Temperature dependence of the energy band structure of electrons in metallic lithium

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A procedure is developed that allows for exact calculations of the band energy of a solid in the Hartree–Fock approximation. The starting point is a self-consistent calculation that employs a Gaussian basis of functions. The method is used to establish the energy structure of the electrons in metallic lithium as a function of temperature. The calculated density of states, optical conductivity, the K-edge of the x-ray emission spectrum, and other properties of the electrons agree with the experimental data. Small variations in the band energies for lithium are discovered. The most important ones are the broadening of the core electron states and the transition of outer-shell electrons from s-symmetry states to p-symmetry states as the temperature grows. © *1996 American Institute of Physics.* [S1063-7761(96)02310-4]

1. INTRODUCTION

Modern band theory assumes that the energy structure of electrons experiences no significant changes when the atoms are thermally excited. The present paper discusses the most important variations in the band structure of the electrons in metallic lithium. Lithium was chosen as the object of investigation for two reasons. First, this metal has been studied fairly well both experimentally and theoretically, so that it can be considered a suitable test material. Second, thanks to the anomalies in the elastic properties of lithium at high pressures and low temperatures discovered in experiments[1] and the theoretical predictions of the transition of lithium to a magnetically ordered state at large values of the lattice constant[2] there is an unflagging interest in this material.

2. THE HARTREE–FOCK EQUATIONS

The problem of finding the spectrum of atoms and molecules within the Hartree–Fock method can be assumed solved and realized numerically by computer calculations that employ either difference schemes or basis approaches.[3–6] An unfortunate feature of this problem, however, is the presence of branches of divergent solutions. But even this difficulty can be resolved, at least in principle.[7] The problem of establishing the single-particle spectrum $E_{i\mathbf{k}}$ of the wave functions $\Psi_{i\mathbf{k}}$ of the electrons in a crystal requires solving a system of more complicated Hartree–Fock equations, which for monatomic lattices can be written as

$$\left\{-\frac{\hbar^2}{2m}\Delta+4\pi e^2\int_{\Omega'}G_0(\mathbf{r}-\mathbf{r}')[Z\delta(\mathbf{r}')-\rho(\mathbf{r}')]d^3r'\right\}$$

$$\times\Psi_{i\mathbf{k}}(\mathbf{r})+2\pi e^2\sum_{j\mathbf{k}'}^{\mathrm{occ}}\int_{\Omega'}G_{\mathbf{k}-\mathbf{k}'}(\mathbf{r}-\mathbf{r}')$$

$$\times\Psi^*_{j\mathbf{k}'}(\mathbf{r}')\Psi_{j\mathbf{k}'}(\mathbf{r})\Psi_{i\mathbf{k}}(\mathbf{r}')d^3r'=E_{i\mathbf{k}}\Psi_{i\mathbf{k}}(\mathbf{r}).\qquad(1)$$

Here m is the electron mass, e^2 is the square of the electron charge, $\hbar$ is the Planck constant (in the atomic system of units we can assume $m=\frac{1}{2}$, $\eta^2=2$, and $\hbar=1$), Z is the atomic number of the element, Δ is the Laplace operator, $\delta(\mathbf{r})$ is the Dirac's delta function, and

$$\rho(\mathbf{r})=\sum_{j\mathbf{k}}^{\mathrm{occ}}|\Psi_{j\mathbf{k}}(\mathbf{r})|^2\qquad(2)$$

is the probability density of discovering an electron at a point defined by the vector $\mathbf{r}$ within a cell of volume Ω. Note that both on the right-hand side of Eq. (2) and in the exchange term in Eq. (1) the summation is over occupied states with quantum numbers j and wave vectors $\mathbf{k}$. We write the Green's function in the form of a sum over the vectors $\mathbf{R}_p$ of the direct lattice:

$$G_{\mathbf{k}}(\mathbf{r})=-\frac{1}{4\pi}\sum_p\frac{\exp(i\mathbf{k}\cdot\mathbf{R}_p)}{|\mathbf{R}_p-\mathbf{r}|}.\qquad(3)$$

To solve Eq. (1) we select $\Phi_{j\mathbf{k}}(\mathbf{r})$ in the form

$$\Psi_{j\mathbf{k}}(\mathbf{r})=\sum_i C_{ji}\chi_i(\mathbf{r}),\qquad(4)$$

where for $\chi_i(\mathbf{r})$ it is convenient to take a linear combination of Gaussian functions[8] that satisfies the Bloch theorem. For s-symmetry states,

$$\chi_i(\mathbf{r}-\mathbf{a})=\sum_p\exp(-\alpha_i|\mathbf{R}_p-\mathbf{r}+\mathbf{a}|^2+i\mathbf{k}\cdot\mathbf{R}_p).\qquad(5)$$

By differentiating (5) with respect to the components of the parameter $\mathbf{a}$ we can easily obtain functions with p-, d-, and f-symmetry.

Representing the wave function in the form (4) makes it possible to reduce the problem of solving Eqs. (1) to the algebraic problem of finding the eigenvalues E and the coefficients $\{C\}$:

$$FC=ESC.\qquad(6)$$

Here F is the Fock matrix. Its elements can be written as follows:

$$F_{kk'}=K_{kk'}+N_{kk'}+\sum_{nm}U_{nm}(B_{kk',nm}+D_{kn,k'm}),\qquad(7)$$

where

$$U_{nm}=\sum_{j}^{\mathrm{occ}}\sum_{pq} C_{jp}(S^{-1/2})_{pn}C_{jq}(S^{-1/2})_{qm}, \tag{8}$$

where S is the overlap integral matrix, $K_{kk'}$ are the matrix elements of the kinetic-energy operator, $N_{kk'}$ is the Coulomb electron–nucleus interaction integral, $B_{kk',nm}$ is the Coulomb electron–electron interaction integral, and $D_{kn,k'm}$ is the exchange integral. For the functions (5) these matrix elements can be calculated by the method described in Ref. 8.

3. THE AVERAGED GREEN'S FUNCTION

If we assume that each atom in a crystal lattice undergoes small vibrational displacements $\mathbf{u}_p$ about the equilibrium position determined by the vector $\mathbf{R}_p$, then the new position of the atom can be specified by the radius vector $\mathbf{R}_p+\mathbf{u}_p$. Substituting $\mathbf{R}_p+\mathbf{u}_p$ for $\mathbf{R}_p$ in the expression of the structural Green's function (3) and averaging over an ensemble of displacements $\{\mathbf{u}_p\}$ within the adiabatic approximation, we get

$$\langle G_{\mathbf{k}}(\mathbf{r})\rangle=G_{\mathbf{k}}(\mathbf{r})+\frac{1}{4\pi}\sum_{p}{}' \operatorname{erfc}\left(\frac{|\mathbf{R}_p-\mathbf{r}|}{\sqrt{2\langle u^2\rangle}}\right)\frac{\exp(i\mathbf{k}\cdot\mathbf{R}_p)}{|\mathbf{R}_p-\mathbf{r}|}. \tag{9}$$

Here $\operatorname{erfc}(x)$ is the complementary error function, and $\langle u^2\rangle$ is the standard deviation of the atoms.

Note that the method used here to average the Green's function makes it possible to take into account only elastic and coherent electron–phonon scattering. For this reason it could prove inapplicable in describing the electron states near the Fermi level.

4. RESULTS AND DISCUSSION

In the first stage of our iterative search for a self-consistent solution of the Hartree–Fock equations we use matrix elements averaged over the wave vector $\mathbf{k}$. Calculations of such matrix elements do not take much time. In this case the procedure is similar to that of self-consistent atomic calculations but involving "crystal" matrix elements. The subsequent calculation of the spectrum as a function of the wave vector $\mathbf{k}$ requires practically no iterations. The variations in the spectrum are even smaller if matrix elements with $\langle u^2\rangle\neq 0$ are employed. For this reason here too we use the same set of variational expansion coefficients $\{C\}$ found in the iteration process involving matrix elements averaged over the wave vector $\mathbf{k}$. We used the REDUCE program[9] in the analytical calculations of p- and d-symmetry matrix elements, in resolving the indeterminancies in these matrix elements, and in subsequent FORTRAN programming.

Now let us discuss the results of self-consistent calculations of the spectrum and the properties of electrons in metallic lithium with a body-centered cubic lattice. The lattice constant was assumed constant and equal to the experimentally established value of 6.597 a.u. The basis set of functions was the same as in Ref. 10. Figure 1 depicts the energy bands along some symmetric directions. The results obtained by Ching and Callaway[10] with a different exchange potential differ little from those of the present work. The shape of the spectrum curve also changes little under thermal excitation. However, some differences do exist, and we discuss them below.

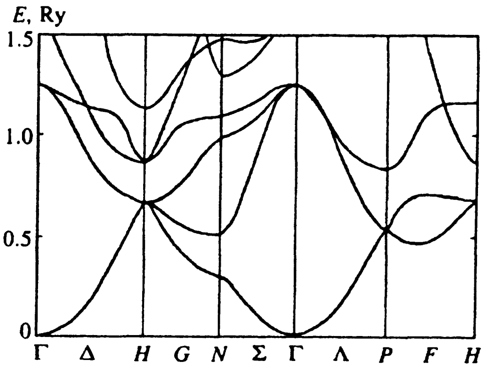

FIG. 1. The energy band structure of the electrons of outer-shell states in metallic lithium along some symmetry directions of the Brillouin zone.

We discovered that the outer-shell electrons are redistributed according to symmetry types: $N(s)=0.32$ and $N(p)=0.68$ at $\langle u^2\rangle=0$, and $N(s)=0.15$ and $N(p)=0.85$ at $T=0$ and $\langle u^2\rangle=0.16(\mathrm{a.u.})^2$. This transition of electrons from s-symmetry states to p-symmetry states can be interpreted as the strengthening of directional bonds. This tendency is observed with the increases in temperature, but the strengthening is insignificant. Figure 2 depicts the density of outer-shell states, with the partial densities of states designated by the letters s, p, and d. Thermal excitation has practically no effect on the shape of these curves. In particular, at the Fermi energy we have $D(s)=0.69$, $D(p)=5.67$, and $D(d)=0.00$ at $\langle u^2\rangle=0$; $D(s)=0.58$, $D(p)=5.69$, $D(d)=0.02$ at $T=0$ and $\langle u^2\rangle=0.16(\mathrm{a.u.})^2$; and $D(s)=0.54$, $D(p)=5.40$, and $D(d)=0.02$ at $T=450\,\mathrm{K}$ and $\langle u^2\rangle=1.00(\mathrm{a.u.})^2$. These values show that the variations in the densities of states are small and are different for each symmetry type. The width of the band occupied by electrons increases from 0.267 Ry to 0.274 Ry with temperature. On the whole, though, our results of calculations of the energy band structure of the electrons prove to be satisfactory when

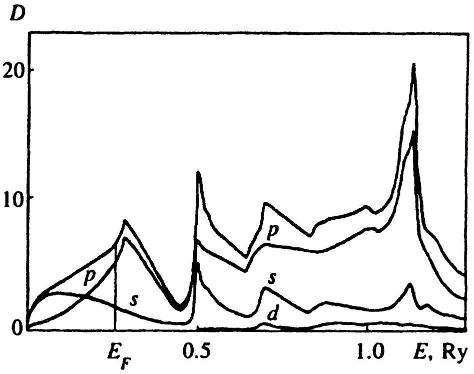

FIG. 2. The total density D of the outer-shell states and its s-, p-, and d-components for lithium electrons measured in number of states per atom per rydberg unit.

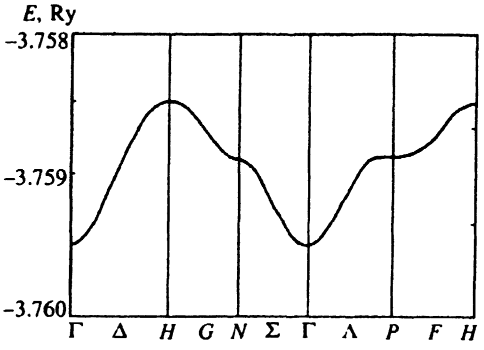

FIG. 3. The energy band structure of the electron of the core states in lithium along some symmetry directions of the Brillouin zone.

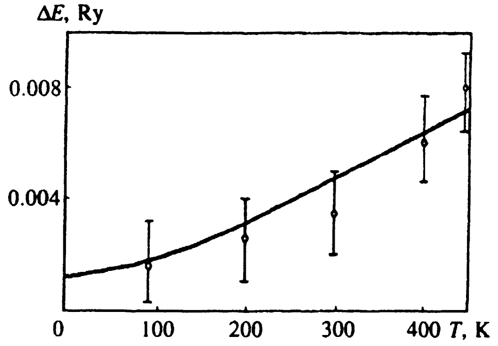

FIG. 5. The temperature dependence of the K-edge of x-ray emission spectrum in lithium. The solid curve represents the results of calculations and the dots correspond to the experimental values.

compared with previous calculations cited in the literature and with the experimental data.[10]

The temperature dependence of the core states is quite different, however. The band structure and the density of the core states at $\langle u^2 \rangle = 0$ are depicted in Figs. 3 and 4, respectively. All these states have the $1s$-symmetry, which does not change under thermal excitation. But the width of the band increases from 0.0010 Ry to 0.0013 Ry (at $T=0$) and then to 0.0063 Ry (at $T=450$ K). This phenomenon (broadening of the band of the core states caused by an increase in temperature) corresponds to the current ideas and leads to an experimentally observed broadening of spectral lines and weakening of the intensity of the peaks in x-ray spectra.

The calculated position of the Fermi level, 4.036 Ry, in relation to the peak in the density of core states fully agrees with the experimentally discovered value 4.03 Ry of the position of the edge of x-ray spectra.[11] The temperature dependence of the K-edge of the x-ray emission spectrum in lithium is depicted in Fig. 5, where the solid curve represents the results of calculations. These results coincide (within experimental errors) with the experimental data,[12] depicted by dots. Note that in Fig. 5 the position of the K-edge of the x-ray spectrum is measured from the value of ΔE with $\langle u^2 \rangle = 0$.

The calculations of optical conductivity were done with the model of direct interband transitions. The results are depicted in Fig. 6 (curve *1*). The resulting value of 0.27 Ry for the lower edge of the direct transitions is somewhat lower on the energy scale than the values calculated by other researchers.[10] The results in the literature suggest that the beginning of interband transitions is located even lower on the energy scale than the present result. The discrepancy between the calculated results and the experimental data is believed to be caused by indirect transitions. The results of calculations of optical conductivity done with the model of indirect interband transitions is also depicted in Fig. 6 (curve *2*). The resulting value of the gap in indirect interband transitions is in good agreement with the experimental data: ~ 0.18 Ry at 125 K. Thus, inelastic electron–phonon scattering has proved to play an important role in the formation of the optical conductivity spectrum of lithium under thermal excitation.

On the whole, atomic vibrations in the lattice (averaged over the displacement ensemble) lead to small changes in the energy band structure of the electron in lithium. The following changes are the most significant: the shift and broadening of the core bands, and the transition of outer-shell electrons from s-symmetry states to p-symmetry states with increasing temperature.

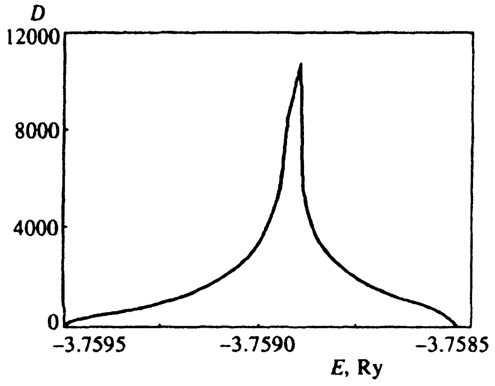

FIG. 4. The total density D of the core states for lithium electrons measured in number of states per atom per Rydberg unit.

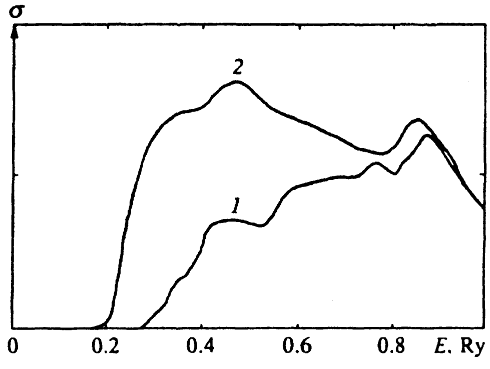

FIG. 6. The optical conductivity σ of lithium electrons obtained in the models of direct (curve *1*) and indirect (curve *2*) interband transitions.

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