[7] L. N. Cooper, Phys. Rev. **104**, 1189 (1956).

[8] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[9] K. Maki and P. Fulde, Phys. Rev. **140**, A1586 (1965).

[10] M. A. Woolf and R. Reif, Phys. Rev. **137**, A557 (1965); D. K. Finnemore, D. L. Johnson, J. E. Ostenson, F. H. Spedding, and B. J. Beaudry, Phys. Rev. **137**, A550 (1965); J. J. Hauser, H. C. Theuerer, and N. R. Werthamer, Phys. Rev. **142**, 118 (1966).

[11] A. K. Bhatnagar and E. A. Stern, Department of Physics and Astronomy Technical Report No. 755, University of Maryland, 1967 (unpublished).

[12] A. K. Bhatnagar and E. A. Stern, Phys. Rev. Lett. **21**, 1061 (1968).

[13] A. K. Bhatnagar, Bull. Am. Phys. Soc. **14**, 191 (1969).

[14] O. P. Hansen, Phys. Rev. **181**, 671 (1969).

[15] R. P. Groff and R. D. Parks, Phys. Rev. **176**, 567 (1968).

[16] A. Schmid, J. Low Temp. Phys. **1**, 13 (1969).

[17] E. Brun Hansen and P. Voetmann Christiansen, University of Copenhagen, Denmark, 1970 (report of work prior to publication); P. V. Christiansen, E. B. Hansen, and C. J. Sjöström, J. Low Temp. Phys. **4**, 349 (1971).

[18] V. L. Ginzburg and L. D. Landau, Zh. Eksp. Teor. Fiz. **20**, 1064 (1950).

[19] C. D. Mitescu, Rev. Mod. Phys. **36**, 305 (1964); also, in *Proceedings of the Tenth International Conference on Low-Temperature Physics, Moscow, 1966*, edited by M. P. Malkov (VINITI, Moscow, 1967), Vol. 2B, p. 336.

[20] J. L. Levine, Phys. Rev. Lett. **15**, 154 (1965).

[21] J. E. Mercereau and L. T. Crane, Phys. Rev. Lett. **9**, 381 (1962).

[22] K. Rose and M. D. Sherrill, Phys. Rev. **145**, 179 (1966).

[23] D. H. Douglass, Jr., Phys. Rev. **132**, 513 (1963).

[24] S. Tolansky, *Multiple Beam Interferometry of Surfaces and Films*, 1st ed. (Clarendon, Oxford, England, 1948).

[25] A. K. Bhatnagar and J. A. Stark, Department of Physics and Astronomy Technical Report No. 606, University of Maryland, 1966 (unpublished).

[26] W. S. Smyth, *Static and Dynamic Electricity* (McGraw-Hill, New York, 1950).

[27] The authors are thankful to Hungerford and Terry Inc., Arlington, Va., for supplying the zeolite free of charge.

[28] M. Tinkham, Phys. Rev. **110**, 26 (1959).

[29] P. G. de Gennes, *Superconductivity of Metals and Alloys* (Benjamin, New York, 1966).

[30] D. H. Douglass, Jr., Phys. Rev. **124**, 735 (1961).

[31] S. Skalski, O. Betbeder-Matibet, and P. R. Weiss, Phys. Rev. 136, A1500 (1964).

[32] D. H. Douglass Jr., Phys. Rev. Lett. **6**, 346 (1961).

[33] M. Tinkham, Phys. Rev. **129**, 2413 (1963).

[34] A. K. Bhatnagar, Bull. Am. Phys. Soc. **14**, 196 (1969).

PHYSICAL REVIEW B VOLUME 8, NUMBER 3 1 AUGUST 1973

Transition Temperature of d-f-Band Superconductors

J. Appel

I. Institut für Theoretische Physik, der Universität Hamburg, Germany

(Received 20 November 1972)

The theory of Appel and Kohn is used to calculate T_c for a narrow-band superconductor, where the conduction electrons near the Fermi suface have both d and f character. The vertex equations for the symmetrized pair states formed from d and f orbitals are solved in the contact model. The result is used for a parameter study of T_c; one pertinent parameter is the pairing interaction due to phonon exchange between d and f electrons. The experimental situation for La is discussed in terms of the T_c results.

I. INTRODUCTION

We address ourselves to the question: What is the effect on the superconducting transition temperature T_c that is caused by a narrow f band at or near the Fermi surface of a d band? The f band may be "infinitely narrow," corresponding to nonmagnetic and nonconducting f states, or it may have a finite width on account of $f-f$ overlap or covalent $d-f$ admixture. One reason for studying this question is the considerable interest in the mechanism for superconductivity in La and La-Ce alloys.[1-15] Also U has an unusual superconductive behavior, for example, with respect to the pressure dependence of T_c.[6] In metallic La, the electrons at the Fermi surface (FS) have a predominant d character, according to the large d-orbital contribution to the Knight shift and the nuclear spin relaxation in the normal state.[7] The $4f$ levels lie above the Fermi energy, but the distance is not known at present. However, the rare-earth element next to La, namely Ce, in the free atomic state has one bound $4f$ electron, whereas La has none. In the metallic state, Ce has $4f$ levels at or below the Fermi energy. The electrons occupying these levels cause a strong exchange enhancement of the magnetic susceptibility[8] and are responsible for the absence of superconductivity in Ce metal. Therefore, it is reasonable to assume that in La metal the $4f$ levels are close to (but above) the Fermi energy, the distance ϵ_f being of the order of a typical phonon energy $\hbar\omega_0$, where ω_0 is the maximum phonon frequency.

Under the assumption $\epsilon_f \leq \hbar\omega_0$, Kuper, Jensen, and Hamilton[1] have developed a theory of superconductivity in La based on a two-band model. The first band is the conduction band arising from the $5d\,6s^2$ valence electrons. In this band, the BCS mechanism of phonon exchange pairs the electrons at the FS. The second band is a narrow *f* band the width of which is less than $\hbar\omega_0$. Electrons from the conduction band can be virtually excited into the *f* band. Hence electrons at the FS spend short periods of time in 4*f* states. During these times, the electrons are paired through an antiferromagnetic exchange interaction provided their distance is equal to or larger than the interatomic separation. For smaller distances the Coulomb interaction is ignored, that is, the intra-atomic Coulomb repulsion is neglected. The authors justify the neglect by postulating that the Cooper pair wave function has a node at small electron separations. To achieve this, they assume that the orbital or relative wave function of a pair has 2*s* rather than 1*s* character. Then, it is found that the pairing between 4*f* electrons leads to a strong enhancement of T_c.

Another theoretical model which also involves the inner 4*f* shells has been developed by Ratto, Coqblin, and D'Agliano[2] to explain the pressure dependence of T_c observed on La. The authors presume a one-band model, where the 4*f* levels, lying above the FS, are covalently admixed into the conduction-band states. Thus the electrons at and near the FS have a certain *f* character, depending on the distance ϵ_f. During the time fractions which two electrons at the FS spend in *f* orbitals either at one and the same atom, or at near-neighbor pairs of atoms, they experience a large Coulomb repulsion. The leading term of this repulsion is the intra-atomic Coulomb interaction. The repulsion inhibits superconductivity more the closer the 4*f* levels lie to the FS. The plausible assumption, not yet experimentally verified, that with increasing pressure the 4*f* levels move away from the FS, leads to a continuous increase of T_c, parallel with the decrease in the 4*f* character of the electrons at the FS. Eventually, at high pressures, the 4*f* character is negligible and T_c saturates at a value given by the pairing interaction between electrons which have no 4*f* character left. This picture of Ratto *et al.* has been criticized by Wittig,[9] one reason being that Ratto *et al.* have no explanation for the high-T_c values observed at large pressures. At 130 kbar, the transition temperature T_c equals 12 °K, higher than any known T_c for pure elements.

In this paper we present a discussion of the transition temperature of an *f*-band superconductor, taking into account the important pairing interaction that is due to phonon exchange between *d* and *f* electrons. The BCS mechanism has a particular feature here since the electron-phonon interaction has matrix element coupling a *d* orbital and an *f* orbital both at the same site through the gradient of the ion potential at this site. This matrix element does not vanish for symmetry reasons since the parity of a *d* orbital and an *f* orbital differ by one and since the ion-potential gradient is odd under inversion symmetry. By the same token, the matrix element between two *d* orbitals is zero if the three sites are identical. The parity argument for the electron-phonon interaction is the central point in a theory by Hopfield[10] and by Chui[11] who discuss the transition temperature and the phonon structure of transition metals, where the *p*-*d* matrix element is important. For tightly bound electrons, the parity argument is immediately seen from the formulation of the theory of superconductivity by Appel and Kohn.[12] They use atomic or Wannier functions to write the pairing interactions. Their theory is applied to a *d*-*f*–band superconductor and T_c is calculated as a function of ϵ_f and a few other parameters which measure the strength of the intra- and inter-orbital pairing interactions.

In Sec. II, we first define our one-band model and its density of states and then we formulate the vertex equations for the electron-electron interaction. Assuming that the *d* and *f* orbitals are sufficiently localized, we use the contact model defined in I. The equations defining T_c conclude this section. In Sec. III we proceed the calculate T_c. The frequency dependence of the pairing interaction is parameterized in the manner of BCS. Then T_c is obtained as a function of the density-of-states parameters and a few pairing parameters. The results are discussed in relation to the transition temperature of La and its pressure dependence.

II. VERTEX EQUATIONS FOR *d*-*f*–BAND SUPERCONDUCTOR

A. Energy-Band Model

We define the energy-band structure which is used to set up the vertex equations for a Cooper pair. Spin-orbit coupling effects of the periodic lattice are ignored. They are important for atomic *f* states and also for the actual band structure of *f*-band metals and should be taken into account for quantitative calculations of T_c. However, we solve here the vertex equation with other approximations, such as the contact model and the BCS parametrization of the electron-electron interaction, which are sufficient to demonstrate the qualitative dependence of T_c on ϵ_f and the pairing interactions. Spin-orbit effects will not change the pertinent qualitative features of the results.

Let us now define our nonrelativistic *d*-*f* band for a cubic lattice. If the covalent admixture between *d* and *f* orbitals is negligible, the band model consists of a partly filled and degenerate *d* band of either Γ'_{25} or Γ_{12} symmetry and of a narrow *f* band of one of the symmetries Γ'_2, Γ_{25}, and Γ_{15}. The restriction to one *d* band and one *f* band is not necessary. It has the advantage that eventually only two coupled vertex equations determine T_c.

The Bloch functions for the *d* band are given by

$$\psi_{\nu_d,\vec{k}}(\vec{r})=\frac{1}{N^{1/2}}\sum_{\vec{n}}\sum_{i_d}a_{i_d}(\nu_d,\vec{k})\,e^{i\vec{k}\cdot\vec{n}}\,w_{i_d}(\vec{r}-\vec{n}), \tag{1}$$

where ν_d is the subband index, $w_{i_d}(\vec{r}-\vec{n})$ is a Wannier orbital of *d* symmetry centered at $\vec{n}$, and N is the number of atoms in the crystal. The Γ'_{25} and Γ_{12} bands have three and two subbands, respectively, and the Wannier orbitals are given by Eqs. (A1) and (A2). The wave functions for the *f* band are

$$\psi_{\nu_f,\vec{k}}(\vec{r})=\frac{1}{N^{1/2}}\sum_{\vec{n}}\sum_{i_f}a_{i_f}(\nu_f,\vec{k})\,e^{i\vec{k}\cdot\vec{n}}\,w_{i_f}(\vec{r}-\vec{n}). \tag{2}$$

The Γ'_2, Γ_{25}, and Γ_{15} bands have one, three, and three subbands, respectively, and the Wannier orbitals of *f* symmetry are given by Eqs. (A3)–(A5).

When the covalent admixture between *d* and *f* orbitals is not negligible, the Bloch functions have the form

$$\psi_{\nu,\vec{k}}(\vec{r})=\frac{1}{N^{1/2}}\sum_{\vec{n}}\sum_{i}a_{i}(\nu,\vec{k})\,e^{i\vec{k}\cdot\vec{n}}\,w_{i}(\vec{r}-\vec{n}), \tag{3}$$

where ν is now a subband index of the admixed *d*-*f* band. For example, if the Γ'_{25} *d* band is admixed with the Γ'_2 *f* band, $\nu=1, 2, 3, 4$ and $i=1, 2, 3, 6$ [Eqs. (A1) and (A3)]. All of the a_i's can be different than zero.

The wave functions, Eq. (3), and the energy eigenvalues $\epsilon(\nu,\vec{k})$ define our *d*-*f* band. The density of states per atom is given by

$$N(\epsilon)=\sum_{i}N_i(\epsilon), \tag{4}$$

where

$$N_i(\epsilon)=\frac{1}{8\pi^3 n}\sum_{\nu}\int_{\substack{\text{surface}\\ \epsilon=\text{const.}}}\frac{|a_i(\nu,\vec{k})|^2}{|\vec{\nabla}_{\vec{k}}\,\epsilon(\nu,\vec{k})|}\,dS_\nu \tag{5}$$

is the density of states for orbital i and n is the number of atoms per cm^3, from hereon $\hbar=1$.

B. Vertex Equations; Contact Model

The equations for the vertex functions of a Cooper pair are set up according to the prescription given in II. In the contact model, the symmetrized pair states formed from *d* and *f* orbitals are given by Eqs. (A7)–(A11) of Appendix A. We note that no mixed *d*-*f* pair states occur. Of the different contact states, we choose one *d* state, $|\eta_d\rangle$, and one *f* state, $|\eta_f\rangle$, corresponding to the particular *d*-*f*-band model. For our example of a Γ'_{25} *d* band admixed with a Γ'_2 *f* band, we have $|\eta\rangle\equiv|\eta_1\rangle$ and $|\eta_f\rangle\equiv|\eta_3\rangle$, Eqs. (A7) and (A9).

The vertex equations for $|\eta_d\rangle$ and $|\eta_f\rangle$ are in the notation of II given by

$$\Gamma(\eta_d,\omega)=-\frac{1}{\beta}\sum_{\omega'}[\Gamma(\eta_d,\omega')\langle\eta_d\omega'|K|\eta_d\omega\rangle$$

$$+\Gamma(\eta_f,\omega')\langle\eta_f\omega'|K|\eta_d\omega\rangle], \tag{6a}$$

$$\Gamma(\eta_f,\omega)=-\frac{1}{\beta}\sum_{\omega'}[\Gamma(\eta_f,\omega')\langle\eta_f\omega'|K|\eta_f\omega\rangle$$

$$+\Gamma(\eta_d,\omega')\langle\eta_d\omega'|K|\eta_f\omega\rangle]. \tag{6b}$$

The kernel K has four components, *d*-*d*, *f*-*d*, *d*-*f*, and *f*-*f*.

Let us write down explicitely the *d*-*d* component. Omitting the frequency variables ω and ω', it is given by [cf. II (3.26)]

$$\langle\eta_d|K|\eta_d\rangle=\langle\eta_d|\vec{0}g_d\rangle\sum_{\vec{m}'}\tfrac{1}{2}[\langle\vec{m}'g_d|\mathcal{K}|\vec{0}g_d\rangle$$

$$+\langle P\vec{m}'g_d|\mathcal{K}|\vec{0}g_d\rangle]\langle\vec{0}g_d|\eta_d\rangle. \tag{7}$$

Here $|\vec{m}'g_d\rangle$ is the basic (unsymmetrized) pair state of two *d* electrons at site $\vec{m}'$, $g_d\equiv(d_1,d_2)$. Instead of the subindex i, we use d_1, d_2 and f_1, f_2 as orbital indices of a *d* pair and an *f* pair, respectively; e_1 and e_2 are used below as summation indices over both *d* and *f* pairs. In Eq. (7) the kernel $\mathcal{K}$ occurs between basic pair states; it is given by

$$\sum_{\vec{m}'}\langle\vec{m}'g_d|\mathcal{K}|\vec{0}g_d\rangle=\sum_{e_1,e_2}F_{d_1d_2e_1e_2}(\omega')\,I_{e_1e_2d_1d_2}(\omega',\omega), \tag{8}$$

where the pair Green's function F can be be expressed by products of single-particle Green's functions G,

$$F_{d_1d_2e_1e_2}(\omega)=\sum_{\vec{m}}G_{d_1d_2e_1e_2}(\vec{m},\omega)\,G_{d_1d_2e_1e_2}(\vec{m},-\omega), \tag{9}$$

and where I is the contracted irreducible interaction [cf. I (2.30)],

$$I_{e_1e_2d_1d_2}(\omega',\omega)=\sum_{\vec{m}'}I_{e_1e_2d_1d_2}(\vec{m}',\vec{m}',\omega';\vec{0},\vec{0},\omega). \tag{10}$$

Finally, inserting (8) into Eq. (7), we have the *d*-*d* component of K in the following form:

$$\langle\eta_d|K|\eta_d\rangle=\sum_{\substack{d_1,d_2\\ e_1,e_2}}\langle\eta_d|d_1d_2\rangle\tfrac{1}{2}(F_{d_1d_2e_1e_2}+F_{d_2d_1e_1e_2})$$

$$\times I_{e_1e_2d_1d_2}\langle d_1d_2|\eta_d\rangle. \tag{11}$$

In an analogous manner, we can write the *f*-*d*, *d*-*f*, and *f*-*f* components of K.

C. Solution of Vertex Equations

To solve Eqs. (6a) and (6b) which determine T_c, we proceed in exactly the same manner as described in I. The irreducible interaction is the sum of a phonon part and a Coulomb part, $K=K^{\text{ph}}+K^{C}$, the latter being frequency independent. Hence the vertex functions are also composed of a frequency-dependent part $\Gamma_1(\omega)$, which vanishes in the limit $\omega\to\infty$, and a frequency-independent part Γ_2. The equations for the Γ_1's are

$$\Gamma_1(\eta_d,\omega)=-\frac{1}{\beta}\sum_{\omega'}\{[\Gamma_1(\eta_d,\omega')+\Gamma_2(\eta_d)]\langle\eta_d\omega'|K^{\mathrm{ph}}|\eta_d\omega\rangle+[\Gamma_1(\eta_f,\omega')+\Gamma_2(\eta_f)]\langle\eta_f\omega'|K^{\mathrm{ph}}|\eta_d\omega\rangle\},\tag{12a}$$

$$\Gamma_1(\eta_f,\omega)=-\frac{1}{\beta}\sum_{\omega'}\{[\Gamma_1(\eta_f,\omega')+\Gamma_2(\eta_f)]\langle\eta_f\omega'|K^{\mathrm{ph}}|\eta_f\omega\rangle+[\Gamma_1(\eta_d,\omega')+\Gamma_2(\eta_d)]\langle\eta_d\omega'|K^{\mathrm{ph}}|\eta_f\omega\rangle\}.\tag{12b}$$

Here, for example, the *d-d* component of K^{ph} is given by

$$\langle\eta_d\omega'|K^{\mathrm{ph}}|\eta_d\omega\rangle=\sum_{\substack{d_1,d_2\\e_1,e_2}}\langle\eta_d|d_1d_2\rangle\tfrac{1}{2}[F_{d_1d_2e_1e_2}(\omega')+F_{d_2d_1e_1e_2}(\omega')]\times I^{\mathrm{ph}}_{e_1e_2d_1d_2}(\omega-\omega')\langle d_1d_2|\eta_d\rangle.\tag{13}$$

The quantities $\Gamma_2(\eta_d)$ and $\Gamma_2(\eta_f)$ are given by Eqs. (B1) and (B2).

Equations (12a) and (12b) are two coupled integral equations in ω. They are exact equations, in the contact model. We solve these equations in an approximate manner by using the BCS parametrization of $I^{\mathrm{ph}}(\omega-\omega')$. The cutoff of this interaction at $\pm\omega_0$ leads to a corresponding truncation of the kernel K^{ph}. Its *d-d* component, Eq. (13), is given by

$$\langle\eta_d\omega'|K^{\mathrm{ph}}|\eta_d\omega\rangle=\begin{cases}-\langle\eta_d\omega'|K^{\mathrm{ph}}|\eta_d\rangle, & |\omega| \text{ and } |\omega'|\le\omega_0\\ 0, & \text{otherwise.}\end{cases}\tag{14}$$

This truncated kernel has the form of the right-hand side of Eq. (13) with $I^{\mathrm{ph}}(\omega-\omega')$ replaced by $-I^{\mathrm{ph}}$. For this simple form of the kernel, the vertex functions $\Gamma_1(\eta_d,\omega)$ and $\Gamma_1(\eta_f,\omega)$ are zero if $|\omega|>\omega_0$ and they are constants $\Gamma_1(\eta_d)$ and $\Gamma_1(\eta_f)$, respectively, if $|\omega|\le\omega_0$. Thus Eqs. (12a) and (12b) become the following algebraic equations:

$$\Gamma_1(\eta_d)=-[\Gamma_1(\eta_d)+\Gamma_2(\eta_d)]K^{\mathrm{ph}}_{dd}+[\Gamma_1(\eta_f)+\Gamma_2(\eta_f)]K^{\mathrm{ph}}_{fd},\tag{15a}$$

$$\Gamma_1(\eta_f)=-[\Gamma_1(\eta_d)+\Gamma_2(\eta_d)]K^{\mathrm{ph}}_{df}+[\Gamma_1(\eta_f)+\Gamma_2(\eta_f)]K^{\mathrm{ph}}_{ff}.\tag{15b}$$

Here the quantities $\Gamma_2(\eta_d)$ and $\Gamma_2(\eta_f)$ are given by Eqs. (B9) and (B10); and

$$K^{\mathrm{ph}}_{dd}=\frac{1}{\beta}\sum_{|\omega'|\le\omega_0}\langle\eta_d\omega'|K^{\mathrm{ph}}|\eta_d\rangle,\tag{16a}$$

$$K^{\mathrm{ph}}_{fd}=\frac{1}{\beta}\sum_{|\omega'|\le\omega_0}\langle\eta_f\omega'|K^{\mathrm{ph}}|\eta_d\rangle,\tag{16b}$$

$$K^{\mathrm{ph}}_{df}=\frac{1}{\beta}\sum_{|\omega'|\le\omega_0}\langle\eta_d\omega'|K^{\mathrm{ph}}|\eta_f\rangle,\tag{16c}$$

$$K^{\mathrm{ph}}_{ff}=\frac{1}{\beta}\sum_{|\omega'|\le\omega_0}\langle\eta_f\omega'|K^{\mathrm{ph}}|\eta_f\rangle.\tag{16d}$$

Equations (15a) and (15b) are two homogeneous linear equations for $\Gamma_1(\eta_d)$ and $\Gamma_1(\eta_f)$. The conditions that the determinant of the coefficients vanishes defines T_c. This completes the formal solution of the vertex equations in the contact model and for the BCS parametrization of the pairing interaction.

III. T_c CALCULATIONS; DISCUSSION

To determine T_c, we must first calculate quantities such as those defined by Eqs. (16a)–(16d). For a threefold-degenerate *d* band of Γ'_{25} symmetry, K^{ph}_{dd} is calculated in I. Following this example, we find for a *d-f* band the following results:

$$K^{\mathrm{ph}}_{dd}=\frac{N_d(0)}{N(0)}\left(N_d(0)I^{\mathrm{ph}}_{dd}+N_f(0)I^{\mathrm{ph}}_{fd}\right)\ln(1.13\beta\omega_0),\tag{17a}$$

$$K^{\mathrm{ph}}_{fd}=\frac{N_f(0)}{N(0)}\left(N_f(0)I^{\mathrm{ph}}_{fd}+N_d(0)I^{\mathrm{ph}}_{dd}\right)\frac{c_f}{c_d}\ln(1.13\beta\omega_0),\tag{17b}$$

$$K^{\mathrm{ph}}_{df}=\frac{N_d(0)}{N(0)}\left(N_d(0)I^{\mathrm{ph}}_{df}+N_f(0)I^{\mathrm{ph}}_{ff}\right)\frac{c_d}{c_f}\ln(1.12\beta\omega_0),\tag{17c}$$

$$K^{\mathrm{ph}}_{ff}=\frac{N_f(0)}{N(0)}\left(N_f(0)I^{\mathrm{ph}}_{ff}+N_d(0)I^{\mathrm{ph}}_{df}\right)\ln(1.13\beta\omega_0).\tag{17d}$$

Here $N_d(0)$ and $N_f(0)$ are the density of states for *d* and *f* orbitals at the Fermi energy; c_d and c_f are the normalization constants $\langle\eta_d|d_1d_2\rangle$ and $\langle\eta_f|f_1f_2\rangle$, respectively, given in Appendix A. The interaction parameters for phonon exchange are

$$I^{\mathrm{ph}}_{dd}=c_d^2\sum_{d_2}I^{\mathrm{ph}}_{d_1d_1d_2d_2},\tag{18a}$$

$$I^{\mathrm{ph}}_{fd}=c_f^2\sum_{d_2}I^{\mathrm{ph}}_{f_1f_1d_2d_2},\tag{18b}$$

$$I^{\mathrm{ph}}_{df}=c_d^2\sum_{f_2}I^{\mathrm{ph}}_{d_1d_1f_2f_2}=I^{\mathrm{ph}}_{fd},\tag{18c}$$

$$I^{\mathrm{ph}}_{ff}=c_f^2\sum_{f_2}I^{\mathrm{ph}}_{f_1f_1f_2f_2}.\tag{18d}$$

The expressions for the kernel parameters due to phonon exchange, Eqs. (17a)–(17d), are valid under the assumption that both density-of-states functions $N_d(\epsilon)$ and $N_f(\epsilon)$ are smooth in the vicinity of the Fermi energy, $|\epsilon|\le\omega_0$. This assumption holds here if $\epsilon_f>\omega_0$[cf. Eq. (29) below]. The leading contribution to I^{ph}_{df} is determined by an *atomic* parameter, namely, the matrix element of an ion-potential gradient between two Wannier orbitals (*d* and *f*) both centered at the ion site.

As for the kernel parameters of the Coulomb interaction, there are two kinds, both defined in Appendix B. The first kind results from the Coulomb interaction in the vicinity of the Fermi energy where $|\epsilon|\le\omega_0$, Eqs. (B10)–(B13). The corresponding parameters, k^C_{dd}, etc., have the form, Eqs. (17a)–(17d), with I^C being substituted for I^{ph}.

The second kind of Coulomb parameter is determined by the interaction between electrons which can be far away from the Fermi surface, Eqs. (B4)–(B7). K^C_{dd}, etc., depend on $N(\epsilon)$ over the whole bandwidth. For a nondegenerate band it is seen from Eq. (A14) in I that structure of $N(\epsilon)$ can be important, if it occurs not too far away from the Fermi energy. Thus in calculating these parameters the structure in $N(\epsilon)$ due to the $4f$ states is taken into account. We write the orbital density of states for one f electron per atom (spin up or down) as

$$N_f(\epsilon) = \frac{1}{\pi}\,\frac{\Gamma}{(\epsilon - \epsilon_f)^2 + \Gamma^2}\,, \tag{19}$$

where Γ measures the width of the $4f$ level density due to the covalent d-f admixture.[13] For simplicity we assume one $4f$ electron per atom only, corresponding to Γ_2' symmetry. For this case, the $4f$ density of states used by Ratto *et al.*[2] is of the same form as our $N_f(\epsilon)$.

With Eq. (19) the second type of Coulomb parameters can be obtained in closed form. The *d-d* parameter, for example, is given by

$$K^C_{dd} = \frac{N_d^2(0)}{N(0)}\, I^C_{dd}\Big([\ln(1.13\beta\omega_0) + \kappa_{dd}] + \frac{N_d(0)N_f(0)}{N(0)}\, I^C_{fd}[\ln(1.13\beta\omega_0) + \kappa_{fd}]\Big) \tag{20}$$

The *f-d*, *d-f*, and *f-f* parameters also can be written down in this form, by analogy with Eqs. (17b)–(17d), respectively. The κ's are calculated in Appendix C.

We can now proceed to calculate T_c. The condition that the determinant of Eqs. (15a) and (15b) vanishes yields an equation for T_c which is general can only be solved numerically. This applied to a real case where all the pairing parameters I^{ph} and I^C are calculated on the basis of known wave functions and potentials.

In simple cases, sufficient for a parameter study, T_c is obtained in the BCS form. Such a special case is now adopted. It is characterized by

$$I^{\text{ph}}_{dd},\ I^{\text{ph}}_{df},\ I^C_{ff} \neq 0, \tag{21}$$

$$I^C_{dd},\ I^C_{df},\ I^{\text{ph}}_{ff} = 0, \tag{22}$$

Here I^{ph}_{ff} vanishes because it was assumed that the *f-f* overlap between nearest neighbors is negligible. As for $I^C_{dd} = 0$, we take into account that I^{ph}_{dd} can be adjusted to incorporate the *d-d* Coulomb repulsion. The same holds for I^C_{df} and I^{ph}_{df}. With the pairing interaction given by (21) and (22), we get

$$T_c = 1.13\omega_0 \exp[-1/(\lambda_{dd} + \lambda_{ff} - \mu^*_{ff})], \tag{23}$$

where

$$\lambda_{dd} = \frac{N_d(0)}{N(0)}\Big(N_d(0) I^{\text{ph}}_{dd} + N_f(0) I^{\text{ph}}_{fd}\Big), \tag{24}$$

$$\lambda_{ff} = \frac{N_f(0)N_d(0)}{N(0)}\, I^{\text{ph}}_{df}, \tag{25}$$

$$\mu^*_{ff} = \frac{\mu_{ff}}{1 + \mu_{ff}[\kappa_{ff} + \ln(\epsilon_b/\omega_0)]}\,. \tag{26}$$

Here

$$\mu_{ff} = \frac{N_f^2(0) I^C_{ff}}{N(0)}\,, \tag{27}$$

and [cf. Eq. (C5)]

$$\kappa_{ff} = \ln\frac{(\epsilon_f^2 + \Gamma^2)^{1/2}}{\epsilon_b} + \frac{\epsilon_f}{\Gamma}\tan^{-1}\frac{\epsilon_f}{\Gamma}\,; \tag{28}$$

ϵ_b is an effective half-width of the d-f band defined according to Eq. (A11) of I. The above expression for T_c holds provided

$$(\epsilon_f^2 + \Gamma^2)^{1/2} \geq \omega_0\,. \tag{29}$$

Otherwise, $N_f(\epsilon)$ is not sufficiently smooth around the FS, $|\epsilon| \leq \omega_0$, to permit the approximation $N_f(\epsilon) = N_f(0)$ in calculating the components of K^{ph}, Eqs. (16a)–(16d), and of K^C, Eqs. (B10)–(B13).

The T_c equation (23) is used for a parameter study. We take the following parameters as fixed:

$$\begin{aligned} &\omega_0 = 142\ ^\circ\text{K}\ (= 0.0122\ \text{eV}),\\ &N_d(0) = 2\ \text{states/eV atom},\\ &I_{dd} = 0.152\ \text{eV}. \end{aligned} \tag{30}$$

The corresponding transition temperature (no $4f$ states) is $T_{c0} = 6\ ^\circ$K. As variable parameters we take those which characterize the effect of the f electrons on T_{c0}. These are ϵ_f, Γ, I^{ph}_{df}, and I^C_{ff}. Note that $I^C_{ff} \equiv U_{ff}$, the intra-atomic Coulomb integral for $4f$ electrons. In Fig. 1, T_c vs ϵ_f is plotted for a fixed value of Γ and for four values of I^{ph}_{df}. In Figs. 2 and 3, I^{ph}_{df} is finite and zero, respectively, and Γ has different values. In all of these cases $U_{ff} = 10$ eV. Let us briefly discuss the results.

The important feature of the curves in Fig. 1 is the occurence of a maximum for sufficiently large values of I^{ph}_{df}. A maximum occurs for the following reason. The relative importance of the additional attractive interaction due to phonon exchange between d and f electrons and of the additional Coulomb repulsion depends on ϵ_f via $N_f(\epsilon)$. From Eqs. (24) and (27) we see that I^{ph}_{df} is multiplied by $N_d(0)\, N_f(0)$, whereas U_{ff} has the factors $N_f^2(0)$. If, to begin with, the $4f$ levels are far away from the FS corresponding to large values of ϵ_f, T_c is determined by the d-electron parameters, Eq. (30). As ϵ_f decreases, T_c increases due to the enhancement effect of $I^{\text{ph}}_{df}/(\epsilon_f^2 + \Gamma^2)$. Eventually, the diametral effect of $U_{ff}/(\epsilon_f^2 + \Gamma^2)^2$ compensates for the phonon enhancement; T_c goes through a maximum and rapidly decreases as the $4f$ levels move toward the Fermi energy. In this region the

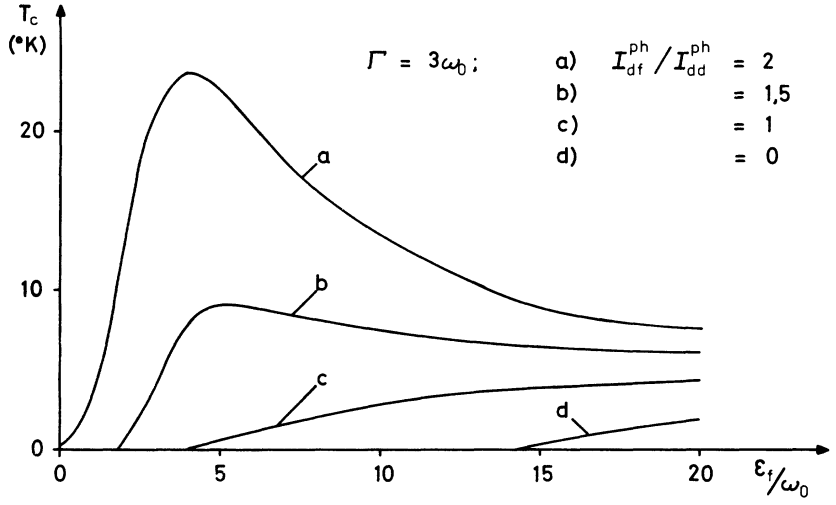

FIG. 1. Transition temperature T_0 as a function of the distance ϵ_f between the $4f$ levels and the Fermi energy, Eq. (23). I_{df}^{ph} is the pairing interaction between d and f electrons due to phonon exchange.

slope $dT_c/d\epsilon_f$ depends crucially on both U_{ff} *and* I_{df}^{ph}, and to a smaller extent on Γ (see Fig. 2). In the case where $I_{df}^{ph}=0$, $\partial T_c/\partial\epsilon_f \sim 1\ ^\circ\mathrm{K}/3\omega_0$, Fig. 3, in agreement with the result of Ratto *et al.*[2]

On the basis of these results, we now discuss the transition temperature of La. As pointed out in Sec. I, our d-f-band model should be applicable since the electrons at the FS of La have a predominant d character.

There are two experimental facts about La which are unusual and which require a consistent explanation. The transition temperature of La is high, $T_c = 6$ °K for fcc La. Other early transition metals are either not found to be superconducting at zero pressure (Sc, Y) or they have a low transition temperature, of the order of 1 °K (Ti, Zr, Hf). The second fact is the large increase of T_c(La) with pressure P. For other early transition metals T_c increases also with P, but the slope dT_c/dP is much smaller.[14]

Kasuya[15] has made the interesting suggestion that the high transition temperature of La is due to a soft lattice. The low Debye temperature $\Theta_D = 142$ °K, is attributed to a large electron density of states somewhat above the Fermi energy owing to empty $4f$ levels. A high density of states contributes to the screening of the ion-ion interaction and tends to make the lattice soft. However, the last rare-earth element, Lu, also has a soft lattice, $\Theta_D = 162$ °K; but here the $4f$ shell is filled and $T_c < 0.018$ °K.

We suggest that the transition temperature of La is directly affected by $4f$ levels close to the Fermi energy and that the high value of T_c is due to phonon exchange between d and f electrons. The pressure dependence of T_c is attributed to the change in the

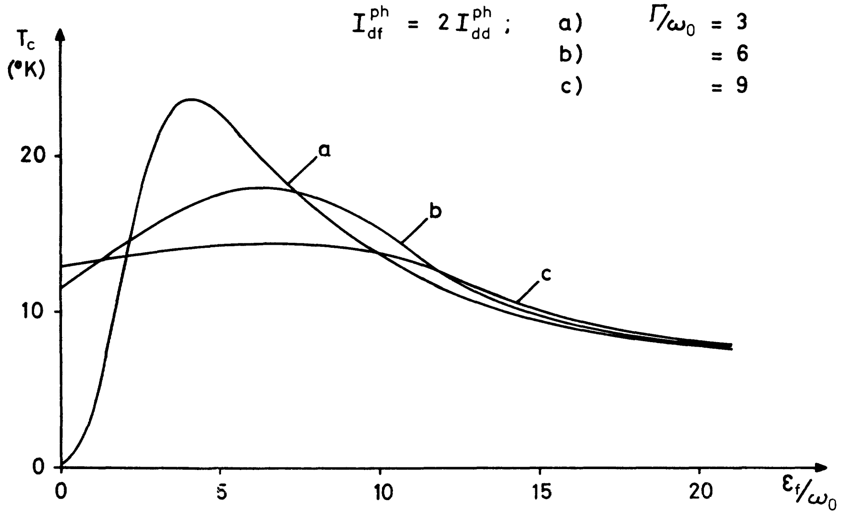

FIG. 2. T_c vs ϵ_f for different values of Γ, the half-width of the $4f$-level distribution defined by Eq. (19).

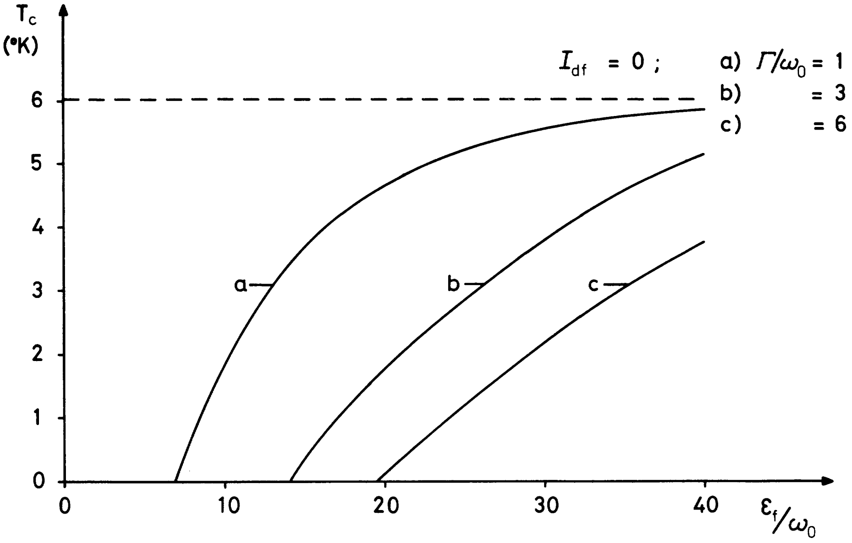

FIG. 3. T_c vs ϵ_f for $I_{df}^{ph}=0$. The intra-atomic Coulomb repulsion between $4f$ electrons, U_{ff}, is assumed to be 10 eV.

effect of I_{df}^{ph} and U_{ff} as the $4f$ levels move away from the Fermi energy. We mentioned before that I_{df}^{ph} and U_{ff} are atomic parameters, characteristic of the La atom, and rather insensitive to the environment of this atom. In Fig. 4 we have plotted the experimental data of Ref. 3, T_c vs P, together with the curve T_c vs ϵ_f, which is calculated with the parameters given in the figure. This is not a quantitative comparison between theory and experiment. The pairing interactions, for example, were not calculated but were chosen to give this T_c vs ϵ_f dependence. Furthermore, Γ is assumed to be a constant, whereas it may actually depend on ϵ_f. However, some qualitative features are obvious when one compares the two curves in Fig. 4. The rates at which $T_{c,\mathrm{calc}}$ and $T_{c,\mathrm{expt}}$ change with ϵ_f and P, respectively, are such that an increase of ϵ_f by about $5\omega_0$ corresponds to rise of P from 0

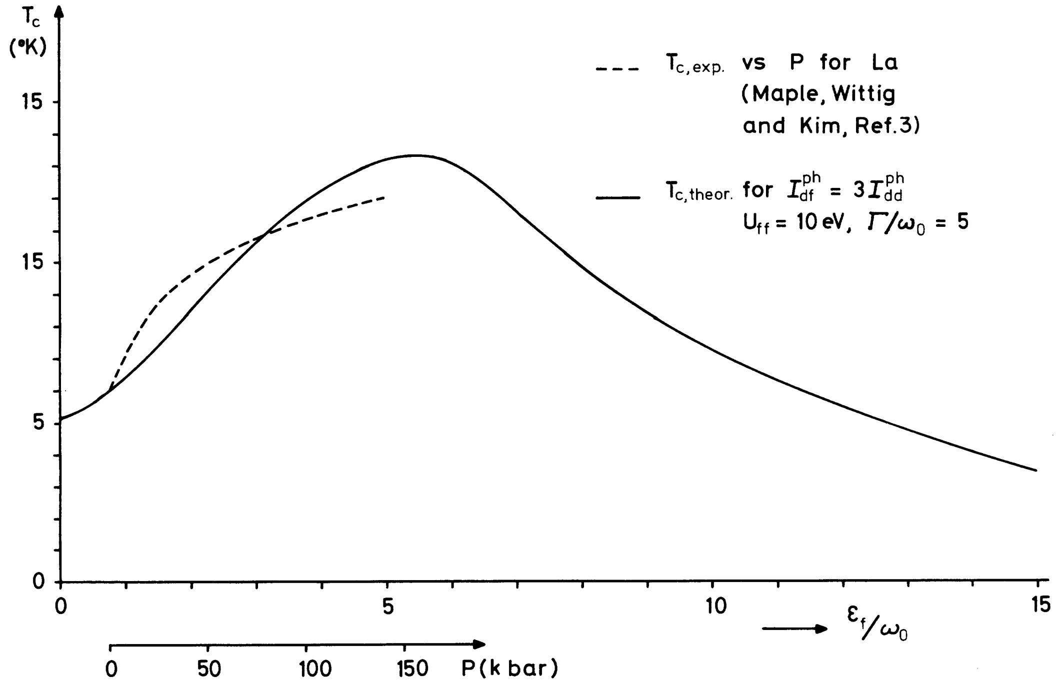

FIG. 4. T_c vs ϵ_f for a special case of the parameters determining the density of states of the *d*-*f* band and the pairing interactions. Also, the experimental values of T_c vs P are shown for La.

to 140 kbar. At this time, we could not find any direct experimental evidence for the changes of ϵ_f and Γ with P.[18] Furthermore, $T_{c,\text{calc}}$ exhibits a maximum, whereas there is no experimental indication of a maximum in the pressure dependence of $T_{c,\text{expt}}$. In summary, our suggestion that phonon exchange between d and f electrons causes the high T_c values of La at all pressures and that T_c vs P is due to the combined effect of I_{df}^{ph} and U_{ff} appears plausible but has no direct experimental foundation at this time. In particular, direct evidence for a shift of the $4f$ levels under pressure, perhaps from optical-absorption experiments, could be used to support or invalidate our suggestion.

ACKNOWLEDGMENT

It is a pleasure to thank Professor W. Kohn for helpful discussions.

APPENDIX A: WANNIER ORBITALS AND CONTACT PAIR STATES

We have five Wannier orbitals of d symmetry and seven orbitals of f symmetry. These orbitals together with the irreducible representations of the cubic group, according to which they transform under symmetry operations, are given by

$$\left.\begin{aligned} w_1 &= (15/4\pi)^{1/2} yzf(\vec{r}), \\ w_2 &= (15/4\pi)^{1/2} zxf(\vec{r}), \\ w_3 &= (15/4\pi)^{1/2} xyf(\vec{r}), \end{aligned}\right\} \Gamma_{25}' ; \tag{A1}$$

$$\left.\begin{aligned} w_4 &= (15/16\pi)^{1/2}(x^2-y^2)g(\vec{r}), \\ w_5 &= (15/16\pi)^{1/2}(2z^2-x^2-y^2)g(\vec{r}), \end{aligned}\right\} \Gamma_{12} ; \tag{A2}$$

$$w_6 = (105/4\pi)^{1/2} xyzh(\vec{r}), \quad \Gamma_2' ; \tag{A3}$$

$$\left.\begin{aligned} w_7 &= (105/16\pi)^{1/2} x(y^2-z^2)k(\vec{r}), \\ w_8 &= (105/16\pi)^{1/2} y(z^2-x^2)k(\vec{r}), \\ w_9 &= (105/16\pi)^{1/2} z(x^2-y^2)k(\vec{r}), \end{aligned}\right\} \Gamma_{25} ; \tag{A4}$$

$$\left.\begin{aligned} w_{10} &= (175/16\pi)^{1/2} x(x^2-\tfrac{3}{5})l(\vec{r}), \\ w_{11} &= (175/16\pi)^{1/2} y(y^2-\tfrac{3}{5})l(\vec{r}), \\ w_{12} &= (175/16\pi)^{1/2} z(z^2-\tfrac{3}{5})l(\vec{r}), \end{aligned}\right\} \Gamma_{15} . \tag{A5}$$

These functions are normalized:

$$\int w_i^2(\vec{r})\,d^3r = 1. \tag{A6}$$

The functions f, g, h, k, and l have cubic symmetry.

To write out the contact pair states we use the notation $|ij\rangle$ = *pair state, where orbitals* w_i *and* w_j *centered at the same atom are occupied.* Then the contact pair states, constructed from the Wannier oribtals, Eqs. (A1)–(A5), are, according to II, given by

$$|\eta_1\rangle = (1/\sqrt{3})(|11\rangle + |22\rangle + |33\rangle), \tag{A7}$$

$$|\eta_2\rangle = (1/\sqrt{2})(|44\rangle + |55\rangle), \tag{A8}$$

$$|\eta_3\rangle = |66\rangle, \tag{A9}$$

$$|\eta_4\rangle = (1/\sqrt{3})(|77\rangle + |88\rangle + |99\rangle), \tag{A10}$$

$$|\eta_5\rangle = (1/\sqrt{3})(|10\,10\rangle + |11\,11\rangle + |12\,12\rangle). \tag{A11}$$

Hence $|\eta_d\rangle = |\eta_1\rangle$ or $|\eta_2\rangle$ and $|\eta_f\rangle = |\eta_3\rangle$ or $|\eta_4\rangle$ or $|\eta_5\rangle$.

APPENDIX B: QUANTITIES $\Gamma_2(\eta_d)$ AND $\Gamma_2(\eta_f)$

These quantities are determined from Eqs. (6a) and (6b). We take the limit $\omega \to \infty$ and solve for $\Gamma_2(\eta_d)$ and $\Gamma_2(\eta_f)$. This gives

$$\begin{aligned} \Gamma_2(\eta_d) = -\frac{b}{\beta} \sum_{\omega'} \{ &\Gamma_1(\eta_d, \omega') [\langle \eta_d \omega' | K^C | \eta_d \rangle (1 + K_{dd}^C) \\ &- \langle \eta_d \omega' | K^C | \eta_f \rangle K_{fd}^C] \\ &+ \Gamma_1(\eta_f, \omega') [\langle \eta_f \omega' | K^C | \eta_f \rangle K_{fd}^C \\ &- \langle \eta_f \omega' | K^C | \eta_d \rangle (1 + K_{ff}^C)]\}, \end{aligned} \tag{B1}$$

$$\begin{aligned} \Gamma_2(\eta_f) = -\frac{b}{\beta} \sum_{\omega'} \{ &\Gamma_1(\eta_f, \omega') [\langle \eta_f \omega' | K^C | \eta_f \rangle (1 + K_{ff}^C) \\ &- \langle \eta_f \omega' | K^C | \eta_d \rangle K_{df}^C] \\ &+ \Gamma_1(\eta_d, \omega') [\langle \eta_d \omega' | K^C | \eta_d \rangle K_{df}^C \\ &- \langle \eta_d \omega' | K^C | \eta_f \rangle (1 + K_{dd}^C)]\}. \end{aligned} \tag{B2}$$

Here

$$b = \frac{1}{(1 + K_{dd}^C)(1 + K_{ff}^C) - K_{fd}^C K_{df}^C} \tag{B3}$$

and

$$K_{dd}^C = \frac{1}{\beta} \sum_{\omega'} \langle \eta_d \omega' | K^C | \eta_d \rangle, \tag{B4}$$

$$K_{fd}^C = \frac{1}{\beta} \sum_{\omega'} \langle \eta_f \omega' | K^C | \eta_d \rangle, \tag{B5}$$

$$K_{df}^C = \frac{1}{\beta} \sum_{\omega'} \langle \eta_d \omega' | K^C | \eta_f \rangle, \tag{B6}$$

$$K_{ff}^C = \frac{1}{\beta} \sum_{\omega'} \langle \eta_f \omega' | K^C | \eta_f \rangle. \tag{B7}$$

The frequency-dependent components of the Coulomb kernel K^C are found from those of K when I^C is substituted for $I(\omega', \omega)$. When the vertex equations (6a) and (6b) are solved in the manner of BCS (see Sec. II), Eqs. (B1) and (B2) become

$$\begin{aligned} \Gamma_2(\eta_d) = -b\, \{&\Gamma_1(\eta_d) [k_{dd}^C (1 + K_{dd}^C) - k_{df}^C K_{fd}^C] \\ &+ \Gamma_1(\eta_f) [k_{ff}^C K_{fd}^C - k_{fd}^C (1 + K_{ff}^C)]\}, \end{aligned} \tag{B8}$$

$$\begin{aligned} \Gamma_2(\eta_f) = -b\, \{&\Gamma_1(\eta_f) [k_{ff}^C (1 + K_{ff}^C) - k_{fd}^C K_{df}] \\ &+ \Gamma_1(\eta_d) [k_{dd}^C K_{df}^C - k_{df}^C (1 + K_{dd}^C)]\}, \end{aligned} \tag{B9}$$

where

$$k_{dd}^C = \frac{1}{\beta} \sum_{|\omega'| \leq \omega_0} \langle \eta_d \omega' | K^C | \eta_d \rangle, \tag{B10}$$

$$k^C_{fd}=\frac{1}{\beta}\sum_{|\omega'|\leq\omega_0}\langle\eta_f\,\omega'|K^C|\eta_d\rangle, \tag{B11}$$

$$k^C_{df}=\frac{1}{\beta}\sum_{|\omega'|\leq\omega_0}\langle\eta_d\,\omega'|K^C|\eta_f\rangle, \tag{B12}$$

$$k^C_{ff}=\frac{1}{\beta}\sum_{|\omega'|\leq\omega_0}\langle\eta_f\,\omega'|K^C|\eta_f\rangle. \tag{B13}$$

APPENDIX C: COULOMB KERNEL K^C

The components of the Coulomb kernel K^C are readily calculated, as shown in Appendix A of I. As an example, the d-d component K^C_{dd} is given above, Eq. (20).

The components of K^C contain the following parameters:

$$\kappa_{dd}=\int_{\epsilon_{\min}}^{\epsilon_{\max}}\left(\frac{N_d^2(\epsilon)N(0)}{N_d^2(0)N(\epsilon)}-1\right)\frac{d\epsilon}{2|\epsilon|} \tag{C1}$$

$$\kappa_{fd}=\int_{\epsilon_{\min}}^{\epsilon_{\max}}\left(\frac{N_f(\epsilon)N_d(\epsilon)N(0)}{N_f(0)N_d(0)N(\epsilon)}-1\right)\frac{d\epsilon}{2|\epsilon|}, \tag{C2}$$

$$\kappa_{ff}=\int_{\epsilon_{\min}}^{\epsilon_{\max}}\left(\frac{N_f^2(\epsilon)N(0)}{N_f^2(0)N(\epsilon)}-1\right)\frac{d\epsilon}{2|\epsilon|}. \tag{C3}$$

To evaluate these parameters, it is assumed that $N_d(\epsilon)$ is a smooth function of ϵ. Hence, we may set

$$\kappa_{dd}=0. \tag{C4}$$

The parameter κ_{df} does not occur in our T_c result, Eq. (23)[19]; κ_{ff} is easily calculated if $N(\epsilon)$ in the denominator of (C3) is replaced by $N_d(0)+N_f(\epsilon)$. The result is

$$\kappa_{ff}=\ln\frac{(\epsilon_f^2+\Gamma^2)^{1/2}}{\epsilon_b}+\frac{\epsilon_f}{\Gamma}\tan^{-1}\frac{\epsilon_f}{\Gamma},\qquad \epsilon_{\max},\ |\epsilon_{\min}|\gg\epsilon_f. \tag{C5}$$

---

[1] C. G. Kuper, M. A. Jensen, and D. C. Hamilton, Phys. Rev. **134**, A15 (1964).

[2] C. F. Ratto, B. Coqblin, and E. Galleani D'Agliano, Adv. Phys. **18**, 489 (1969).

[3] M. B. Maple, J. Wittig, and K. S. Kim, Phys. Rev. Lett. **23**, 1375 (1969).

[4] B. Matthias, Am. Sci. **58**, 80 (1970).

[5] T. F. Smith, in *Superconductivity in d- and f-band Metals*, edited by D. H. Douglass (AIP, New York, 1972).

[6] Reference 5, pp. 309–313.

[7] Y. Masuda, J. Phys. Soc. Jap. **19**, 239 (1964). The result of Masuda agrees with a rough estimate from band-structure calculations by H. Myron (private communication), d character $\approx$ 60–90% at the FS.

[8] A. S. Edelstein, Phys. Rev. Lett. **20**, 1348 (1968).

[9] J. Wittig, Phys. Rev. Lett. **24**, 812 (1970).

[10] J. J. Hopfield, Phys. Rev. **186**, 443 (1969).

[11] S. T. Chui (unpublished).

[12] J. Appel and W. Kohn, Phys. Rev. B **4**, 2162 (1971); Phys. Rev. B **5**, 1823 (1972). These papers are referred to as (I) and (II). Equations from these papers have their numbers preceded by I and II, respectively.

[13] Whether a finite Γ is caused by covalent d-f admixture or by p-f hybridization is not pertinent here.

[14] C. Probst and J. Wittig, Proceedings of the Thirteenth International Conference on Low Temperature Physics, Boulder, Colo., 1972 (unpublished).

[15] T. Kasuya, in *Magnetism*, edited by R. T. Rado and H. Suhl (Academic, New York, 1966), Vol. II B.

[16] J. Wittig, C. Probst, and W. Wiedemann, in Ref. 14.

[17] A maximum in T_c vs P has been observed by Smith on α-U, Ref. 5, p. 312.

[18] D. Lynch (private communication) also points out that the position of the 4f level and of its pressure dependence is not known at present.

[19] $\kappa_{df}=\kappa_{fd}$ is given by the right-hand side of Eq. (C5) with Γ replaced by $\Gamma(1+1/\pi N_d(0)\Gamma)^{1/2}$.