

## MODIFIED TIGHT-BINDING APPROXIMATION AND ELECTRON-PHONON SPECTRAL FUNCTION FOR TRANSITION METALS

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The modified tight-binding approximation has been analyzed in detail and is applied to the derivation of an expression for electron-phonon spectral function (EPSF) which enters the strong coupling equations of superconductivity. Numerical calculations of the EPSF and the electron phonon coupling parameter  $\lambda$  for five transition metals, V, Nb, Mo, W, Ta have been performed.

### 1. Introduction

In order to understand quantitatively the electrical, thermal and superconducting properties of metals one needs a proper description of the electronic states. A systematic, self-consistent treatment of the electron-electron and electron-phonon interactions plays an important role in this aspect.<sup>1,2</sup> For simple metals one can introduce a weak pseudopotential to describe the interaction between the ions and electrons and, therefore, this part of the problem can be treated in perturbation theory.

On the other hand, for transition metals and their compounds (TMC) where the electron-ion interaction potential is in no sense weak, such a first-principle theory does not exist. Furthermore, the electron properties of most transition metals and their compounds are dominated by relatively tightly bound *d*-electrons. Therefore, the tight-binding approximation for the *d*-electrons has been used widely for a qualitative description of the electronic and thermal properties of TMC.<sup>3-6</sup>

Over the last decades there have been many attempts to develop a microscopic theory of phonon spectra and electron-phonon coupling in TMC. There are mainly two approaches for dealing with the electron-phonon interaction in TMC. Firstly, it has been suggested that in transition metals the electron-phonon interaction may be described by the rigid muffin-tin approximation (RMTA).<sup>2,5</sup> There has been a significant step towards understanding the electron-phonon interaction in TMC. Unfortunately, the correct calculations of RMTA electron-phonon matrix elements  $\langle K' | \nabla V | K \rangle$  is a very difficult task, especially for low momentum transfer and in low temperature region.<sup>5-9</sup> Moreover, one must explicitly require the knowledge of the wave functions and potential gradients at all points in space.

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Another question referring to very general properties concerns the problem of the superconductivity in TMC and related materials.<sup>10</sup> In order to understand quantitatively this phenomenon one needs a proper description of electron-phonon interaction, too. This has been one of the central themes in the theory of metals.<sup>1,2</sup> The recent discovery of high temperature superconductivity in ceramic compounds has stimulated great efforts towards its theoretical understanding. A number of theories has been proposed that essentially involves strong electron-phonon interaction.<sup>11–14</sup> The isotope shift, though small in the oxide superconductors, is however not zero and seems to suggest a syncretic mechanism in which phonon mediation plays a role.<sup>15</sup> The primary determinant of the superconducting transition temperature  $T_c$  is the electron-phonon coupling parameter  $\lambda$ . It is therefore of considerable importance to attempt to predict in a qualitative way from the first principles how  $\lambda$  varies from one material to another. Of special interest in this regard are the transition metals, their alloys and their compounds for it is their electronic structure which cannot be usefully viewed in terms of weakly perturbed free-electron bands. The advantage of the tight-binding approximation for the description of  $d$ -band transition metals and their compounds has long been recognized. In particular, great efforts have been devoted to the calculation of the electron-phonon coupling in this approach. Stimulating ideas have been initiated by Frohlich.<sup>16</sup> More detailed formulation was developed in Refs. 17–21. It was argued that with Bloch functions constructed from atomic orbitals, the modified tight-binding approximation (MTBA) is more appropriate for calculating the electron-phonon coupling than the ordinary Bloch formulation.

The most important function related to the electron-phonon interaction is the electron-phonon spectral (or Eliashberg) function  $\alpha^2F(\omega)$ ,<sup>10</sup> that describes the average coupling of electrons at the Fermi surface to phonons of energy  $\hbar\omega$ . From this function other important parameters can be derived.<sup>5,10</sup> In this paper we calculate EPSF of transition metals in MTBA. Our goal is a realistic calculation which can be compared with experiments. It should be stressed that the way we treat the problem gives rise then to the fundamental principles of the MTBA and results that are the main subject of the present study.

## 2. Modified Tight-Binding Approximation

The tight-binding theory of electrons considers the wave functions of electrons in crystals prescribed in principle by the theory of atomic structure. According to the tight-binding theory, we accept the wave functions of electrons around each atom as the basic wave functions of the problem. Frohlich pointed out<sup>16</sup> that the situation in metals with incomplete inner shells is radically different from the situation in metals with complete inner shells already in the proper treatment of electron-phonon interaction. It is evident that the free electron model leads to a description of a single electron in terms of a Bloch wave function which in zero order is independent of the lattice vibrations. Now consider an inner shell. In contrast to the ordinary approach where the atomic orbitals are centred on the mean ionic positions, the wave function of an electron in a deformed lattice is written in the MTBA as a Bloch sum of atomic orbitals centred on the displaced ionic positions  $\mathbf{R}e = \mathbf{R}e^0 + \mathbf{u}e$

$$\psi_k(r) = N^{-1/2} \sum_{R_e} e^{i\mathbf{k}\mathbf{R}_e} \phi_a(\mathbf{r} - \mathbf{R}_e). \quad (1)$$

Frohlich<sup>16</sup> supposed that when the lattice oscillates the parts of the electronic wave function near an ion should follow it adiabatically. In the tight-binding approximation this implies the whole localized wave function. Of course, this wave function can be developed in the displacement  $\mathbf{u}_j = \mathbf{R}_j - \mathbf{R}_j^0$

$$(\mathbf{r} - \mathbf{R}_e) \approx (\mathbf{r} - \mathbf{R}_e^0) + \mathbf{u} \frac{\partial}{\partial \mathbf{r}} (\mathbf{r} - \mathbf{R}_e^0) + \frac{1}{2} u_e u_s \frac{\partial}{\partial r_e} \frac{\partial}{\partial r_s} (\mathbf{r} - \mathbf{R}_e^0) + \dots \quad (2)$$

This approximation is usually called the MTBA. The detailed investigation of the electron-phonon interaction matrix element has been examined in Refs. 16–21. It was shown<sup>22</sup> that this scheme describes quite well the superconductivity in the case of transition metal alloys.

The MTBA was clarified and generalized in recent years in great detail.<sup>23–26</sup> Varma *et al.*<sup>27</sup> have demonstrated that the tight-binding scheme yields accurate quantitative results when the non-orthogonality of the orbitals is incorporated. A very important aspect of this approach is that phonon dynamics has also been calculated by this method.<sup>28</sup> This approach and the Bloch approach under the RMTA lead to the same physical results within the harmonic approximation.<sup>25</sup> However, there is a considerable difference between the tight-binding and RMTA results in predicting anisotropic properties for Nb.<sup>25,28,29</sup> In Kuzemsky *et al.*<sup>30</sup> we developed further the ideas of MTBA, showing that the BLF<sup>18</sup> approach gives a constructive and workable formalism for the description of the interaction between the tight-binding electrons and phonons in TMC. In Vujicic *et al.*<sup>31</sup> the BCS-Bogolubov theory of the superconductivity was formulated on a general basis using the language and technique of the two-time thermal Green's functions. According to this, the problem reduces to finding the self-energy of a quasi-particle in the generalized Hartree-Fock-Bogolubov approximation. The strong coupling equations of superconductivity have been derived. The Cooper pairing was described in the Wannier representation to highlight the atomic nature of the electrons responsible for superconductivity in transition metals. In the next section we will briefly recapitulate the main points of the BLF model.

### 3. The Model

Following Refs. 18 and 30 we consider a system of tightly-bound electrons in the one-band approximation, described by the Hubbard Hamiltonian

$$H = \sum_{ij\sigma} t_{ij} a_{i\sigma}^+ a_{j\sigma} + \frac{U}{2} \sum_{i\sigma} n_{i\sigma} n_{i-\sigma} \quad (3)$$

where  $a_{i\sigma}^+$ ,  $a_{i\sigma}$  are creation and annihilation operators for electrons at the site  $\mathbf{R}_i$ ,  $U$  is the Coulomb repulsion energy of the electrons at one site. The hopping integral  $t_{ij}$  is given by

$$t_{ij} = \int d^3r \phi^*(\mathbf{r} - \mathbf{R}_j) \left[ \frac{p^2}{2m} + \sum_l V_s(\mathbf{r} - \mathbf{R}_l) \right] \phi(\mathbf{r} - \mathbf{R}_i) \quad (4)$$

where  $\{\phi(\mathbf{r} - \mathbf{R}_j)\}$  are a complete orthonormal set of Wannier wave functions. Considering small vibrations of ions we replace in Eq. (3) the ion position  $\mathbf{R}_i$  by  $(\mathbf{R}_i^0 + \mathbf{u}_i)$ , i.e. its equilibrium position plus displacement. To further illuminate the problem under consideration we emphasize that in order to describe the electron motion in deformed lattices in our formalism, the Frohlich-Mitra MTBA must be generalized. The unperturbed electronic wave function must be written as a Bloch sum of displaced and suitably orthonormalized Wannier functions

$$\int d^3r \phi^*(\mathbf{r} - \mathbf{R}_j - \mathbf{u}_j) \phi(\mathbf{r} - \mathbf{R}_i - \mathbf{u}_i) \approx \delta_{ij}. \quad (5)$$

As it follows from Eq. (5), the creation and annihilation operators  $a_{i\sigma}^+$ ,  $a_{i\sigma}$  may be introduced in the deformed lattice so as to take partly into account the adiabatic follow up of the electron upon deformation of the lattice. Hamiltonian (3) may be rewritten in the form

$$H = t_0 \sum_{i\sigma} h_{i\sigma} + \sum_{\substack{ij\sigma \\ i \neq j}} t(\mathbf{R}_j^0 + \mathbf{u}_j - \mathbf{R}_i^0 - \mathbf{u}_i) a_{i\sigma}^+ a_{i\sigma} + \frac{1}{2} U \sum_{i\sigma} n_{i\sigma} n_{i-\sigma}. \quad (6)$$

For small displacements  $\mathbf{u}_i$ , we may expand  $t(\mathbf{R})$  as

$$t(\mathbf{R}_j + \mathbf{u}_j - \mathbf{R}_i - \mathbf{u}_i) = t(\mathbf{R}_j - \mathbf{R}_i) + \left. \frac{\partial t(\mathbf{R})}{\partial \mathbf{R}} \right|_{\mathbf{R}=\mathbf{R}_j-\mathbf{R}_i} \times (\mathbf{u}_j - \mathbf{u}_i) + \dots \quad (7)$$

In the BLF paper<sup>18</sup> the following approximation, based on the nature of tight-binding functions, was introduced

$$\frac{\partial t(\mathbf{R})}{\partial \mathbf{R}} = -q_0 \frac{\mathbf{R}}{|\mathbf{R}|} t(\mathbf{R}). \quad (8)$$

Here  $q_0$  is a coefficient characterizing the exponential decrease of the radial part of the  $d$ -function  $\phi(\mathbf{r}) \sim \phi_0 \exp(-q_0|\mathbf{r}|)$  (usually  $q_0$  is the order of  $1 \text{ \AA}^{-1}$ ).

Finally, the full electronic Hamiltonian may be rewritten in the following form

$$H = H_e^0 + H_{e-i}, \quad (9)$$

$$H_e^0 = t_0 \sum_{i\sigma} n_{i\sigma} + \sum_{\substack{ij\sigma \\ i \neq j}} t_{ij}^0 a_{i\sigma}^+ a_{j\sigma} + \frac{1}{2} U \sum_{i\sigma} n_{i\sigma} n_{i-\sigma} \quad (10)$$

where  $t_{ij}^0 = t(\mathbf{R}_j - \mathbf{R}_i)$  at equilibrium positions,

$$H_{e-i} = q_0 \sum_{\substack{ij\sigma \\ i\pm j}} t_{ij}^0 \frac{(\mathbf{R}_j - \mathbf{R}_i)}{|\mathbf{R}_j - \mathbf{R}_i|} \cdot (\mathbf{u}_i - \mathbf{u}_j) a_{i\sigma}^+ a_{j\sigma}. \quad (11)$$

The operator  $H_{e-i}$  (11) describes the interaction between lattice vibrations and tightly bound electrons in the localized Wannier basis.

The Hamiltonian for the ionic subsystem is assumed to have the usual form

$$H_i = \sum_i \frac{P_i^2}{2M} + \frac{1}{2} \sum_{ij\alpha\beta} u_i^\alpha \phi_{ij}^{\alpha\beta} u_j^\beta. \quad (12)$$

The total Hamiltonian is a sum of (10), (11) and (12). The localized basis representation, used above, underlines the localized nature of  $d$ -electrons. It should be emphasized that such a form is necessary when one must consider disordered transition metal alloys.

In the case of the crystal it is convenient to introduce the normal co-ordinate operators

$$\mathbf{u}_i = \frac{1}{\sqrt{MN}} \sum_{q\nu} Q_{q\nu} \mathbf{e}_{q\nu} e^{i\mathbf{q}\mathbf{R}_i} \quad (13)$$

where  $M$  is the mass of the ion and  $N$  their number in the crystal,  $\mathbf{e}_{q\nu}$  is the polarization at the wave vector  $q$  and branch index  $\nu$  of bare phonon frequency  $\omega_{0q\nu}$ . It follows that

$$H_{e-i} = \sum_{i,j} \sum_{q\nu} A_{q\nu}(i, j) Q_{q\nu} a_{i\sigma}^+ a_{j\sigma} \quad (14)$$

where

$$A_{q\nu}(i, j) = \frac{q_0}{\sqrt{MN}} t_{ij}^0 \frac{(\mathbf{R}_j - \mathbf{R}_i) \cdot \mathbf{e}_{q\nu}}{|\mathbf{R}_j - \mathbf{R}_i|} \times [e^{i\mathbf{q}\mathbf{R}_i} - e^{i\mathbf{q}\mathbf{R}_j}] \quad (15)$$

represents the matrix element of the electron phonon interaction in terms of parameters  $q_0$ ,  $t_{ij}^0$ ,  $M$ ,  $\mathbf{e}_{q\nu}$ , characterizing the transition metal. Thus, as in the Hubbard model, the  $d$ - and  $S(p)$  bands are replaced by one "effective" band in our model. However, the  $s$  electrons give rise to screening effects and are taken into account by choosing proper values of Coulomb integral  $U$  and the acoustical phonon frequencies  $\omega_{0q\nu}$ . Note that our representation of BLF Hamiltonian is valid for any Bravais lattices.

#### 4. The Electron-Phonon Spectral Function

A very important aspect of the electron-phonon problem is the understanding of the electron-phonon spectral functions. In this section we shall calculate and compare them with experiment and previous calculations.

In order to understand how such a concept naturally arises let us consider the scattering process of electron and phonon. The transition probability of this process is given by

$$W = \frac{2\pi}{\hbar} |\langle f | H_{e-p} | i \rangle|^2 \delta(E_i - E_f). \quad (16)$$

It is obviously more satisfactory to have a general technique. To do this let us consider the scattering rate in thermal equilibrium of an electron in state  $|\mathbf{K}\rangle$  at the Fermi surface

$$I_{\pm}(\mathbf{k}) = \frac{V}{2\pi^2\hbar} \sum_{\nu 1,2,3} \int_0^{\infty} d\omega L^{\pm} \int_{\text{FS}} \frac{d^2k'}{v_{k'}} |M_{\nu}(\mathbf{k}, \mathbf{k}')|^2 \delta(\hbar\omega - \hbar\omega_{q\nu}). \quad (17)$$

Here the occupation of final electron states and the occupation number of phonons have been taken into account and also the emission of phonons have been allowed. Signs ( $\pm$ ) denote the scattering rate due to phonon absorption and emission, respectively. The functions  $L^{\pm}$  are given by

$$\begin{aligned} L^+ &= \nu(\omega_{q\nu}) (1 - n(E_{k'})) \\ L^- &= (1 + \nu(\omega_{q\nu})) (1 - n(E_{k'})) \end{aligned} \quad (18)$$

where  $\nu(\omega_{q\nu})$  and  $n(E_k)$  are the Bose and Fermi distribution functions, respectively. Alternatively, we can express the same information in the following form

$$I_{\pm}(\mathbf{k}) = 4\pi \int_0^{\infty} d\omega \alpha^2 F(\omega, \mathbf{k}) L_{\pm}. \quad (19)$$

This suggests a reason for introducing the coupling function<sup>2</sup>

$$\alpha^2 F(\omega, \mathbf{k}) = \frac{V}{(2\pi)^3\hbar} \sum_{\nu} \int_{\text{FS}} \frac{d^2k'}{v_{k'}} |M_{\nu}(\mathbf{k}, \mathbf{k}')|^2 \delta(\hbar\omega - \hbar\omega_{q\nu}). \quad (20)$$

This function describes the electron-phonon interaction between an initial state  $|\mathbf{K}\rangle$  on the Fermi surface and all other states  $|\mathbf{K}'\rangle$  on the Fermi surface which differ in energy from the initial state by  $\hbar\omega$ . The quantity  $\alpha^2 F(\omega, \mathbf{k})$  is dimensionless and is independent of the volume of the specimen.

We can now explain how the electron-phonon spectral or Eliashberg function may be defined. The electron-phonon spectral distribution function is the average of  $\alpha^2 F(\omega, \mathbf{K})$  over all  $\mathbf{K}$  on the Fermi surface

$$\alpha^2 F(\omega) = \frac{V}{(2\pi)^3\hbar} \frac{\sum_{\nu} \int_{\text{FS}} \frac{d^2k}{v_k} \int_{\text{FS}} \frac{d^2k'}{v_{k'}} |M_{\nu}(\mathbf{k}, \mathbf{k}')|^2 \delta(\hbar\omega - \hbar\omega_{q\nu})}{\int_{\text{FS}} \frac{d^2k}{v_k}}. \quad (21)$$

The electron-phonon mass enhancement is perhaps the single most relevant parameter for superconductivity since it gives an average strength of the electron-phonon coupling. It is given by<sup>2</sup>

$$\lambda = 2 \int \alpha^2 F(\omega) \omega^{-1} d\omega. \quad (22)$$

The electron-phonon spectral distribution function  $\alpha^2 F(\omega)$  enters the Eliashberg equations<sup>2,10</sup> that govern the superconductive properties of strong coupling superconductors. Before going into concrete calculations it will be worthwhile to note that there is a great similarity between the Eliashberg spectral function and the transport coupling function  $\alpha_{tr}^2 F(\omega)$ . The latter gives another method to probe the electron-phonon interaction. The function  $\alpha_{tr}^2 F(\omega)$  differs from the Eliashberg spectral function by the scattering factor  $K_{tr}(P, P')^2$ . Experimentally, much effort has been made to determine accurately both types of functions.

Turn now to the Eliashberg equations. In Ref. 31 the system of equations of superconductivity for the tight-binding electrons in the transition metal has been derived. The equations of superconductivity have been obtained in localized Wannier basis and give an alternative approach to the theory of superconductivity in TMC. Our equations are analogous to the Eliashberg equations for the Bloch electrons. In momentum representation<sup>30</sup> the obtained system of equations reduces to the standard form of Eliashberg equation with the electron-phonon spectral function defined by<sup>30</sup>

$$\alpha^2 F(\omega) = \int_{\text{SF}} \frac{d^2 k}{v_k} \int_{\text{SF}} \frac{d' k'}{v_{k'}} \sum_{\nu} |V_{\nu}(\mathbf{k}', \mathbf{k})| \left( \frac{-1}{\pi} \right) \text{Im} D_{k\nu}(\omega + i\delta) \bigg/ \int \frac{d^2 k}{v_k}. \quad (23)$$

Here  $D_{k\nu}(\omega)$  is the phonon Green functions, defined in Ref. 30. It is obvious from the comparison (23) and (21) that at non-zero temperature the phonon Green function in (23) describes the thermal broadening. To interpret (23) let us note that the meaning of the  $\alpha^2 F(\omega)$  is that it counts at fixed frequency  $\Omega$ , how many phonons with  $\omega_q = \Omega$  there are, and weighs each phonon by the strength and number of electron transitions from  $|\mathbf{k}\rangle$  to  $|\mathbf{k} + \mathbf{q}\rangle$  across the Fermi surface in which this phonon can participate. It is interesting to point out here that as a way of using Eliashberg equations some authors<sup>32</sup> make the following ansatz:

$$\alpha^2 F(\omega) = \frac{\lambda \Omega}{2} \delta(\omega - \Omega) \quad (24)$$

which corresponds to the system of electron and phonon with the Einstein spectrum. Contrary to such phenomenological approach, in the present paper we take into account the real phonon spectrum of transition metal.

### 5. Numerical Results

Let us apply the results of previous sections to reasonable model calculations of the electron-phonon spectral functions of five bcc transition metals. We rewrite the expression (14) for the electron-phonon interaction in the form

$$H_{e-i} = \sum_{q\nu} \sum_{k\delta} V_\nu(\mathbf{k}, \mathbf{k} + \mathbf{q}) Q_{q\nu} a_{k+q\delta}^+ a_{k\delta} \quad (25)$$

$$V_\nu(k, k + q) = \frac{iq_0}{\sqrt{NM}} \sum_{\mathbf{x}} t^0(R_x) \frac{\mathbf{R}_x \cdot \mathbf{e}_{q\nu}}{|\mathbf{R}_x|} [\sin(\mathbf{k}\mathbf{R}_x) - \sin(\mathbf{k} + \mathbf{q})\mathbf{R}_x]. \quad (26)$$

It is well known that the transfer integral  $t^0(R)$  determines the band width  $W$  for the cubic lattices by

$$W = 2 \cdot z \cdot t^0(R_x) \quad (27)$$

where  $Z$  is the number of n.n. The band energy is given by

$$\begin{aligned} \varepsilon_k &= t_0 + \sum_{\mathbf{k}} t^0(\mathbf{R}_x) e^{i\mathbf{k}\mathbf{R}_x} \\ &= \sum_{\mathbf{x}} t^0(R_x) \cos(\mathbf{k} \cdot \mathbf{R}_x). \end{aligned} \quad (28)$$

For the bcc transition metals like V, Nb, Mo, W, Ta the band energy<sup>22</sup> may be written as ( $z = 8$ )

$$\varepsilon_k = 8 \cos\left(\frac{1}{2} k_x a\right) \cos\left(\frac{1}{2} k_y a\right) \cos\left(\frac{1}{2} k_z a\right) t^0(a) = t^0 \cdot \bar{\varepsilon}_k. \quad (29)$$

The calculations were done with the appropriate set of metal parameters. The experimental band width  $W$  lead to appropriate value of  $t^0$ , as it follows from Eq. (27). A special problem is to find the polarization  $\mathbf{e}_{q\nu}$  at the wave vector  $\mathbf{q}$  and branch index  $\nu$ . For our aims it is reasonable to accept the Born-Karman model (cf. Refs. 33, 34). It is the phenomenological scheme allowing to calculate the energies and polarization vectors of phonons for arbitrary vectors of the BZ in terms of phenomenological parameters called the force constants. The last quantities are obtained by fitting this model to the experimentally available phonon frequencies.<sup>35-37</sup>

We are now ready to calculate the EPSF taking the Born-Karman scheme mentioned above into account. An explicit calculation yields the following EPSF



$$\alpha^2(\omega)F(\omega) = \frac{V}{(2\pi)^3 \hbar^2} \frac{q_0^2 t_0^2}{a^2 MN} \int_{\text{SF}} \frac{d^2 k}{v_k} \int \frac{d^2 k'}{v_k'} \times \sum_{\nu\alpha} \frac{\left[ e_{k-k'\nu}^\alpha \left( \frac{\partial \bar{\epsilon}_{k'}}{\partial k'^\alpha} - \frac{\partial \bar{\epsilon}_k}{\partial k^\alpha} \right) \right]^2}{2\omega_{k-k'\nu}} \delta(\omega - \omega_{k-k'\nu}) / \int_{\text{SF}} \frac{d^2 k}{v_k} \quad (30)$$

It is convenient to write down the following equality

$$\left[ e_{k-k'\nu}^\alpha \left[ \frac{\partial \bar{\epsilon}_{k'}}{\partial k'^\alpha} - \frac{\partial \bar{\epsilon}_k}{\partial k^\alpha} \right] \right]^2 = \frac{8a^2}{4} [A_\nu^\alpha(\mathbf{k}', \mathbf{k})]^2. \quad (31)$$

It is easy to calculate

$$\int_{\text{SF}} \frac{d^2 k}{v_k} = \frac{V}{(2\pi)^3} \cdot \frac{(2\pi)^3}{V} \int_{\text{SF}} \frac{d^2 k}{v_k} = \frac{(2\pi)^3}{V} \mathcal{N}(\epsilon_f) = \frac{(2\pi)^3}{V} \cdot \mathcal{N} \cdot \mathcal{N}_a(\epsilon_f) \quad (32)$$

where  $\mathcal{N}_a(\epsilon_f)$  is the density of state per unit cell and  $\mathcal{N}$  is the number of unit cells. For the bcc lattice we have

$$\mathcal{N} = \frac{V}{\Omega_c} = \frac{2V}{a^3}. \quad (33)$$

Now we get the final expression for the EPSF

$$\alpha^2 F(\omega) = \frac{V^2}{(2\pi)^6 \hbar^2} \frac{q_0^2 t_0^2}{MN^2 \mathcal{N}_a(\epsilon_f)} \int_{\text{SF}} \frac{d_2 k}{v_k} \int_{\text{SF}} \frac{d^2 k'}{v_k'} \sum_{\nu\alpha} \frac{|A_\nu^\alpha(\mathbf{k}', \mathbf{k})|^2}{\omega_{k-k'\nu}} \times \delta(\omega - \omega_{k-k'\nu}). \quad (34)$$

Using (22), the electron-phonon enhancement parameter  $\lambda$  may be expressed as

$$\lambda = \frac{V^2}{(2\pi)^6 \hbar^2} \cdot \frac{2q_0^2 t_0^2}{M \cdot \mathcal{N}^2 \cdot \mathcal{N}_a(\epsilon_f)} \int_{\text{SF}} \frac{d^2 k}{v_k} \int \frac{d^2 k'}{v_k'} \sum_{\nu\alpha} \frac{[A_\nu^\alpha(k', k)]^2}{\omega_{k-k'\nu}^2}. \quad (35)$$

The calculations were done for the spherical Fermi surface for the sake of simplicity. The radii of the Fermi sphere can be calculated as

$$\epsilon_f = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}; \quad n = \frac{Z}{\Omega_c} \quad (36)$$

where  $Z$  is the valence of an ion. The integrals which appear in Eq. (34) were calculated by the Monte-Carlo method.<sup>38</sup> In Fig. 1 the electron-phonon spectral functions for five bcc transition metals have been calculated in the approximation  $Z = 2$ . Then, we may see that the present calculations give relatively good description of the EPSF despite very rough approximation which consists of integration on the spherical Fermi surface. Roughly speaking, the common feature of our results presented in Fig. 1 is similarity of the obtained histograms to the phonon DOS (cf. Refs. 39–42). Especially for the W our results are very close to phonon DOS  $F(\omega)$  which have been obtained within the angle forces model.<sup>36</sup> In Table 1 we presented the results for the parameter  $\lambda$  which was calculated using Eq. (34). There is remarkable consistency between our  $\lambda$  and published data.<sup>43–45</sup>

Table 1. Values of various parameters for the five transition metals.

No	$Z$	$Z^{eff}$	$W = 2tz$ Ry	$q_0 \text{ \AA}^{-1}$	$a \text{ \AA}$	$M_{a.e.M.}$	$\lambda$
V	5	3.34	0.58	0.93	3.040	50.94	1.04
Nb	5	3.95	0.69	0.91	3.300	92.91	1.376 (1.48)
Mo	6	4.54	0.72	0.91	3.147	95.94	0.71 (0.803)
Ta	5	4.3084	0.75	0.87	3.306	180.95	0.92 (0.97)
W	6	5	0.77	0.87	3.165	183.85	0.36

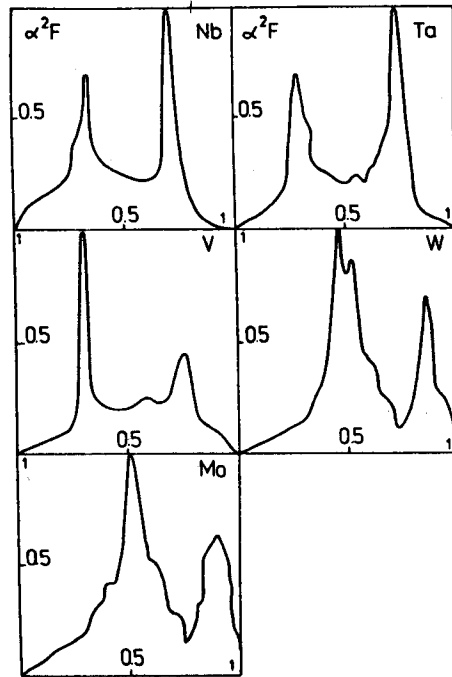


Fig. 1. The electron-phonon spectral function in MTBA for five bcc transition metals.

## 6. Discussion and Conclusion

We have shown that the MTBA enables one to calculate the EPSF for transition metals. From Fig. 1 it follows that the agreement of the experimental EPSF with theoretical EPSF is quite good. The small differences in the shape of our spectral functions and those by other authors<sup>39–42</sup> are very natural. The reason for the difference in the predictions of MTBA method and experiment is probably due to the averaging over the spherical Fermi surface. It must be stressed that of course the effective number of electron per ion  $Z$  is not equal to 2 but is closer to the atomic values, as was shown in Ref. 46. Nevertheless, it is evident that the phonon DOS is the most important factor, which determines the structure of the EPSF.

The theoretical calculation of the superconducting critical temperature<sup>43,45</sup> is a very important task. Unfortunately, at present the most serious problem in the theory of calculating the superconducting transition temperature from first principles is that we do not have a complete understanding about the effect of electron-electron interaction on  $T_c$ .<sup>47</sup> In Ref. 48 it was shown that we can obtain the same value of  $T_c$  for various combinations of  $\lambda$  and Coulomb pseudopotential  $\mu^*$ . It is also important to estimate the effects of the electron-phonon vertex corrections, including high order correction, on the superconducting transition temperature,<sup>49</sup> which was omitted in our calculations.<sup>30,31</sup>

In summary, in the present paper it was shown that the BLF approach gives a constructive and workable formalism for the description of the interaction between the tight-binding electrons and phonons in TMC. It is worth noting that the BLF model has proved to be useful in the case of the theory of electroconductivity for the one-band model for the transition metal, including shift of the Fermi surface and its deformation.<sup>50</sup> Essentially new temperature dependence of the electroresistance in the low temperature region was obtained there. The generalization of the electron-phonon interaction Hamiltonian for disordered binary alloy  $A_xB_{1-x}$  of transition metals have been done in Ref. 51. Using methods of Refs. 30 and 31 the theory for strong coupling superconductivity in disordered transition metal alloys has been developed.<sup>52</sup> The calculation of electroconductivity in disordered alloys has been performed in Ref. 53. The results of the papers<sup>30,31,50–53</sup> and the present paper demonstrate the effectiveness of the MTBA in the description of a variety of properties in the transition metals and their alloys. This is achieved through the use of the Frohlich-Friedel idea that in TMC the change of the electronic charge caused by the displacements of the ions is described in the best way by using orbitals which move with the ions.

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