal systems, in which the Coulomb effect may be more important in determining the relevant parameters and superconducting T_c. If the variation of μ^* with ω_E is taken into account, we expect the T_c change due to vertex correction to be much stronger than that shown in curve 2 of Fig. 5, or even the appearance of superconductivity to be suppressed by vertex correction, as discussed in Ref. 7.

Of course the present results are based on the oversimplified Einstein spectrum. In a real system, the spectrum $\alpha^2F(\omega)$ may be much more complicated and the vertex correction may be spectrum dependent. To see the vertex correction on T_c for a realistic spectrum, extensive numerical calculation is necessary especially in the case beyond the ladder approximation. Fortunately our calculation for an Einstein spectrum shows that in the case of λ less than 2 and ω_E less than 1, the results obtained in the ladder graphs are very close to those in the nonladder approximation. Thus, we may expect that Eq. (15) with ladder approximation is a reasonable starting point for the estimation of the vertex-correction effects on the superconducting T_c for mediate coupling constant and mediate characteristic frequency. The detailed calculation according to Eq. (15) will be reported later.

ACKNOWLEDGMENTS

The authors wish to express their thanks to Professor Chien-Hua Tsai for helpful discussion. This work was supported by the National Science Foundation of China.

[1]W. Weber, Phys. Rev. Lett. **58**, 1371 (1987).
[2]J. Blezius and J. P. Carbotte, Phys. Rev. B **36**, 3622 (1987); J. Rammer, Phys. Rev. B **36**, 5665 (1987).
[3]V. Z. Kresin, Phys. Rev. B **35**, 8716 (1987); J. Ruvalds, *ibid.* **35**, 8869 (1987).
[4]C. M. Varma, A. Schmitt-Rink, and E. Ahrahams, Solid State Commun. **62**, 681 (1987).
[5]G. H. Eliashberg, Zh. Eksp. Teor. Fiz. **38**, 966 (1960) [Sov.

Phys. JETP **11**, 716 (1960)].
[6]A. B. Migdal, Zh. Eksp. Teor. Fiz. **34**, 1638 (1958) [Sov. Phys. JETP **7**, 996 (1958)].
[7]M. Grabowski and L. J. Sham, Phys. Rev. B **29**, 6132 (1984).
[8]D. J.Scalapino, in *Superconductivity,* edited by R. D. Parks (Dekker, New York, 1969), Vol. 2, p. 665; P. B. Allen and B. Mitrovic, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1982), Vol. 37, p. 1.
[9]G. D. Mahan, Phys. Rev. **142**, 366 (1966).
[10]G. D. Mahan, in *Many-Particle Physics* (Plenum, New York, 1981).
[11]S. Engelsberg and J. R. Schrieffer, Phys. Rev. **131**, 993 (1963).
[12]H. Rietschel and L. J. Sham, Phys. Rev. B **28**, 5100 (1983).
[13]J. C. Ward, Phys. Rev. **78**, 182 (1950).
[14]Hang-sheng Wu *et al.*, J. Phys. Chem. Solid **48**, 395 (1987).