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Van Hove excitons and high-T_c superconductivity: II. Toward a calculation of T_c

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Abstract. T_c is estimated for the excitonic model developed in an earlier paper. It is shown that, by inclusion of transverse phonon coupling and retardation effects, the high values of T_c and small isotope effects can readily be understood. The connection of the excitons with covalent bond formation is stressed, as well as the relation of high-T_c oxide superconductors to other exotic superconducting materials.

1. Introduction

The very high values of critical temperature in the new oxide superconductors [1], along with the very weak isotope effect [2], suggest that the pairing in these materials is brought about by a non-phonon mechanism. An excitonic mechanism [3–5], associated with some virtual electronic excitation of the system, has frequently been postulated [6–9], and this picture is supported by observation of an optical feature [10] which strongly correlates with T_c [11]. However, detailed calculations must still be carried out for these models. Can a microscopic gap theory be derived (or a modified BCS/Eliashberg equation shown to be valid) and can appropriate parameters be estimated to show that the mechanism does produce high T_cs? For the excitonic mechanism, there exists a large theoretical literature [3–5, 12–15], although without experimental examples a number of questions have not been answered.

The new high-T_c oxides afford an opportunity to re-analyse these ideas. Marsiglio *et al* [16] have used empirical values for the various coupling strengths to see what the properties of a strong-coupling excitonic superconductor would be. The present paper will try to estimate these parameters from a particular model of the electronic excitation. While a number of models for the exciton currently exist [5–9], the present calculations are based on the particular model introduced earlier (paper I [9]), associated with the van Hove singularity of the CuO_2 planes. The relevant antibonding band is shown in figure 1, identifying the proposed excitons and free holes. The excitons are generated by a (charge or spin) density-wave (DW) transition which gaps the Fermi surface only near the van Hove singularity (X points), leaving the relatively small hole pockets which are responsible for the observed Hall effect. These holes are considered to be responsible for the superconductivity, coupled into Cooper pairs by a combination of phonons and

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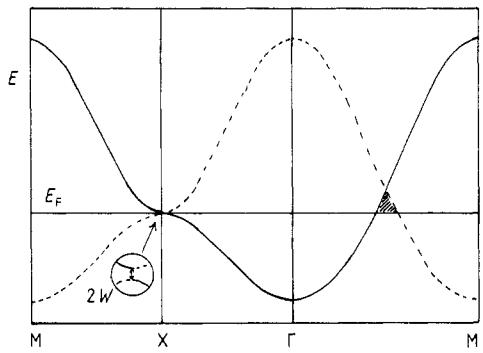

Figure 1. Idealised band structure of equation (1). Full curve, structure of equation (1); broken curve, extra bands produced by M → Γ zone folding; shaded region, light holes; inset, density-wave gap at the X point.

virtual electronic excitations across the DW gap. The above model applies directly to $La_{2-x}Sr_xCuO_4$(LSCO); a similar model, but with a three-dimensional charge DW (CDW), holds for $BaPb_{1-x}Bi_xO_3$(BPBO). In $YBa_2Cu_3O_7$(YBCO) and the new Bi and Tl compounds, the extra carriers present in the chain and Bi and Tl layers may also condense, leading to the higher T_Cs. The present considerations will concentrate predominantly on LSCO.

The DW transition has a simple interpretation: the transition from a metallic to a covalent Cu–O bond; the condensing holes are associated with direct O–O hopping [9]. In BPBO, there is a real CDW transition, and in the two-dimensional (2D) oxides, there are low-temperature transitions [17] which may possibly be identified with the DWs. However, evidence for short-range DW order (including the optical features [10, 11]) persists up to room temperature, and the possibility remains that no long-range order exists down to the superconducting transition.

Although the excitonic mechanism is applied here to the high-T_c oxide superconductors, it may have considerably wider validity. In the A15 compounds, a similar competition between superconductivity and DW formation exists [18, 19]. The calculations of paper I were in fact based on a modified Bilbro–MacMillan Hamiltonian [18]. Mazumdar [20] has postulated a close relation with the organic and heavy-fermion superconductors. As the covalent bond forms, the relevant carriers become more localised, leading to a band narrowing and enhanced effective mass. The heavy-fermion systems could be locked in close to the point of this localisation.

2. Ingredients for a calculation of T_c

Even in dealing with the usual electron–phonon mechanism, first-principles calculations of T_c are plagued by what Rainer calls 'superflexibility' [21]: too many parameters are too poorly known. In his words, 'We must at least consider the possibility that *although the present theory of T_c is able to explain every known experimental result, it is nevertheless unable to make reliable predictions.*' These same problems arise in trying to deal with the excitonic mechanism. Hence the present section carefully discusses the various steps of the calculation, and points out approximations which are made.

2.1. Migdal's theorem

Fundamentally, excitonic superconductivity should be very similar to phonon superconductivity, differing only in the nature of the boson exchanged. Hence the same type

of Eliashberg- or BCS-type of theory should apply. However, in dealing with phonons there is a small parameter, m/M, where $m(M)$ is the electronic (ionic) mass, which greatly simplifies the calculations. By Migdal's theorem [22], the electron–phonon coupling need be calculated only to lowest order in $(m/M)^{1/2}$, allowing neglect of vertex corrections. For an electronic excitation, this small parameter is in general absent. However, in the present case DW formation produces a mass renormalisation of the nearly localised holes $m \rightarrow m_d^*$, and the ratio m/m_d^* may again serve as a small parameter. In what follows, it will be assumed that Migdal's theorem is approximately valid.

With this assumption, the standard weak- and strong-coupling theories follow. In the phonon case the average electron–electron interaction can be written as $\mu - \lambda_{ph}$, where μ is the Coulomb repulsion and λ_{ph} is the phonon-mediated attraction. Once μ and λ_{ph} are known, T_c can be written in terms of them. Thus, in weak coupling,

$$T_c = 1.14\Theta \exp[-1/(\lambda - \mu^*)] \tag{1}$$

where Θ is an average phonon energy, μ^* is a renormalised Coulomb energy [23, 24],

$$\mu^* = \mu/(1 + \mu \ln(E^*/\omega_c)) \tag{2}$$

and E^* and ω_c are appropriate cut-off energies. For the phonon case, $\omega_c \simeq \Theta$; $E^* \simeq E_F$, the electron Fermi energy, and $\lambda = \lambda_{ph}$. If excitonic pairing is also important, it is tempting to substitute $\lambda_{ph} \rightarrow \lambda = \lambda_{ph} + \lambda_{ex}$, where λ_{ex} is the exciton-mediated electron attraction, and use an appropriately averaged value of Θ in equation (1). This substitution must be carefully justified, however, since it is no longer true that $E_F \gg \Theta$. Before this can be discussed, however, it is necessary to recognise a fundamental limitation on the allowed values of λ and μ.

2.2. *Lattice stability*

The parameters λ and μ can be related to the total dielectric constant of the medium, $\varepsilon = \varepsilon_{el} + \varepsilon_{ph} - 1$, where $\varepsilon_{el}(\boldsymbol{q}, \mu)$ is the electronic dielectric constant and $\varepsilon_{ph}(\boldsymbol{q}, \mu)$ is the phonon part. Then the pair potential seen by two electrons is

$$V_{pair}(\boldsymbol{q}, \psi) = v(\boldsymbol{q})/\varepsilon \simeq v/\varepsilon_{el} - v(\varepsilon_{ph} - 1)/\varepsilon_{el}^2 \equiv V_{ee} + V_{ph} \tag{3}$$

where $v = 4\pi e^2/q^2\varepsilon_0$ is the Fourier transform of the bare Coulomb potential and ε_0 is the background dielectric constant. Then $\mu(\lambda_{ph})$ is given by an appropriate average of $V_{ee}(-V_{ph})$ in the low frequency ($\omega \rightarrow 0$) limit. Cohen and Anderson [25, 26] pointed out that the stability of the lattice imposes restrictions on equation (3). In particular, they suggested that the lattice is only stable if $\varepsilon(q, 0) > 0$, in which case

$$\lambda < \mu. \tag{4}$$

Now μ may be written as [13]

$$\mu = \mu_0 \int_0^{2k_F} \frac{dq}{q\varepsilon_{el}(q, o)} \tag{5}$$

where k_F is the Fermi momentum, $\mu_0 = e^2 m/\pi\hbar^2\varepsilon_0 k_F \equiv \alpha r_s/\pi$, $\alpha = (4/9\pi)^{1/3}$ and r_s is the normalised electron radius. Hence, for any approximation to the dielectric constant,

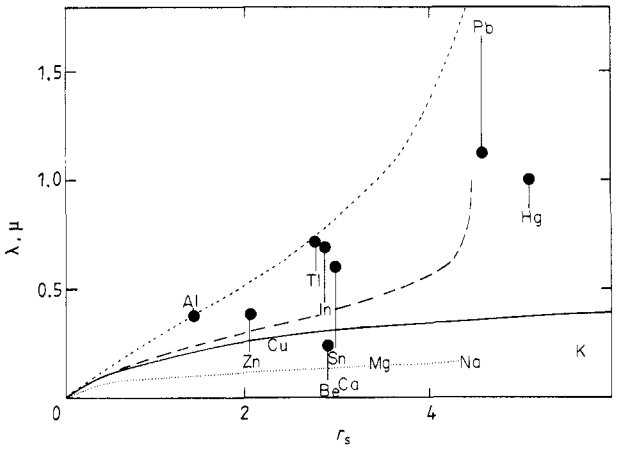

Figure 2. Test of equation (4): experimental λ values (symbols) against theoretical μ values (curves). Chemical symbols are from reference [28]; full circles are from reference [27]. Full curve, μ_L; long-broken curve, μ_{RPA}; short-broken curve, $\mu_{\beta=3}$; dotted curve, $\mu^*_{\beta=3}$.

the value of μ can be readily calculated. Figure 2 shows μ calculated (full curve) for the Lindhard dielectric constant appropriate to the free-electron gas:

$$\varepsilon_L(q,0) = 1 + (\mu_0/2\hat{q}^2)\{1 + [(1-\hat{q}^2)/2\hat{q}]\ln[(1+\hat{q})/(1-\hat{q})]\} \equiv 1 + \kappa^2(\hat{q})/\hat{q}^2 \qquad (6)$$

where $\hat{q} = q/2k_F$. Shown also are realistic estimates [27, 28] for λ_{ph}, based on analyses of experimental data. From the figure, it would appear that equation (4) is violated for the majority of superconductors. While it is possible to improve the calculation of μ by the incorporation of many-particle effects, this does not greatly improve matters. For instance, away from the high-density limit ($r_s \to 0$), μ_0 is renormalised by Fermi-liquid effects. Within the random-phase approximation (RPA) [29], μ_0 is replaced by

$$\mu_{0RPA} = \mu_0/[1 - \mu_0 - \mu_0^2(1 - \ln 2)\ln r_s]. \qquad (7)$$

Substituting this expression into equation (5) enhances μ significantly (long-broken curve in figure 2). However, for large values of r_s the RPA itself becomes inaccurate—the lattice becomes unstable, $\mu_{0RPA}^{-1} = 0$, at $\mu_0 = 0.745$. Moreover, at large r_s exchange and correlation effects modify the form of ε_L; typical Hubbard corrections [30] to ε will reduce the difference between μ and μ_{RPA}. In all cases, equation (4) is violated: $\lambda_{ph} > \mu$.

The solution to this problem was suggested, in general terms, by Cohen and Anderson [25]. They pointed out that ε is not a scalar, but a tensor $\tilde{\varepsilon}(q, \omega)$, in reciprocal lattice space, with matrix elements $\varepsilon_{KK'}$, where K and K' are reciprocal lattice vectors. The criterion for lattice stability deals with the direct dielectric constant: instability first occurs at a value of $q = q_0$ for which $\det \tilde{\varepsilon}(q_0, 0) = 0$ is satisfied. On the other hand, the dielectric constant entering into equation (3) is $1/[\tilde{\varepsilon}^{-1}]_{00}$, i.e., the inverse of the $K = K' = 0$ element of the tensor $\tilde{\varepsilon}^{-1}$. This tensor-inversion process could explain the deviations from equation (4). The elements of ε with K or $K' \neq 0$ refer to Umklapp processes, and hence to short-range interactions. The local fields seen by the electrons and the ions are not exactly the same, so screening cannot be described by a simple average dielectric constant (ε_{00}). In first-principles calculations of λ_{ph}, Umklapp processes are known to make a significant contribution (e.g. reference [31]). Such local-field effects are expected to be large in the high-T_c superconductors, since the average carrier separation is larger

than the Cu–O separation distance [32]. Moreover, the pile-up of charge associated with a covalent bond must be described in terms of off-diagonal elements of the dielectric constant tensor [33].

However, it is still not clear how Umklapp processes alleviate the disagreement between equation 4 and experiment (figure 2). This is a perfect example of superflexibility. In what follows, a number of possible explanations are listed.

(1) Dolgov *et al* [34] have pointed out that lattice stability only requires $\varepsilon_{00}^{-1}(q, 0)$ to be positive at $q = 0$. Hence, in averaging equation (3) to find μ and λ, it would be possible for $\mu - \lambda < 0$ if $\varepsilon_{00}^{-1}(q, 0) < 0$ for most finite q. Mathematically, it is possible to have $\det(\bar{\varepsilon}) > 0$ while $\varepsilon_{00}^{-1} < 0$. However, it is hard to construct a simple model dielectric constant which has this property.

(2) A second possibility is that inclusion of Umklapp processes enhance the value of μ, as well as λ, to the point where equation (4) is satisfied. In this view, superconductivity is possible because $\mu^* \ll \mu$, so $\lambda - \mu^* > 0$ is possible. Why does Umklapp enhance μ? Because dielectric screening must break down at short range ($\varepsilon \rightarrow 1$): in particular, the on-site Coulomb repulsion U is only weakly screened, and it is the Umklapp processes which describe this short-range renormalisation. A simple example will illustrate how this occurs. An element of the dielectic tensor can be written

$$\varepsilon_{KK'}(\boldsymbol{q}, \omega) = \delta_{KK'} - v(\boldsymbol{K} + \boldsymbol{q})\pi_{KK'}(\boldsymbol{q}, \theta) \tag{8}$$

where $\tilde{\pi}$ is a polarisation tensor. Because of the factor $v(\boldsymbol{K} + \boldsymbol{q})$, the largest off-diagonal elements of $\bar{\varepsilon}$ are in general those with $\boldsymbol{K} = 0$. Hence, a good first approximation to the dielectric tensor should be to neglect all off-diagonal matrix elements unless either $\boldsymbol{K}$ or $\boldsymbol{K}'$ is zero. then

$$\bar{\varepsilon} \equiv 1/[\bar{\varepsilon}^{-1}]_{00} = \varepsilon_{00} - \sum_{K \neq 0} \varepsilon_{0K}\varepsilon_{K0}/\varepsilon_{KK}. \tag{9}$$

Since $\pi_{0K} = \pi_{K0}$, equation (9) shows that $\bar{\varepsilon} < \varepsilon_{00}$ if all the ε_{KK} are positive. Since it is $\bar{\varepsilon}$ that enters into equation (3), the value of μ will be enhanced over that shown in figure 2, which assumed $\varepsilon = \varepsilon_{00}$. In the present model, $\bar{\varepsilon}$ may also be written as $\det \bar{\varepsilon}/\Pi_{K \neq 0}\, \varepsilon_{KK}$, so $\bar{\varepsilon}$ can only be negative if some ε_{KK} is negative. Local-field corrections are likely to be particularly large in the high-T_c materials, since the carrier density is low and macroscopic screening is not likely to set in until the carriers are several lattice constants apart [32].

(3) Finally, there will be coupling via transverse phonons. For simple, nearly-free-electron metals, the electrons only interact with longitudinal phonons; in more complicated d-band metals, interaction with transverse phonons is of a comparable strength—particularly since this transverse coupling is only poorly screened. While the importance of transverse phonons has been recognised theoretically [35] and confirmed in first-principles calculations of λ [31], it has proven difficult to provide a simple treatment of them. In this paper a simplified procedure is followed. An extra term $-V_{\mathrm{ph}}^{\mathrm{tr}}$ is added to equation (3), producing an extra contribution , $\lambda_{\mathrm{ph}}^{\mathrm{tr}}$. The calculation of $\lambda_{\mathrm{ph}}^{\mathrm{tr}}$ will follow that of λ_{ph}, but electronic screening will be neglected ($\varepsilon_{\mathrm{L}} \rightarrow 1$). Lattice stability (equation (4)) involves only $\lambda_{\mathrm{ex}} + \lambda_{\mathrm{ph}}$, so $\mu - \lambda_{\mathrm{ex}} - \lambda_{\mathrm{ph}} - \lambda_{\mathrm{ph}}^{\mathrm{tr}}$ can be negative. In general, if λ_{ex} is neglected, it would be expected that $\lambda_{\mathrm{ph}}^{\mathrm{tr}} \simeq \lambda_{\mathrm{ph}}$, so $\lambda_{\mathrm{ph}} + \lambda_{\mathrm{ph}}^{\mathrm{tr}} \leqslant 2\mu$. This relation is satisfied for all the data in figure 2 taking $\mu = 2\mu_{\mathrm{RPA}}$.

A priori, there is little reason to choose either (2) or (3) as the dominant effect. Below, it will be seen that effect (3), transverse coupling, is likely to be important in the high-T_c superconductors. It should be noted from figure 2 that for metals without a

significant d-band contribution, λ is always less than the Lindhard value of μ. This is expected, since local-field corrections should be small in these materials.

2.3. Estimating parameters

Rather than carry out a full solution of the Eliashberg equations [24], the parameters of equations (1) and (2) will be estimated following the calculations of Kirzhnits *et al* (KMK) [13]. It should be cautioned that the KMK equation is only approximate, and it has been shown that their equation may severly *underestimate* T_c when electronic mechanisms are dominant [36]. Nevertheless, for ordinary phonon coupling their equation is usually an improvement (closer to the Eliashberg results) over the BCS treatment [37]. In the present case, the sharp DW gap produces well defined structure in the dielectric constant, and so the KMK treatment should be adequate.

The KMK analysis provides simple analytic expressions for μ (equation (5)) and λ, if the phonon and excitonic features are characterised by Einstein oscillators[38]. The dielectric constant is written in the form

$$\varepsilon(q,\omega) = \varepsilon_L(q,\omega) + \sum_\nu f_\nu/(\omega_{0\nu}^2 - \omega^2 - i\omega\tau_\nu) \tag{10}$$

where ε_L is the Lindhard dielectric function, ν is an index running over phonon and electronic modes, f_ν is the oscillator strength, $\omega_{0\nu}$ the bare frequency and τ_ν the relaxation time of the νth mode. In the present calculation, only a single phonon and exciton mode $\nu = \mathrm{ph}, \mathrm{ex}$ will be included, and the limit $\tau_\nu \to 0$ will be assumed. In the model of van Hove excitons, for $La_{2-x}Sr_xCuO_4$,

$$f_{ex} \simeq \omega_{pl,ex}^2 \simeq \omega_{pl}^2/x \tag{11}$$

where ω_{pl} is the plasma frequency of the holes away from the van Hove singularity and $\omega_{pl,ex}$ is the plasma frequency of those holes near the van Hove singularity. From the optical spectra, it can be seen that equation (11) is approximately satisfied. In terms of the dielctric constant equation (10) the pair potentials can be written [13]

$$\lambda_\nu = \mu(f_\nu/\omega_{0\nu}^2)/(1 + \Sigma f_\nu/\omega_{0\nu}^2). \tag{12}$$

Equation (12) has the expected features that $\lambda < \mu$ and $\lambda_{ex} \propto 1/\omega_{0ex}^2$ as $\omega_{0ex} \to \infty$.

For the transverse phonons, an equation similar to equation (12) is assumed to hold, involving only transverse contributions. In particular, it is assumed that there are no transverse electronic contributions in the denominator (corresponding to the neglect of a possible λ_{ex}^{tr}). Finally, while a single-mode approximation is probably adequate for the exciton mode, it is undoubtedly a poor estimate for the electron–phonon coupling, which is an integral over all phonon modes. To roughly account for this, both λ_{ph} and λ_{ph}^{tr} are multiplied by three. This factor is highly approximate, but takes into account the idea that since f_{ph} will be comparable to ω_{0ph}^2, many modes will make comparable contributions. It seems highly improbable that an enhancement factor will be less than three; indications from other calculations [16], discussed below, suggest that the factor is closer to six. Finally, KMK show that the remaining parameters of equations (1) and (2) can be written;

$$\Theta^\lambda = \omega_{ex}^{\lambda ex}\omega_{ph}^{\lambda ph} \tag{13}$$

and $\omega_c = \Theta/\mu_{0RPA}^{1/3}$. The approximate value of E^* is comparable to the full band

width [27, 39]; in the present case, the band is approximately half full, suggesting $E^* \simeq E_B/2$.

2.4. Numerical estimates

Most of the parameters for $La_{1.85}Sr_{0.15}CuO_4$ can be derived from experiment. From optical studies [10, 11, 40] $\varepsilon_0 = 4.5$, $\omega_{pl.ex} = 0.84$ eV, $\omega_{0.ex} = 0.45$ eV, $\omega_{pl} = 0.36$ eV; the free-hole density $n \simeq 3 \times 10^{21}$ cm^{-3} from Hall-effect studies [41]; while the band mass is estimated to be $2m_0$ (m_0 is the free-electron mass). In the van Hove exciton model, the free carriers are associated with Fermi-surface sections away from the high-DOS regions, and so may have smaller masses. On the other hand, there are then four carrier pockets, and this degeneracy affects r_s in the same manner as a higher mass. Hence the assumption $m = 2m_0$ is made to include approximately both band mass and degeneracy factors. The bandwidth is probably between 2–3 eV. In the present calculation, the value $E_B \simeq 2.4$ eV is chosen.

The in-plane phonon modes do not show up well in the optical spectra, because of free-carrier absorption. However, the oscillator strength should be comparable to the square of a phonon plasma frequency [42]:

$$f_{ph} \simeq \Omega_{pl.ph}^2 = 4\pi N(Ze)^2/\varepsilon_L M \tag{14}$$

where N, M and Ze are the appropriate ionic density, reduced mass and valence charge of the particular phonon mode. For the highest-frequency modes, N is the oxygen density, M the reduced mass of two oxygen atoms and $Z \simeq 2$, giving $\Omega_{pl.ph} \simeq 28$ meV. The corresponding f_{ph} is of approximately the order of magnitude observed for transverse phonons. For this mode, $\omega_{o.ph} \simeq 60$ meV. For simplicity, the same values are assumed for λ_{ph}^{tr}.

These parameters give $r_s = 3.6$ and $\mu_0 = 0.59$. Hence, assuming $\mu = \mu_{RPA} = 0.48$, $\lambda_{ex} = 0.36$, $\lambda_{ph} = 0.069$, $\lambda_{ph}^{tr} = 0.26$, $\lambda = 0.69$ and $\Theta = 0.17$ eV. Hence, $E^* \simeq 1.2$ eV, $\omega_c \simeq 0.13$ eV, so $\mu^* \simeq 0.23$ and, from equation (1), $T_c = 220$ K. However, for such large values of λ, a strong-coupling calculation of T_c is required. Simply plugging λ and μ^* into a McMillan-type formula [27] yields

$$T_c = 1.14\Theta \exp -\left\{\frac{(1+\lambda)}{[\lambda - \mu^*(1+0.62\lambda)]}\right\} = 20\ \text{K} \tag{15}$$

comparable to the experimental value ~38 K. However, the McMillan formula was not designed to deal with the situation where μ^* is comparable to λ and hence is likely to overestimate the T_c reduction.

A comparison with the work of Marsiglio *et al* [16] is illuminating. They showed that the properties of the high-T_c superconductors could be explained by a strong-coupling excitonic model if the following parameter values were assumed: $\lambda_{ex} = 0.4$, $\lambda_{ph} = 0.6$, $\mu^* = 0.15$. The present calculation finds comparable values for the parameters. (The choice of phonon enhancement factor of three was purely for illustrative purposes; doubling that would bring λ_{ph} into agreement.) Note, however, that agreement for the phonon modes was achieved only by inclusion of the transverse phonons. From equation (12), it is seen that the longitudinal phonons are screened by the low-frequency polarisability of the electronic mode. A similar effect is found in the optical spectra, where the background dielectric constant ε_0 must be taken to be considerably larger in the infrared than in the visible, to account for the electronic excitations. This reduction of λ_{ph} seems inevitable as long as a purely longitudinal dielectric constant is assumed. Hence, to

explain the relatively large isotope effect [43] in $La_{2-x}Sr_xCuO_4$ it is necessary to include the effects of transverse phonons.

In the present model, $1 < \lambda/\mu = 1.44 < 2$. Thus superconductivity is due to both the presence of transverse phonons (allowing $\lambda > \mu$) and retardation effects ($\mu > \mu^*$). The retardation effects are similar to those found in ordinary phonon-induced coupling: the exciton response is sufficiently slower than the free-carrier relaxation to allow time-delayed carrier pairing. The importance of retardation effects can be seen by repeating the above calculation in the absence of retardation (i.e., assuming $\mu^* = \mu$). Using the weak-coupling formula (equation (1)) $T_c = 19$ K, but from equation (15) the system is found not to be superconducting.

It is likely that a full strong-coupling calculation will show that the effects of μ^* are even less significant. Rietschel and Sham [44] showed that within the RPA, a correct strong-coupling calculation would predict superconductivity based on μ alone, even in the absence of λ, for $r_s > 2.5$; in the KMK approximation T_c would be orders of magnitude smaller. However, this also shows the problems with such calculations. Since there are real metals with $r_s > 2.5$ which are non-superconducting, a correct calculation of T_c must go beyond the RPA [44].

3. Discussion

3.1. Connection with the model of paper I

It is important to stress precisely which features of the model introduced in paper I are relevant to the above calculations. The model of paper I describes the carriers in each $Cu–O_2$ plane as a correlated Fermi liquid, with a well defined Fermi surface. These carriers naturally fall into two groups, a high-DOS group (heavy holes) near the van Hove singularity and a low-DOS group (light holes) associated with other parts of the Fermi surface. In short, it is proposed that the heavy holes have a charge (or spin) density-wave instability, and that excitations across the resulting charge-transfer excitonic gap produce Cooper pairing among the light holes. The specific features of the model relevant to the present calculations are as follows.

(i) Knowledge of the Fermi surface allows estimates of the relevant hole densities and effective masses. Moreover, as shown in figure 1, the Fermi energy is small compared with the full bandwidth, E_B. This feature is essential for minimising the effect of the Coulomb term, μ^*, as discussed in § 2.3.

(ii) While long-range DW order may set in only at or below the superconducting transition temperature, a short-range (2D) DW gap persists up to temperatures above room temperature. It is this short-range gap which is relevant both for superconductivity and in the optical spectra. Hence, the exciton energy $\hbar\omega_{ex}$ can be considered to be a temperature-independent constant.

(iii) The effect of the strong on-site Coulomb repulsion has been incorporated [45] into the model via a slave boson calculation [46]. It is found that in LSCO, where the van Hove singularity coincides with the Fermi level for a Sr excess $x \simeq 0.18$, the material phase separates for Sr concentrations away from this special value. The high-T_c values are associated with this special x value, and hence need only be calculated for this particular case. If the domains of the two phases are small enough and intimately mixed, proximity effects can both reduce T_c in the van Hove phase and induce a (lower) T_c in the second phase. On the other hand, if the domains are large enough, T_c may be

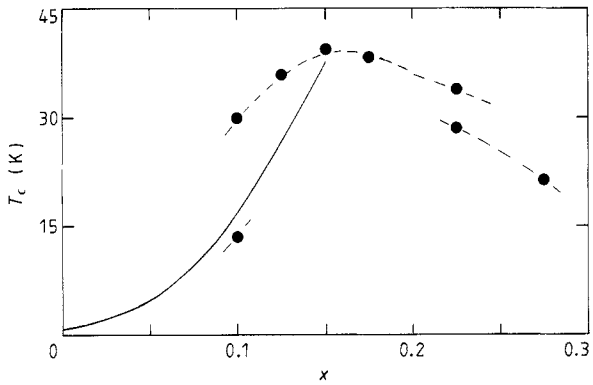

Figure 3. Sr-doping dependence of T_c in LSCO. Full circles, data of reference [50]; full curve, equations (16) and (17); broken curves, guides to the eye.

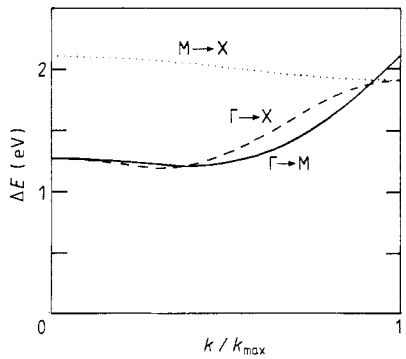

Figure 4. Renormalised interband (bonding to non-bonding Cu–O_2 bands) transitions, calculated in the slave boson scheme, following reference [45], for several directions in the Brillouin zone. Bare parameters are $t_{CuO} = 1.2$ eV, $t_{OO} = 0.48$ eV, $\Delta E = 5.4$ eV.

completely unaffected by the second phase. Interestingly, both phenomena can be observed in LSCO. Since Sr diffusion is slow, domains formed in Sr-doped material should be small, and proximity effects large. This is seen to be the case in the data of reference [46], where there appear to be two T_cs away from optimum doping. The values deduced from the resistive transitions are shown in figure 3. The reduction in T_c is consistent with proximity effects. However, La_2CuO_4 can also be hole doped by excess O [47]. In this case, the rapid O diffusion allows large domains to form, leading to an observed superconducting T_c which is independent of O doping (although the fraction of the sample which goes superconducting is proportional to the excess O concentration).

(iv) This same microscopic calculation [45] can be used in interpreting the optical spectra. In particular, the model predicts the location of interband transitions, both at the bare-energy separations and at the interband gaps renormalised by the slave boson effects. The smallest renormalised interband gaps are found only at energies above 1 eV (see discussion in paper I and figure 4). Hence the observed [10, 11, 40] optical transition at 450 meV in LSCO cannot be interpreted as an interband transition. This is consistent with the present model, in which it is attributed to the DW transition, i.e. it is identified as $\hbar\omega_{ex}$.

3.2. Superflexibility

The above estimates have shown that, by incorporating the excitons into a dielectric constant formalism, the high values of T_c arise rather prosaically. The key ingredient

has been in understanding the role of equation (4). This still remains unsatisfactory, but the problem exists for ordinary superconductors as well as for the high-T_c materials. It would be most useful to repeat first-principles calculations of λ_{ph} in ordinary superconductors, calculating μ at the same time. The optimum procedure would consist in sorting contributions to μ and λ (i.e. the $\varepsilon_{KK'}$ terms) as to whether they enhance μ above the Lindhard value μ_L, contribute to λ_{ph}^{tr}, or contribute to $\lambda > \mu$ in some other fashion. However, it would be interesting just to have values of μ to see whether $\mu > \mu_L$ or $\lambda > \mu$.

Some insight into alternative possibilities can be obtained by repeating the calculations of § 2, but neglecting λ_{ph}^{tr} and assuming that μ is enhanced above μ_L, so that $\mu > \lambda$. (This corresponds to choosing alternative 2 rather than alternative 3 in § 2.2.) From equation (8), the off-diagonal terms are seen to reduce the magnitude of κ^2 in equation (6). If the reduction is taken to be uniform: $\kappa^2 \rightarrow \kappa^2/\beta$, where β is a q-independent constant, then the effect of these terms is easily accounted for. The short-broken curve in figure 2 shows the resulting μ_β, with $\beta = 3$, the smallest value consistent with $\mu > \lambda$. The dotted curve shows that μ_β^*, calculated from equation (2), is physically plausible: for most r_s it satisfies $0.08 \leqslant \mu_\beta^* \leqslant 0.15$, which is in the range generally used in calculations of T_c. For estimating μ_β^*, ω_c was taken as a fixed value $\omega_c = 150$ K, and $E^* = E_F = \alpha^2 E_R / r_s^2$, where $E_R = 13.6$ eV is the Rydberg energy. Using $\mu_{\beta=3}$, the calculations of § 2 yield $\mu = 1.05$, $\lambda_{ph} = 0.15$, $\lambda_{ph}^{tr} = 0$, $\lambda_{ex} = 0.79$, $\Theta = 0.33$ eV and $\mu^* = 0.40$, giving $T_c = 600$ K (from equation (1)). However, the large value of μ^* leads to a low value $T_c = 5.8$ K, calculated from the strong-coupling (15). This equation is likely to be inaccurate for such large values of μ^*, and a rigorous calculation [44] might yield acceptable values of T_c. However, as long as $\lambda_{ph}^{tr} = 0$, the ratio $\lambda_{ph}/\lambda_{ex}$ will be small, and it will be difficult to explain the isotope effect in $La_{1.85}Sr_{0.15}CuO_4$. Hence on balance assumption 3 seems more consistent with the data.

3.3. Resonating covalent bond

The problem of superflexibility means that the present calculation can lend only limited insight into the very interesting question of the competition between superconductivity and lattice instability (DW formation). It does help clarify one important point already discussed in paper I of this series. Even after a DW has formed, the large density of states it is associated with is not entirely lost to the superconducting instability—it is merely shifted to higher frequencies in the form of an excitonic pairing mechanism.

A microscopic understanding of the role of Umklapp processes should do much to elucidate the connection between superconductivity and lattice instability, as well as to relate the present dielectric constant formalism to more microscopic tight-binding pictures of the $Cu–O_2$ planes, in terms of on-site and nearest-neighbour Coulomb repulsion (U, Vs) and hopping integrals (ts). The two carrier groups are associated with Cu–O hopping (t_{CuO}) and direct O–O hops (t_{OO}), and the DW formation can be looked on as forming a covalent Cu–O bond. The connection between DWs and covalent bonds has previously been pointed out by Cohen and Anderson [25] and McMillan [48]. It has been shown [33] that Phillips [49] bond charges are associated with off-diagonal elements of the dielectric constant tensor. It would be most interesting to generalise the present calculation to include the role of the DW transition explicitly—instead of taking λ_{ex} as a fixed parameter, to model the DW transition itself, allowing the lattice to soften and ω_{ex} to grow from zero. Such a calculation would be relevant to the high-T_c superconductors, since it appears likely that the DW transition does not occur until low temperatures, and that ω_{ex} observed optically at room temperature is caused by strong two-dimensional

fluctuation effects. Hence it may be that superconductivity in these materials is not associated with a fixed CDW, but with a resonating covalent bond. The connection of this idea with Anderson's resonating valence bond [50] should be obvious. However, the essential difference is that the holes which become superconducting are different from those associated with covalent bond formation. The present calculation suggests that high-T_c superconductivity should persist in the presence of a long-range CDW, although the uncertainty in all parameters does not allow very firm conclusions to be drawn.

3.4. Spin-wave fluctuations

The above calculations have neglected any effects of spin-wave coupling on T_c. Such effects are usually deleterious [51], but an enhancement of T_c is possible in some cases [52], and coexistence of superconductivity and antiferromagnetism is known to occur [53]. A number of experimental observations on the high-T_c oxides could be explained by assuming a spin-wave contribution to T_c of the form [51]

$$T_c = 1.14\Theta \exp\{-(1 + \lambda + \mu_s)/[\lambda - (\mu^* + \mu_s)(1 + 0.62\lambda)]\} \tag{16}$$

where μ_s is the effective electron-spin excitation coupling constant. For instance, as x is varied in $La_{2-x}Sr_xCuO_4$, an interesting phase diagram is found, indicative of a competition between superconductivity and antiferromagnetism. A similar effect occurs in $YBa_2Cu_3O_{7-\delta}$ as a function of the oxygen deficit δ. The data in figure 3 show the values of $T_c(x)$ measured resistively [54]; the full curve is equation (16), with

$$\mu_s = 0.04 + 0.9 \times (0.15 - x). \tag{17}$$

(The other parameters are chosen as $\Theta = 0.17$ eV, $\mu^* = 0.23$, $\lambda = 0.9$, i.e., adjusting λ to give $T_c = 38$ K at $x = 0.15$.) Of course, μ_s should be calculated, but it seems reasonable to assume that it is larger in the $x = 0$ phase, which has long-range antiferromagnetic order. This explanation would hold whether the intermediate-x materials constituted a single homogeneous phase or were a proximity-effect coupled intergrowth of two phases [9]. Moreover, if μ_s is non-zero even at $x = 0.15$, this could explain the strong pressure dependence of T_c, as pressure can rapidly reduce the value of μ_s [55]. With the above parameters, T_c would increase to 66 K if $\mu_s \rightarrow 0$.

3.5. Two-dimensional superconductivity

The above calculations have treated the new oxides using equations appropriate to a three-dimensional material. In reality, these are highly anisotropic, nearly two-dimensional layered compounds. The above calculations would still approximately describe the in-plane coupling, but interlayer coupling is necessary for long-range order. Ordinarily, the weakness of the interlayer coupling would greatly reduce T_c. This would be partially compensated in that screening is poorer in 2D, so μ and hence λ would be larger. However, Tesanovich [56] has shown that three-dimensional coupling could actually enhance T_c if there can be coupling to bands near the Fermi level which have significant c-axis dispersion. While no bands are likely to have a large c-axis dispersion, there are bands near E_F with more interlayer coupling than the antibonding band of figure 1 (e.g., the oxygen p orbitals which point out of the plane). Hence the enhancement of T_c would not be large. Nevertheless, as long as T_c is not reduced by the interlayer couplings, the present calculations show that excitonic couplings can explain the observed T_cs.

3.6. Other high-T_c oxides

The present paper has discussed the superconductivity of a single CuO_2 layer, appropriate for the LSCO superconductors. In paper I it was suggested that the higher T_cs of the other oxide superconductors could be generated by the mechanism discussed by Ginzberg [4] and Allender *et al* [5]. Applied to the oxides, this would work as follows: superconductivity in the CuO_2 plane would be similar to LSCO. Carriers in another plane (e.g. the chains in YBCO) would be coupled via excitons in the CuO_2 planes (a proximity effect), yielding the higher T_c. Now, the appropriateness of such a model can be tested.

Unfortunately, the material parameters for these additional carriers are even harder to estimate, so the present calculation can do no more than establish the plausibility of the proposed mechanism. Within the present framework, the most propitious circumstance would be that the chain carriers have low density (high r_s), to take advantage of larger λ values. In YBCO, the exciton frequency is also known to be higher [10], $\omega_{0,ex} \simeq 0.8$ eV; it will be assumed that $\omega_{pl,ex}$ and E_B are enhanced in the same ratio. Other parameters will be kept the same as in LSCO. Thus, $r_s = 4.4$, $\mu \simeq 1$ and $\lambda_{ex} \simeq 0.75$. Keeping $\lambda_{ph} + \lambda_{ph}^{tr} = 0.33$ yields $\Theta = 360$ meV, $\mu^* = 0.33$ and $T_c = 93$ K (strong coupling, equation (15)). This must be appropriately averaged with the T_c of the CuO_2 layers (which, because of the larger $\omega_{0,ex}$, is $T_c = 34$ K) but the potential enhancement is clear. Considerably higher T_cs would be found using the value [16] $\lambda_{ph} = 0.6$: $T_c(CuO_2) \simeq 98$ K, T_c (chains) $\simeq 189$ K.

3.7. Relation to other systems

The correlation between enhanced T_c and proximity to a lattice instability has long been known, and attributed to electronic effects—high density of states and Fermi-surface nesting—which can enhance either instability. The exact nature of the competition between superconductivity and DW formation has been quite difficult to work out, since Fermi-surface nesting is an 'extended' description of what is essentially a 'localised' phenomenon: the tendency to covalent bond formation. The high-T_c oxides force recognition of an aspect of this competition that has previously been overlooked. Even after a covalent bond (DW) forms, the high density of states is still available, via virtual transitions, for enhancing the superconducting pairing.

The question is, to what extent does this effect exist in other families of unusual superconductors. The A15s show very similar bond structure effects: high DOS, nesting regions near the Brillouin zone boundary coexisting with low-DOS regions near the zone centre, and the calculations of Bilbro and McMillan [18] have served as a paradigm for the present model [9]. These materials also have a small isotope effect, which has prompted speculation of non-phonon coupling mechanisms [57]. Being the highest-T_c non-oxide superconductors, they are natural candidates in which to search for this excitonic mechanism.

As the material approaches the DW transition, the carriers associated with the bond charge become more localised. The DOS peak narrows and the carrier mass m_d^* is enhanced. In this regime of quasi-localisation, when $m_d^* \gg m$, the dielectric response would involve an acoustic plasmon [58], which could be considered as the precursor to the DW exciton, and would also lead to a T_c enhancement. The heavy-fermion systems are locked into this quasi-localised state, with $m_d^* \gg m$. The sharpness of the DOS peak arises because the band involve f electrons rather than d electrons.

A similar two-carrier-group picture can also be applied to the organic superconductors. An interesting variation in both the organic and heavy-fermion superconductors is that the instability involves a SDW. This may explain why the heavy-fermion superconductors show signs of triplet pairing.

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