Effect of Electron-Hole Scattering Resonance on X-Ray Emission Spectrum

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Soft x-ray emission from metals results when an electron in the conduction band makes a radiative transition to an inner hole of the atom. The object of this paper is to study the effect of the electron-hole scattering resonances on the soft-x-ray emission spectra of metals. A detailed theoretical calculation was done for the emission spectra of Li and Na. From this calculation, the qualitative features of the observed K emission spectrum of Li can be explained if a p-scattering resonance exists in the band near the Fermi surface. The resonance is caused by the electron-hole scattering. A resonance violates the Friedel sum rule unless a localized state analogous to a "local moment" is invoked. The crystal was divided into Wigner-Seitz spheres. The normal Li ion was removed from the center of the sphere and replaced by a Li ion with a $1s$ hole. A Hartree-type potential was constructed for this Li ion. Multiple scattering of other ions outside the Wigner-Seitz sphere was treated in the optical model. Scattering wave functions for the electrons inside the Wigner-Seitz sphere were computed numerically and used to calculate the matrix elements. The emission spectrum of Li was computed for various effective masses. The L_{23} emission spectrum of Na was computed along similar lines. No localized state was found in the band. This result may explain why no anomaly exists for the L_{23} emission spectrum of Na. The spectrum of the unobserved L_1 emission of Na has also been computed. Here, there exists a p-scattering resonance, as in the K emission spectrum of Li. From the calculation, it may be concluded that a lack of localized state is the reason why the emission spectra of other substances are normal.

INTRODUCTION

THE soft-x-ray emission of metals results when one of the electrons in the conduction band makes a radiative transition into an empty inner shell. Thus, unlike most of the physical properties of metals which are determined by the energy level of the electron system as a whole (such as cohesive energy), or by the electrons at the Fermi surface (such as cyclotron resonance and electrical conductivity), the x-ray emission is capable of giving direct evidence about the individual energy levels in the conduction and higher bands. Thus, the x-ray emission spectrum has been used to define E_F, the Fermi energy and m^*, the effective mass. The emission spectra also have particular value in helping to decide whether the excitation-band picture should be applied to metals as well as to insulators. It is found that the x-ray spectra of metals show strong discrete lines on contrast with the absorption spectra of the insulators like alkali halides. Because of these properties, the x-ray emission spectra of metals have been well investigated.

The qualitative features of the spectra of most metals are well understood. However, the K emission spectrum of lithium has a feature which has no straightforward interpretation. The spectrum was first measured by Skinner and O'Bryan[1] in 1934. Since then, the measurement has been repeated by Bedo and Tomboulian,[2] Canterall and Trotter,[3] and most recently by Crisp and Williams.[4] All the measurements show that the K emission spectrum of Li has a premature peak about 1.2 eV below the Fermi level. This result cannot be explained by the ordinary density-of-states calculations. The most accurate determination of the energy band of Li was that of Ham,[5] 1962 [see Fig. 5(c)]. His result shows that the Fermi surface is about 0.65 eV below the symmetry point N' of Brillouin zone. This calculation thus disproves the suggestion of Cohen and Heine in 1958[6] that the anomaly is due to the contact with the point N' of Brillouin zone. Ham's result further shows that near the Fermi surface, the density-of-states curve is rising. Tomboulian[7] showed that the discrepancy could be explained neither by the instrumental broadening nor by the lifetime effects. Jones and Schiff[8] advanced the theory that the shape of the K emission of Li could be explained as due to the presence of the $1s$ hole. However, their theory could not explain why emission spectra of other substances do not show the effect.

Goodings,[9] in a simplified model, used a Koster-Slater type of localized approximation to calculate the density of states in the presence of the $1s$ hole. He claimed from physical arguments that the observed shape is due to a change of the density of states and the matrix elements when a $1s$ hole is present. In a recent paper, Shuey[10] considered the peculiar shape of

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[1] H. M. O'Bryan and H. W. B. Skinner, Phys. Rev. **45**, 370 (1934); H. W. B. Skinner, Phil. Trans. Roy. Soc. (London) **A239**, 95 (1940).

[2] D. E. Bedo and D. M. Tomboulian, Phys. Rev. **109**, 35 (1958).

[3] J. A. Catteral and J. Trotter, Phil. Mag. **4**, 1164 (1959).

[4] R. S. Crisp and S. E. Williams, Phil. Mag. **5**, 525 (1960).

[5] F. S. Ham, Phys. Rev. **128**, 82 (1962); **128**, 2524 (1962).

[6] M. H. Cohen and V. Heine, Advan. Phys. **7**, 395 (1958).

[7] D. M. Tomboulian, in *Handbuch der Physik*, edited by S. Flügge, (Springer-Verlag, Berlin, 1957), Chap. XXX, p. 246.

[8] H. Jones and B. Schiff, Proc. Phys. Soc. (London) **A67**, 217 (1954).

[9] D. A. Goodings, Proc. Phys. Soc. (London) **86**, 75 (1965).

[10] R. T. Shuey, Bull. Am. Phys. Soc. **10**, 266 (1966).

the emission spectrum of Li as due to electron-hole scattering. He took into account the band structure of the Li atom. However, he used the first-order Born approximation to compute the oscillator strength. This approximation may not be justified if the phase shifts are not small. His work also indicates a peak just before the Fermi surface.

From a realistic quantitative calculation we have made, the qualitative shape of the K emission spectrum of Li can be explained if a p-scattering resonance exists in the band near the Fermi level. In our calculation the potential of a Li atom with a $1s$ hole was used. The resonance is caused by this potential. Such a resonance violates the Friedel sum rule unless a localized state analogous to a "local moment" is invoked. The importance of such virtual levels in determining the properties of metallic alloys were first recognized by Friedel[11] in connection with the resistivity properties of alloys, where one sees the level as a scattering resonance at the Fermi surface. The idea of localized states has been extended by Clogston,[12] who applied it to the Knight shift, Anderson,[13] and Wolff,[14] who found localized magnetic states in metallic alloys, and by Caroli,[15] who applied the localized state techniques to the study of the optical properties of solids, in particular the AuNi system.

We have also calculated the L_{23} emission spectrum of sodium, finding no localized s state in the band. This may explain why no anomaly exists for the L_{23} emission band of sodium. A similar calculation for the unobserved L_1 emission spectrum of Na was made, showing that there exists a p scattering resonance, as in the K emission band of Li. A summary of the calculations was reported at the 1966 April meeting of the American Physical Society.[16]

We discuss in Sec. 1 the methods used to compute the potentials and the wave functions of Li and Na atoms with inner holes; while in Secs. 2 and 3 brief reviews are given of the Wigner-Seitz method and Hartree-Fock approximation, respectively. In Sec. 4, the model Hamiltonian is derived and solved. A condition for the existence of localized states is also given in this section. We describe the theory of x-ray emission, apply the results to the study of the soft x-ray emission of Li and Na, and compare the observed and calculated emissions in Sec. 4. A summary and some difficulties with the model Hamiltonian are given in the last section. Throughout the paper energy, distance, and angles are measured, respectively, in electron volts (eV), in angstrom units (Å), and in radians.

1. CONSTRUCTION OF THE ATOMIC POTENTIALS

To make a realistic calculation of x-ray emission of an atom, we need to know the potential of an atom with a hole in its inner shell. Such a potential may be obtained by the Hartree-Fock self-consistent-field method.[17–19] However, the labor involved in constructing such a field for an accurate result is considerable. In the computations, therefore, approximate potentials which produced the energy levels of the atomic state of that substance reasonably were used.

For the K emission of Li, a potential for the $1s$ configuration was constructed, while for the L_1 and L_{23} emissions of Na, potentials for the $1s^22s^22p^5$ and $1s^22s2p^6$ configurations of Na^{++}, respectively, were constructed. For the potential of the $1s$ state of the Li atom, a variational calculation gave an effective hydrogenic charge of 2.69. Though the potential constructed using this effective charge gave an energy level which was in excellent agreement with the ionization energy of the $1s^2$ state of Li (the observed energy is 75.62 eV, while the calculated energy using the effective charge of 2.69 is 75.2 eV), it reproduced the energy levels of the excited states, particularly the p states, poorly. It was too strong for the p states. The potential was therefore changed at some points until a compromise potential was obtained. The observed and computed energy levels of Li^{++} are shown in Tables I and II.

An attempt was made to apply the Prokofjwe method[20] to the construction of a potential for Na^{++}, but the accuracy obtained was poor, and this method was discarded. It was found later that earlier attempts by other workers to apply the Prokofjwe method to other substances had also failed.[21,22] The reason for the failure to obtain a Prokofjwe-type potential for Na^{++} may be due to the fact that the potential is not central. The potential used for Na^{++}, in which one $2p$ and the $3s$ electrons were missing, was constructed by trial and error. The initial potential was calculated by

TABLE I. Calculated energy E_c and observed energy E_0 of Na^{++}. Units of E_c and E_0 are in electron volts.

	E_c	E_0
$1s^22s2p^6$	60.00	64.00
$1s^22s^22p^5$	48.70	47.29
$1s^22s^22p^53s$	12.40	14.45
$1s^22s^22p^53p$	9.70	10.95
$1s^22s^22p4s$	5.60	6.20
$1s^22s^22p5s$	3.20	3.51

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[11] P. de Fajet de Castlejan and J. Friedel, J. Phys. Radium **17**, 27 (1956); J. Friedel, Nuovo Cimento **7**, 287 (1958).

[12] A. M. Clogston, Phys. Rev. **125**, 439 (1962).

[13] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

[14] P. A. Wolff, Phys. Rev. **124**, 1020 (1961).

[15] B. Caroli, Physik Kondersierten Materie **1**, 346 (1963).

[16] F. K. A. Allotey and J. J. Hopfield, Bull. Am. Phys. Soc. **11**, 331 (1966).

[17] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).

[18] H. A. Bethe, *Intermediate Quantum Mechanics* (W. A. Benjamin, Inc., New York, 1964), pp. 33–109.

[19] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vols. 1 and 2.

[20] W. Prokofjwe, Z. Physik **58**, 255 (1929).

[21] F. Seitz, Phys. Rev. **47**, 400 (1935).

[22] K. E. Gorin, Physik Z. Sowjetunion, **9**, 328 (1936).

TABLE II.[a] Calculated energy E_c and observed energy E_0 of Li^{++}. Units of E_c and E_0 are in electron volts.

	E_c	E_0
$1s$	74.45	75.62
$1s2s$	12.50	15.77
$1s2p$	16.00	13.91
$1s3s$	6.30	6.64
$1s3p$	6.50	6.16

[a] As is evident from Table II, the best potential we could construct for the Li^{++} was still strong for the p electrons. The effect of this in our calculations has been accounted for by the appropriate choice of U_p and U_s in Sec. 4.

finding the potential as a function of r due to charge distribution on concentric spheres of radii r_{nl} of maximum charge density of nl electrons.

Thus, there were placed at $r_{1s}=0.027$ Å two electrons, at $r_{2p}=0.148$ Å five electrons. The values of r_{nl} used were taken from Slater.[19] For the $1s^22s2p^6$ configuration of Na^{++}, the arrangement of the electrons on the concentric spheres was similar to that described above except that in the present case, one electron was placed at r_{2s}, six electrons at r_{2p}, and two electrons at r_{1s}. Table II shows the observed and calculated energy levels of Na^{++}. Within these approximations, the potentials for the $1s^22s^22p^5$ and $1s^22s2p^6$ configurations of Na^{++} were not very different because $r_{2s}-r_{2p}=0.022$ Å. In Figs. 1(a), 1(b), and 1(c) are shown the computed wave functions for the 1s hole (1s) of Li^{++}, 2p hole ($1s^22s^22p^5$) of Na^{++}, and the 2s hole ($1s^22s2p^6$) of Na^{++}, respectively.

2. WIGNER-SEITZ METHOD

The method is to divide the real space into unit cells as one constructs a Brillouin zone in the reciprocal lattice by bisecting the vectors to their nearest neighbors. In the bcc lattice, the lattice assumed by Li and Na, this gives a regular octahedron. The assumption is then made that this octahedron is not very different from a sphere, and that in the outer regions where departure occurs, the potential is very weak and the wave function is smooth. Compare Figs. 1(a), 1(b), and 1(c). We shall denote by r_s the radius of the s sphere (Wigner-Seitz sphere). The values of r_s for Na and Li are 2.15 Å and 1.71 Å, respectively.

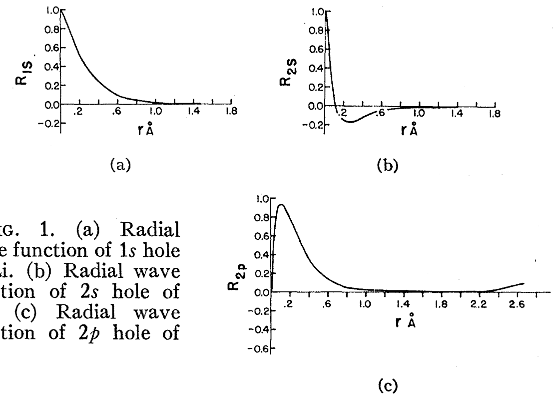

FIG. 1. (a) Radial wave function of 1s hole of Li. (b) Radial wave function of 2s hole of Na. (c) Radial wave function of 2p hole of Na.

The crystal potential at any point in one of the s spheres may be regarded as the sum of three terms: (a) the ion-core potential due to the ion at the center of the octahedron, (b) the Coulomb potential of the $N-1$ other ion cores making up the crystal, (c) the Coulomb potential of $N-1$ electronic charges situated outside the octahedron. The contributions made by (b) and (c) to the crystal potential may be combined to give the Coulomb potential of $N-1$ exterior electrical neutral polyhedra as a first approximation. However, in higher approximations, each octahedron contributes a multipole potential of high order which will be most important near the boundary of the s sphere. A calculation by Wigner and Seitz[23] on alkalis showed that this effect is negligibly small. Therefore, the only surviving term is (a), the ion-core potential which is approximately spherically symmetric within the s sphere. Because of the spherical symmetry, the Schrödinger wave equation within the s sphere is separable.

$$\left(\frac{\hbar^2}{2m}\nabla^2+V(r)-E_k\right)\psi=0, \tag{2.1}$$

$$\psi=\frac{U_{kl}(r)}{r}Y_{lm}(\theta,\phi), \tag{2.2}$$

where $U_{kl}(r)$ satisfies the radial Schrödinger equation

$$\frac{d^2U_{kl}}{dr^2}+\left(k^2-\frac{2m}{\hbar^2}V(r)-\frac{l(l+1)}{r^2}\right)U_{kl}=0. \tag{2.3}$$

In solving Eq. (2.3) inside the s sphere, boundary conditions were imposed such that the wave function and its derivative must be continuous, and also that the Bloch condition

$$\psi_k(\mathbf{r}+\mathbf{R}_i)=e^{i\mathbf{k}\cdot\mathbf{R}_i}\psi_k(\mathbf{r}) \tag{2.4}$$

must be satisfied. In the usual solution of Eq. (2.3), using the Wigner and Seitz approximation, only the wave function corresponding to the bottom of the conduction band is computed, the others being obtained by perturbation expansion. The wave function corresponding to Γ, $k=0$, must have the same symmetry as the crystal; namely, cubic symmetry relative to any nucleus. Hence, ψ_0 may be expanded in the Kubic harmonics in the cell.

$$\psi_0=Rs(r)+g(\theta,\phi)Rg(r)+(\text{term with } l=6), \tag{2.5}$$

where $Rs(r)$ and $Rg(r)$ are the radial functions. In the present approximation, only the first term in Eq. (2.5) is retained.

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[23] E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933); 46, 509 (1934).

The boundary conditions may thus be written

$$\psi_0=Rs(r_s)\,,\quad 0\leqslant r\leqslant r_s\,, \tag{2.6}$$

and

$$(dRs/dr)_{r=r_s}=0\,. \tag{2.7}$$

Equation (2.7) follows because the wave function must approach the cell boundary horizontally, since it must by reflection symmetry be even about the boundary. E_0 was obtained for Na by Wigner and Seitz,[23] and for Li by Seitz,[21] using Eq. (2.3) with $l=0$ and the boundary conditions defined by Eqs. (2.6) and (2.7). These studies used Prokofjwe and Seitz potentials, respectively.

The potential acting within the s sphere has been taken as solely due to the central ion; however, if an account of direct Coulomb interaction of uniform charge distribution inside the s sphere is taken, the potential inside the s sphere should be written

$$V(r)+\int_0^{r_s}\rho_a(r_a,\theta_a,\phi_a)\int_0^{r_s}\left[\rho(r,\theta,\phi)\times\frac{r_<^{\,l}}{r_>^{\,l+1}}Y_{lm}(\theta,\phi)d^3r\right]d^3r_a\,, \tag{2.8}$$

in which $r_>$ is greater and $r_<$ the lesser of r_1 and r_2, the positions of electrons 1 and 2, respectively. $\rho(r,\theta,\phi)$ is the charge density inside the s sphere. We have assumed that the charge distribution inside the s sphere is uniform and constant, hence the potential has spherical symmetry with only $l=0$ component contributing. The last expression on the right-hand side of Eq. (2.8) may thus be written

$$(e^2/2r_s)[3-(r^2/r_s^2)]\,. \tag{2.9}$$

The mean of the extra potential is

$$\frac{e^2}{2r_s}\int_0^{r_s}\left(3-\frac{r^2}{r_s^2}\right)d^3r\bigg/\int_0^{r_s}d^3r=\frac{6}{5}\frac{e^2}{r_s}\,. \tag{2.10}$$

3. MANY-BODY PROBLEM

The electrons interact with each other as well as with the atomic nuclei. The Hamiltonian for the N electrons may be expressed as

$$H=\sum_{i=1}^{N}[\epsilon_i+V(r_i)]+\sum_{j<i}\frac{e^2}{r_{ij}}+I_{ab}\,. \tag{3.1}$$

I_{ab} is the electrostatic interaction between the nuclei and is assumed constant. $\epsilon_i=(\hbar^2/2m)\nabla_i^2$ denotes the kinetic energy of the ith electron. The second term represents the energy of interaction between the electrons and all the nuclei, and the third term is the electrostatic interaction of electrons with each other; r_i is the position of the ith electron and r_{ij} is the distance between electrons i and j; e is the electronic charge. Equation (3.1) has been written in the spirit of Born and Oppenheimer approximations. As a first approximation, it shall be assumed that the atomic nuclei are fixed. Relativistic effects, including the spin-orbit coupling, are also neglected.

The principal approximation for reducing the complexity of the many-body problem is the Hartree-Fock (H-F) method, which in the second quantization may be written

$$\sum_m F_{nm}'C_m^\dagger\Psi_{\text{H-F}}+\sum_n\sum_m(F_{nqnm}^2-F_{qnnm}^2)C_m^\dagger\Psi_{\text{H-F}}=E_mC_m^\dagger\Psi_{\text{H-F}}\,. \tag{3.2}$$

In writing down Eq. (3.2), the off-diagonal terms were neglected as being small. $\Psi_{\text{H-F}}$ is the Hartree-Fock wave function for $N-1$ electrons, and $C^\dagger$ and C are the creation and destruction operators. The F's are defined by

$$F_{nm}'=\langle n|\epsilon+V(r)|m\rangle\,, \tag{3.3}$$

$$F_{nqnm}^2=\left\langle nq\left|\frac{e^2}{r_1-r_2}\right|nm\right\rangle\,, \tag{3.4}$$

and

$$F_{qnnm}^2=\left\langle qn\left|\frac{e^2}{r_1-r_2}\right|nm\right\rangle\,. \tag{3.5}$$

F_{nqnm}^2 is the direct Coulomb interaction between the electrons while F_{qnnm}^2 is the exchange interaction between parallel-spin electrons. Missing in Eq. (3.2) is the correlation energy, which takes into account the fact that because of their Coulomb repulsions, electrons avoid each other.

4. THE MODEL

The normal ion from the center of the s sphere was removed and replaced by the impurity ion. It was assumed, as when the normal ion was present, that the Wigner-Seitz approximation still holds. The multiple scattering of electrons with ions and the electron-electron interactions outside the cell were represented by an optical model potential (Lax,[24] Goldberger and Watson[25]).

The distortion of neighboring ions due to the presence of the impurity ion in their proximity was neglected. The effects of the periodicity of the lattice were also ignored. However, the electron outside the cell was assumed to possess an effective mass. This is justified because no zone-boundary effect was being considered. Inside the cell the effective mass was taken as the free-electron mass. The x-ray emission spectra were computed for Li for various effective masses. For Na, the

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[24] M. Lax, Rev. Mod. Phys. **23**, 287 (1951).

[25] M. L. Goldberger and K. M. Watson, *Collision Theory* (John Wiley & Sons, Inc., New York, 1964), Chap. 11.

effective mass is practically equal to the free-electron mass both inside and outside the cell, and the Fermi surface is almost spherical.

Electrons inside the s sphere in which the hole is located may be described with the following Hartree-Fock equation:

$$H=H_0+H_{imp}(r)+H_c(r_s)+H_{pp}+H_{ss}+H_{ps}. \quad (4.1)$$

Here, H_0 is the unperturbed energy of the free-electron system in the second quantized notation.

$$H_0=\sum_k \sum_l T_l(n_{kl\uparrow}+n_{kl\downarrow}), \quad (4.2)$$

and

$$T_l=\frac{\hbar^2}{2m}\left[-\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{l(l+1)}{r^2}\right]. \quad (4.3)$$

$n_{kl\uparrow}$ is the number operator for electrons in momentum- and angular-momentum states k and l, respectively, with spin up.

$H_{imp}(r)$ is the potential of the atom with the inner hole. The method for obtaining this potential is given in Sec. 1. $H_c(r_s)$ is the lowest energy of the conduction band plus electron-electron interactions outside the s sphere. $H_c(r_s)$ also depends on the angular-momentum states and may be computed by solving the Schrödinger equation. If the cohesive energy of the metal is known, however, $H_c(r_s)$ may be obtained from the equation

$$E_{\text{cohesion}} \approx (E_m+E_0-E_1),$$

where $H_c(r_s)=E_0$ is the energy of the bottom of the band. E_0 calculated from the above equation includes the electron-electron interaction.[26] E_1 is the negative of ionization potential of the metal. E_m is the mean energy of Fermi gas. If $N(E)$ is the density of states, this energy is given by

$$E_m=\int_0^{E_F} EN(E)dE \Big/ \int_0^{E_F} N(E)dE.$$

For a parabolic density of state, we have

$$E_m=\tfrac{3}{5}E_{\text{Fermi}}.$$

Values of E cohesion were taken from Seitz,[27] E_1 was taken from the *Handbook of Atomic Energy Levels*.[28] $H_{pp}+H_{ss}+H_{ps}$ represents the electron-electron interaction part of the Hamiltonian. H_{pp} is the electron-electron interaction of p electrons, H_{ss} represents electron-electron interaction of s electrons, while H_{ps} is the interaction of p electrons with s electrons.

We may write down the general interaction term for any l explicitly as

$$H_{lm_l l'm_{l'}}=\sum_{k=0}^{k_F}\sum_{k'=0}^{k_F}\sum_{l=0}^{\infty}\sum_{l'=0}^{\infty}\sum_{m_l=0}^{2l+1}\sum_{m_{l'}=0}^{2l'+1} J_{kk'lm_l l'm_{l'}}$$
$$\times(n_{klm_l\uparrow}+n_{kl'm_{l'}\downarrow})(n_{k'l'm_{l'}\uparrow}+n_{k'l'm_{l'}\downarrow})$$
$$-\sum_{k}^{k_F}\sum_{k'}^{k_F}\sum_{l=0}^{\infty}\sum_{l'=0}^{\infty}\sum_{m_l=0}^{2l+1}\sum_{m_{l'}=0}^{2l'+1} K_{kk'lm_l l'm_{l'}}$$
$$\times(n_{klm_l\uparrow}n_{k'l'm_{l'}\uparrow}+n_{klm_l\downarrow}n_{k'l'm_{l'}\downarrow}). \quad (4.4)$$

$J_{kk'lm_l l'm_{l'}}$ is the direct Coulomb interaction between the electrons in momentum states k and k', and in the angular-momentum states l and l', with components m_l and $m_{l'}$, respectively; k_F is the value of k at the Fermi surface; $K_{kk'lm_l l'm_{l'}}$ is the exchange integral for electrons in the same spin state. In writing down Eq. (4.4) the off-diagonal terms were neglected. It can be shown[29] that of the density of free noninteracting electrons in an s sphere, the s partial density accounts for about 63%, while the p partial density measures about 29%. Thus we may assume that the role played by the d and f electrons within the sphere is negligible. These electrons were thus omitted in writing Eq. (4.1). Another argument in favor of this omission is that the K emission of Li is due mainly to that of p electrons. However, in the L_{23} emission of Na, there is a small admixture of d and s states. The shape of the wave function within the cell is approximately energy-independent; hence the Coulomb integral does not depend on energy in a first approximation, but only on angular-momentum states. We shall therefore omit the k index on the exchange and the direct Coulomb integrals.

The matrix element of the Coulomb interaction term of Eq. (3.1) may be written

$$\left\langle ab\left|\frac{e^2}{r_{12}}\right|cd\right\rangle=\int\int U_a^*(r_1)U_b^*(r_2)\frac{e^2}{r_{12}}$$
$$\times U_c(r_1)U_d(r_2)d^3r_1d^3r_2. \quad (4.5)$$

Assuming a central-field approximation, we have

$$U_a(r_1)=R_{n^a l^a}(r_1)Y_{l^a m_l^a}(\theta_1\phi_1)(\sigma_1,m_s^a).$$

Here $R_{n^a l^a}(r_1)$ is the radial part of the wave function for a particle at the positional coordinate r_1. $Y_{l^a m_l^a}(\theta_1\phi_1)$ is the spherical harmonic and is a function of the polar angle θ_1 and the azimuthal angle ϕ_1. The spin part of the wave function is denoted by (σ_1,m_s^a).

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[26] J. Friedel, Phil. Mag. 43, 1115 (1952).

[27] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 677–680.

[28] *Atomic Energy Levels*, edited by C. E. Moore, Natl. Bur. Std. (U. S.) Circ. No. 467 (U. S. Government Publishing and Printing Office, Washington, D. C., 1949), Vol. I.

[29] F. K. A. Allotey, Ph.D., thesis, Princeton University, 1966 (unpublished).

The interelectronic distance is given by

$$1/r_{12}=[r_1^2+r_2^2-2r_1r_2\cos\Theta]^{-1/2}$$

$$=\sum_{g=0}^{\infty}\frac{r_<^{g}}{r_>^{g+1}}P_g(\cos\Theta)\,,\qquad(4.6)$$

where Θ is the angle between the radii vectors of electrons 1 and 2 from the origin of the coordinate system. $P_g(\cos\Theta)$ is the Legendre polynomial of order g. g satisfies the so-called triangular condition, which requires that g, l^a and l^b be the sides of a triangle of even perimeter.[30] The methods for computing the integrals in Eq. (4.5) are discussed in Refs. 17, 18, and 19.

As has been mentioned earlier, only p and s electrons will be considered. Thus, for the interaction between p electrons, the triangular condition demands that $g=0$ or 2, while for s-p interaction $g=0$, 1. For the s-s interaction $g=0$.

As a first approximation, only the monopole term ($g=0$) will be considered. Within this approximation the exchange and direct Coulomb interaction terms are identical. The Coulomb interactions between the s electrons, the s and p electrons and the p electrons will be denoted by J_{ss}, J_{sp}, and J_{pp}, respectively.

Density Function

Density functions inside the sphere of radius r_s, in which the hole is located, may be defined by

$$f_{l\alpha}=\sum_{k=0}^{k_{\mathrm{F}}}\int_0^{r_s}|R_{kl}^{\mathrm{scat}}|^2\alpha d^3r.\qquad(4.7)$$

The integration is over the s sphere. R_{kl}^{scat} is the value of R_{kl} when the hole is present. We shall discuss how this is obtained in the later section. α labels a spin component. Inside the band, k is continuous; hence, we shall replace the summation over k by an integration,

$$\sum_k^{k_{\mathrm{F}}}\frac{R}{\pi}\int_0^{k_{\mathrm{F}}}dk.\qquad(4.8)$$

R is the radius of a large sphere and $k_{\mathrm{F}}=k_{\mathrm{Fermi}}$. The integration over k is one-dimensional because the angular dependence of the initial state has already been determined by the impurity ion, hence not all states of the continuum that lie in the interval dk are available to the electron. Thus, Eq. (4.7) may be written

$$f_{l}\alpha=\frac{R}{\pi}\int_0^{k_{\mathrm{F}}}\int_0^{r_s}|R_{kl}^{\mathrm{scat}}|^2\alpha d^3r dk.\qquad(4.9)$$

The Model Hamiltonian

The mean of the Hamiltonian may then be written

$$\langle H\rangle=\sum_{i=1}^{6}E_{pi}f_{pi}+\sum_{i=1}^{2}E_{si}f_{si}+\frac{J_{pp}}{2}\sum_{i=1}^{6}\sum_{j=1}^{6}(f_{pi}+f_{pj})^2$$

$$-\frac{J_{pp}}{2}\sum_{i=1}^{6}f_{pi}^2+\frac{J_{ss}}{2}\sum_{i=1}^{2}\sum_{j=1}^{2}(f_{si}+f_{sj})^2\qquad(4.10)$$

$$-\frac{J_{ss}}{2}\sum_{i=1}^{2}f_{si}^2+J_{sp}\sum_{i=1}^{6}\sum_{j=1}^{2}f_{pi}f_{sj}\,,$$

$$E_{pi}=T_{pi}+H_{imp}(r)+H_c(r_s)\,,$$

$$E_{si}=T_{si}+H_{imp}(r)+H_c(r_s)\,.$$

Minimizing Eq. (4.10) with respect to f_{pi} and f_{si}, we have for the p electrons

$$H_{pi}=T_{pi}+H_{imp}(r)+U_{pi}(r_s)\,,\qquad(4.11)$$

while for the ith s electron we have

$$H_{si}=T_{si}+H_{imp}(r)+U_{si}(r_s)\,,\qquad(4.12)$$

$$U_{pi}(r_s)=H_c(r_s)+J_{pp}\sum_{j=1}^{6}f_{pj}+J_{sp}\sum_{j=1}^{2}f_{sj}$$

$$-J_{pp}f_{pi}\,,\qquad(4.13)$$

and

$$U_{si}(r_s)=H_c(r_s)+J_{sp}\sum_{j=1}^{6}f_{pj}+J_{ss}\sum_{j=1}^{2}f_{sj}-J_{ss}f_{si}.\qquad(4.14)$$

Equations (4.11) and (4.12) have been solved with $U_{pi}(r_s)$ and $U_{si}(r_s)$ as parameters.

Scattering from the Hole

The general solution of Eqs. (4.11) and (4.12) may be written

$$R_{kl}(r)=\left[\frac{k^2}{2\pi R(A_{kl}^2+B_{kl}^2)^{1/2}}\right]^{1/2}$$

$$\times[A_{kl}j(kr)+B_{kl}n_l(kr)].\qquad(4.15)$$

$j_l(kr)$ and $n_l(kr)$ are the spherical Bessel and Neumann functions, respectively. R is the radius of a large sphere surrounding the hole, $l=0$ for the s state and $l=1$ for the p state. $R_{kl}(r)$ is assumed to be regular so that at the origin $B_{kl}=0$. A_{kl} and B_{kl} are calculated from the condition that at a boundary the wave function and its derivative are continuous. Asymptotically, Eq. (4.15) may be written

$$R_{kl}(r)\sim(k^2/2\pi R)^{1/2}\sin(kr+\delta_{kl}-l\pi/2)/kr\,,\qquad(4.16)$$

where δ_{kl} is the phase shift in the presence of the hole. The change of the number of electrons in a sphere of

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[30] E. U. Condon and G. H. Shortley, *The Atomic Spectra* (Cambridge University Press, Cambridge, England, 1963), p. 176.

radius R due to the presence of the hole may be written[31]

$$\Delta n = 4\pi \int_0^R r^2 (|R_{kl}|^2 - |R_{kl}^0|^2) dr .$$

R_{kl}^0 is the solution to radial Schrödinger without the hole.

$$\Delta n = \frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1)\delta_{k_F} . \tag{4.17}$$

The physical meaning of Eq. (4.17) is that if the impurity has a valency z relative to that of the host-lattice self-consistent potential, $U(r)$ will insure that the displaced charge $n|e|$ will cancel $z|e|$ exactly in order that the impurity be screened at large distances. Thus Eq. (4.17) may be written

$$\frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1)\delta_{k_F} = z . \tag{4.18}$$

Equation (4.18) is known as the Friedel sum rule.[31] In deriving it, it was assumed that all the electrons in the angular-momentum state l and the spin state have equal phase shifts. This need not always be the case, particularly when a scattering resonance exists in the conduction band. It is then possible to have different phase shifts for various components of angular momentum state l and spin state α.

Thus, when a scattering resonance exists in the conduction band, the phase shift may be different for each of the electrons in the given l and α states. Instead of Eq. (4.18), self-consistency is obtained by requiring that the generalized Friedel relation be

$$\sum_{j=1}^{2(2l+1)} \delta_{k_F j} = \pi z_l , \quad l = 0, 1, 2, \cdots , \tag{4.19}$$

where z_l is the contribution to the screening by the electrons in the state l. For the p electrons,

$$\delta_{kp1} + \delta_{kp2} + \delta_{kp3} + \delta_{kp4} + \delta_{kp5} + \delta_{kp6} = \pi z_p , \tag{4.20}$$

while for the s electrons

$$\delta_{ks1} + \delta_{ks2} = \pi z_s . \tag{4.21}$$

Many numerical solutions to Eq. (4.11) were made. One symmetrical solution is the solution in which the Friedel sum rule is satisfied. Let us denote by δ_{k_F} and f_{lF} the values of the phase shifts and the density function when the Friedel rule is satisfied. Though the phase shift is evaluated at $k = k_F$, to avoid cumbersome notation the F subscript on k_F has been suppressed. There are also asymmetrical solutions. These solutions occur when localized states exist in the band. This is analogous to Anderson's[13] theory of localized magnetic states. One such solution can be obtained from the configuration in which one p electron is resonant while the others are not and have equal phase shifts. The phase shift of the resonant p electron is denoted by δ_{p1}. That of the nonresonant p electron is denoted by δ_{p2}. Density functions for resonant and nonresonant p electrons are denoted by f_{p1} and f_{p2}, respectively.

The self-consistency condition thus demands that

$$\delta_{p1} + 5\delta_{p2} = \pi z_p . \tag{4.22}$$

Similarly, it is possible to obtain solutions to the models in which two or three p electrons are resonating. For two electrons with parallel spin resonating, we have

$$2\delta_{p1} + 4\delta_{p2} = \pi z_p , \tag{4.23}$$

while for the three electrons with parallel spins resonating, we have

$$3\delta_{p1} + 3\delta_{p2} = \pi z_p . \tag{4.24}$$

Many asymmetrical solutions to Eq. (4.11), in which Eqs. (4.22) and (4.23) are satisfied, have been computed for lithium and sodium. It was found that when there are symmetrical solutions resonance scattering exists above the Fermi levels. For the s electrons in these metals, computations that have been carried out indicated that with reasonable values of J_{ss} and z_s only the symmetrical solutions exist. Thus Eq. (4.4) may be written

$$2\delta_{ksF} = \pi z_s .$$

Numerical Calculation of f

The results of the calculation of Eq. (4.9) indicate that

$$\sum_{j=1}^{6} f_{pj} \quad \text{and} \quad \sum_{i}^{2} f_{si}$$

are almost constants; the reason being that in the calculation, the total phase shift of a given angular-momentum state is assumed to be fixed [see Eqs. (4.20) and (4.21)]. Knowing δ_{p1} from one of the Eqs. (4.22), (4.23), or (4.24), depending on whether one, two, or three electrons are localized, δ_{p2} can be calculated. With this value it is possible to read off the corresponding value of U_{p2} from the graph of phase shift as a function of U_p, and f_{p2} from a graph of f_p as a function of U_p.

Figure 2(a) shows the density function f_p as a function of U_p for various effective masses of Li. The decrease of f_p with the increase of U_p is due to the fact that as U_p is increased the Coulomb interaction term is increased. U_p thus tends to reduce the number of electrons inside the cell. Increase in effective mass is equivalent to increase in the strength of the potential, hence the reduced values of f_p as we increase the effective mass. Figure 2(b) shows the graph of f_p for Na, which has shape similar to that of Li. In Figs. 2(c) and 2(d) are shown graphs of f_s for Li and Na, respectively.

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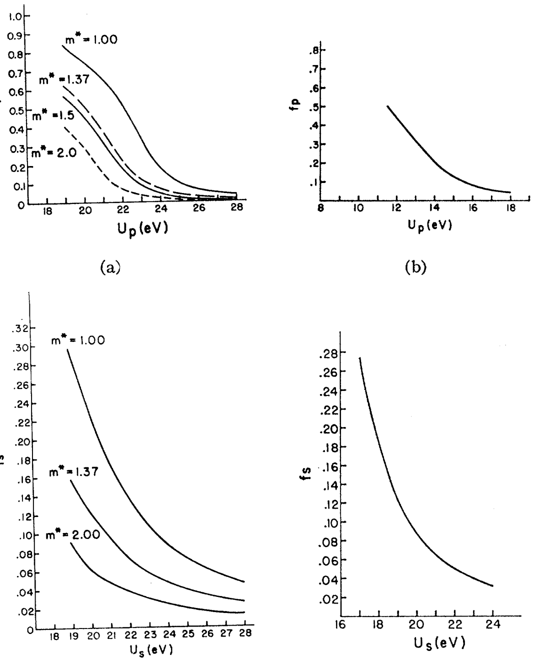
[31] C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1964); or see Ref. 26.



(a) (b)

(c) (d)

FIG. 2. (a) Density function f_p as a function of U_p of Li for different effective masses. (b) Density function f_p as a function of U_p of Na. (c) Density function f_s as a function of U_s of Li for different effective masses. (d) Density function f_s as a function of U_s of Na.

Figures 3(a) and 3(b) show the variations of phase shifts at the Fermi surface as a function of U_p for Li and Na, respectively. It is seen that as U_p is increased, the phase shifts decrease to zero and then become negative. Figures 3(c) and 3(d) show variations of phase shifts with U_s for Li and Na, respectively. These curves show that, unlike the p electrons, the s electrons phase shifts have no structure. The absence of structure in the phase shifts of s electrons explains why the observed spectrum of L_{23} emission of Na is normal.

To compute J_{pp}, we note that from Eq. (4.13) we may obtain

$$U_{p1}(r_s) = H_c(r_s) + B_p - J_{pp} f_{p1}, \tag{4.25}$$

and five equations of the form

$$U_{p2}(r_s) = H_c(r_s) + B_p - J_{pp} f_{p2},$$

$$B_p = J_{pp} \sum_{j=1}^{6} f_{pj} + J_{sp} \sum_{j=1}^{2} f_{sj},$$

where B_p is constant. Thus

$$J_{pp} = (U_{p1} - U_{p2})/(f_{p1} - f_{p2}). \tag{4.26}$$

Similarly, we have for the s electrons

$$\begin{aligned} U_{s1}(r_s) &= H_c(r_s) + B_s - J_{ss} f_{s1}, \\ B_s &= J_{ss} \sum_{j=1}^{2} f_{sj} + J_{sp} \sum_{j=1}^{6} f_{pj}, \end{aligned} \tag{4.27}$$

and another equation for the electron with the opposite spin.

$$U_{s2}(r_s) = H_c(r_s) + B_s - J_{ss} f_{s2}, \tag{4.28}$$

giving

$$J_{ss} = (U_{s1} - U_{s2})/(f_{s1} - f_{s2}). \tag{4.29}$$

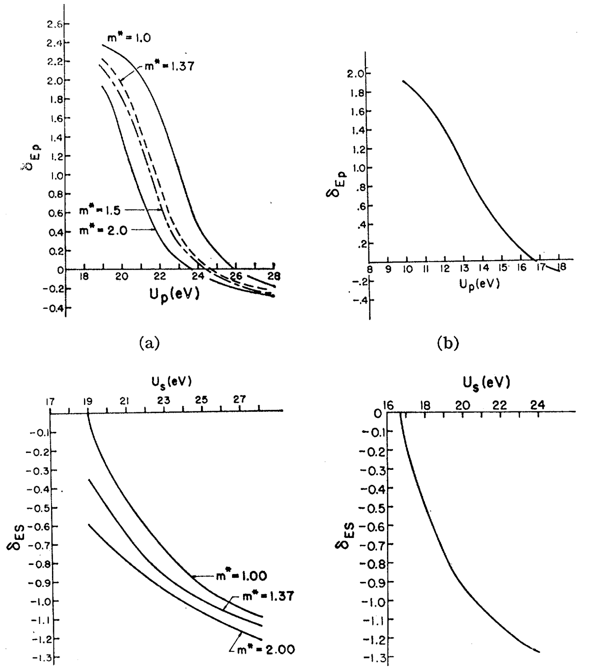
In writing down Eqs. (4.26) and (4.29), we have for convenience suppressed the arguments of U_p and U_s. In the present problem, because of the difficulty with the correlation energy, this is discussed in the last section of this paper. The parameter Up and Us and hence z_p and z_s could not be computed from the first principles. We thus solved the problem for various values of z_p. The values of z_s, however, satisfied the ordinary Friedel relation. In addition, the s electrons "antiscreen," that is, their phase shifts, are negative.

Condition for Stability

The sum of the one-particle energies is just the sum of the kinetic energies of the individual electrons. Thus, this sum may be written

$$\sum_{i=1}^{2(2l+1)} T_{li} = \sum_{i=1}^{2(2l+1)} \frac{\hbar^2}{2m} k_i.$$

The action of the hole is to alter the total energy such that the change in the total energy of the p electrons



(a) (b)

(c) (d)

FIG. 3. (a) Phase shifts δ_{Ep} at the Fermi surface as a function of U_p of Li for different effective masses. (b) Phase shifts δ_{Ep} at the Fermi surface as a function of U_p of Na. (c) Phase shifts δ_{Es} at the Fermi surface of Li as a function of U_s for different effective masses. (d) Phase shifts δ_{Es} at the Fermi surface as a function of U_s of Na.

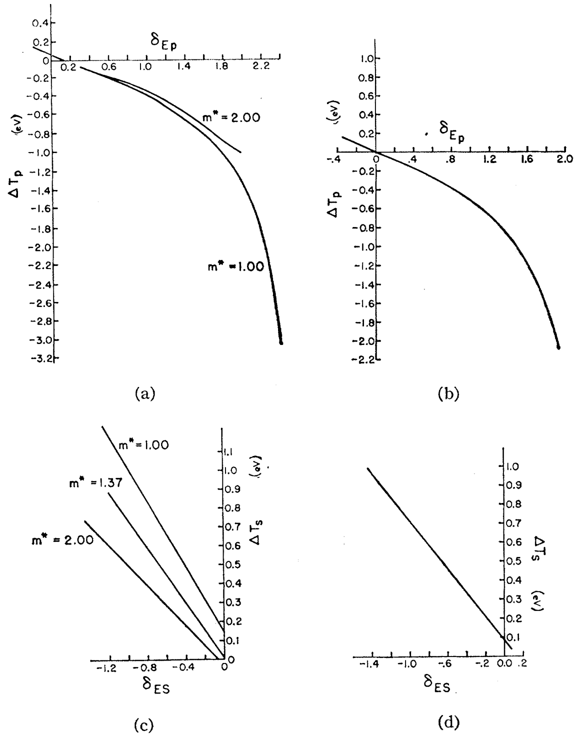


FIG. 4. (a) Change of kinetic energy ΔT_p per particle as a function of phase shifts δ_{Ep} at the Fermi surface of Li as U_p is varied for different effective masses. (b) Change of kinetic energy ΔT_p per particle as a function of phase shifts δ_{Ep} at the Fermi surface of Na as U_p is varied. (c) Change of kinetic energy ΔT_s per particle as a function of phase shifts δ_{Es}, at the Fermi surface of Li as U_s is varied for different effective masses. (d) Change of kinetic energy ΔT_s per particle as a function of phase shifts δ_{Es}, at the Fermi surface of Na as U_s is varied.

from symmetrical to that of the asymmetrical solution may be written with the aid of Eqs. (4.10) as

$$\Delta E_p=\left(\sum_{i=1}^{6}\Delta T_{pi}-6\Delta T_{pF}\right)-\tfrac{1}{2}\left(J_{pp}\sum_{i=1}^{6}f_{pi}^2-6J_{ppF}f_{pF}^2\right). \quad (4.30)$$

ΔT_{pi} is the change of the kinetic energy of the ith p electron when the hole is present. Here the subscript F denotes the Friedel value. Now if we make the wave function of Eq. (4.16) vanish at the boundaries of a large sphere R, the following quantized values of k are obtained:

$$k=\left[\left(n+\frac{l}{2}\right)\pi-\delta_{kl}\right]\Big/R,$$

$$n=0,\,1,\,2,\,\cdots.$$

The action of the hole is to change the wave vector such that

$$\Delta k=-\delta_{kl}/R.$$

Thus,

$$\Delta T_l=\frac{-1}{\pi}\int_0^{E_F}\delta_{El}d_{El}, \quad (4.31)$$

which is independent of the size of the sphere. The condition for stability is

$$\Delta E_l<0. \quad (4.32)$$

For localization of one p electron, Eq. (4.31) is

$$(\Delta T_{p1}+5\Delta T_{p2}-6\Delta T_{pF})-\tfrac{1}{2}[J_{pp}(f_{p1}^2+5f_{p2}^2)-6J_{ppF}f_{pF}^2]<0. \quad (4.33)$$

For localization of two p electrons, the condition is

$$(2\Delta T_{p1}+4\Delta T_{p2}-6T_{pF})-\tfrac{1}{2}[J_{pp}(2f_{p1}^2+4f_{p2}^2)-6J_{pp}f_{pF}^2]<0. \quad (4.34)$$

The integration in Eq. (4.31) was done numerically. In Fig. 4(a) are shown graphs of ΔT_p, the change of kinetic energy per particle as a function of phase shifts at the Fermi surface of Li. ΔT_p is not very sensitive to the changes in the effective mass. Figure 4(b) shows ΔT_p for Na. Graphs of ΔT_s for Li and Na are shown in Figs. 4(c) and 4(d), respectively.

As is evident from the graphs, ΔT_p as a function of phase shift has a curvature while the ΔT_s graph is linear. The difference between the two sets of graphs is due to the fact that p-scattering resonances exist in the band while there are no s-scattering resonances.

We have given here an explicit calculation for the stability condition of two resonant p electrons in Li, $m^*=1.5$ and $z_p=1.3$.

$$U_{p1}=20.50,\quad U_{p2}=23.24,$$
$$\delta_{p1}=1.617,\quad \delta_{p2}=0.212,$$
$$f_{p1}^2=0.66,\quad f_{p2}^2=0.0059,\quad J_{pp}=9.69,$$
$$2\Delta T_{p1}=-1.572,\quad 4\Delta T_{p2}=-0.260,$$
$$2\Delta T_{p1}+4\Delta T_{p2}=-1.832,$$
$$\tfrac{1}{2}J_{pp}(2f_{p1}^2+4f_{p2}^2)=1.546,$$
$$J_{ppF}=12,\quad f_{pF}^2=0.02,\quad 6\Delta T_{pF}=-0.96,$$
$$3J_{ppF}f_{pF}^2=0.72,$$
$$\tfrac{1}{2}J_{pp}(2f_{p1}^2+4f_{p2}^2)-3J_{ppF}f_{pF}^2=0.826,$$

and

$$(2\Delta T_{p1}+4\Delta T_{p2}-6\Delta T_{pF})=-0.872.$$

Hence, $\Delta E_p=-0.046$. The small value of ΔE_p is due to the fact that the scattering resonance occurs very near to the Fermi surface.

5. X-RAY EMISSION

Under electron impact or irradiation by photons, an electron in the inner shell may be removed from an undisturbed atom and be located at a great distance from the parent atom. Subsequent to the removal of the inner electron, a radiative transition may follow when the inner vacancy is filled. Sometimes more than one vacancy is created. When this happens it leads to the so-called satellite lines. In our calculation, an assumption is made that the conduction electrons respond to screen the hole in a relatively short time compared with the emission of the x ray. The screening time is of order V_F/d and is about 10^{-16} sec. V_F and d are, respectively, the Fermi velocity and interatomic distance. An order-of-magnitude calculation, using the intensity curve of the K emission of Li shows that the lifetime of the $1s$ hole is $>10^{-14}$ sec.

X rays are produced by spontaneous emission. This emission occurs regardless of the initial presence of an external field. Thus, unlike the induced emission, one cannot use semiclassical arguments to obtain the transition rate. For a completely satisfactory theory, quantum-field theory is needed. However, it is possible to obtain the correct probability of spontaneous emission from general conditions of equilibrium using Einstein's A and B coefficients for spontaneous and induced transition probabilities, respectively. The probability of spontaneous emission of a photon per unit time per unit solid angle (see Bethe[32] or Dirac[33]) is given by

$$W=\frac{\omega}{2\pi c^3}\left(\frac{e\hbar}{m}\right)^2\left(\frac{E_{\text{eff}}}{E_0}\right)^2|\langle\psi_f|e^{-i\mathbf{k}\cdot\mathbf{r}}\nabla_{\mathbf{A}}|\psi_n\rangle|^2, \quad (5.1)$$

where ψ_n and ψ_f are the wave functions of the atom in the initial and final states. $\nabla_{\mathbf{A}}\psi_n$ is the projection of the gradient of ψ_n on the direction of the vector potential $\mathbf{A}$. E_0 is the field in the cell where the electron is located while E_{eff} is the effective field of the medium outside the cell. Since we are only interested in the qualitative shape of the spectrum, the exact value of the E_{eff}/E_0 will not be needed.

Hence, the intensity per unit frequency is

$$I=\frac{4}{3}\frac{\hbar^2\omega^2e^2n}{m^2c^3}\left(\frac{E_{\text{eff}}}{E_0}\right)^2 N(E)|\langle\psi_f|\nabla_{\mathbf{A}}|\psi_k\rangle|^2, \quad (5.2)$$

where $N(E)$ is the density of states, ψ_k is the wave function in the conduction band, ψ_f is the wave function of the hole, and n is the number of holes.

$$N(E)=\frac{\Omega}{(2\pi)^3}\int\frac{dS_k}{\nabla_k E}, \quad (5.3)$$

where Ω is the volume of the crystal, dS_k is a surface element in the k space; thus,

$$I=F\hbar^2\omega^2N(E)|\langle\psi_f|\nabla_{\mathbf{A}}|\psi_k\rangle|^2, \quad (5.4)$$

where

$$F=\frac{4}{3}\frac{e^2n}{m^2c^3}\left(\frac{E_{\text{eff}}}{E_0}\right)^2.$$

The matrix elements may be shown to take the form

$$\langle\psi_f|\nabla_{\mathbf{A}}\psi_k\rangle=\frac{1}{\hbar\omega}\langle\psi_f|\nabla_{\mathbf{A}}U(r)|\psi_k\rangle, \quad (5.5)$$

where $U(r)$ is the potential the electron moves in in the presence of the hole. Equation (5.4) is general. As outlined earlier, the optical selection rules tell us that only the partial densities and the partial wave functions are needed. The partial density of states is given by

$$n(E)=\frac{R}{\pi}\left(\frac{m}{2\hbar^2E}\right)^{1/2}. \quad (5.6)$$

Thus, from Eqs. (5.4), (5.5), and (5.6), the partial intensity is given by

$$I_j=\frac{4}{3}\frac{R}{\pi}\left(\frac{m}{2\hbar^2E}\right)^{1/2}F\left|\left\langle R_f\left|\frac{dU}{dr}\right|R_{kj}\right\rangle\right|^2. \quad (5.7)$$

j takes the values from 1 to 2 $(2l+1)$; the factor 2 is due to the spin.

Low-Energy Limit

At low energies, Eq. (4.15) may be written

$$R_{kp}\approx k^2r/R,\quad l=1, \quad k\to 0 \quad (5.8)$$

and

$$R_{ks}\approx k/R,\quad l=0. \quad k\to 0 \quad (5.9)$$

R_f and dU/dr do not affect the spectrum very much. Hence, in the limit of low energies, the K emission should, using Eqs. (5.7) and (5.8), be proportional to $E^{3/2}$ while the L_{23} emission, using Eqs. (5.7) and (5.9), is proportional to $E^{1/2}$.

The *K* Emission of Li

We have carried out numerical calculations of Eq. (5.7), using the radial wave function R_{kp} defined by Eq. (4.15), with $l=1$ and the radial wave function R_{1s} obtained for lithium in Sec. 1. The spectrum was computed as a function of U_p. It is possible to obtain the qualitative features of the observed spectrum of K emission of lithium if we assume that two or three parallel electrons are resonating. Thus, when two electrons are resonating,

$$I=\frac{4}{3}\frac{R}{\pi}\left(\frac{m}{2\hbar^2E}\right)^{1/2}F\left[2\left|\left\langle R_{1s}\left|\frac{dU}{dr}\right|R_{kp1}\right\rangle\right|^2+4\left|\left\langle R_{1s}\left|\frac{dU}{dr}\right|R_{kp2}\right\rangle\right|^2\right]. \quad (5.10)$$

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[32] See Ref. 18, p. 143.

[33] P. A. M. Dirac, *Quantum Mechanics* (Oxford University Press, Oxford, England, 1958), p. 245.

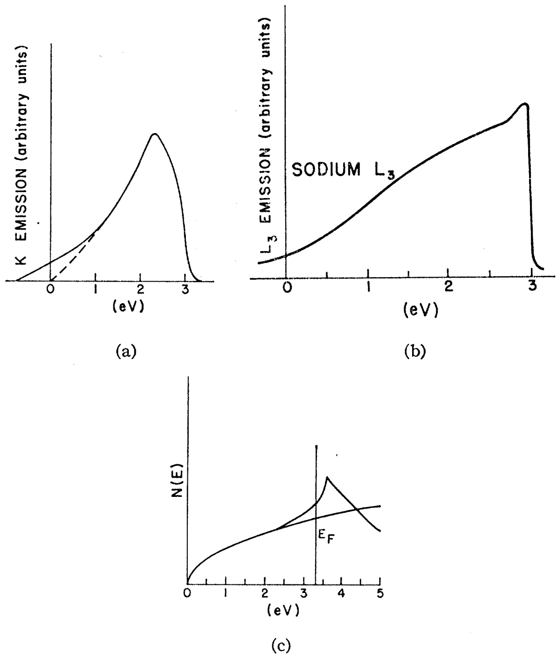

FIG. 5. (a) The observed K emission spectrum of Li, from Crisp and Williams. (b) The observed L_3 emission spectrum of Na, from Skinner. (c) The calculated density-of-states curve of Li from Ham. The smooth curve represents the spherical approximation, and the peaked curve the correct band structure including the nonspherical distortion. E_F is the Fermi energy for the correct band.

R_{kp1} and R_{kp2} are the radial wave functions for the resonating and nonresonating p electrons, respectively, in the presence of the 1s hole.

The L_{23} and L_1 Emissions of Na

Numerical calculation of the L_{23} emission spectrum of sodium was made as a function of U_s. No scattering resonance was found for reasons given earlier, hence

$$I=\frac{8}{3}\frac{R}{\pi}\left(\frac{m}{2\hbar^2E}\right)^{1/2}\left|\left\langle R_{2p}\left|\frac{dU}{dr}\right|R_{ks}\right\rangle\right|^2. \tag{5.11}$$

R_{2p} is the radial wave function of the 2p hole. R_{ks} is the radial wave function for the s electron in the conduction band, in the presence of the sodium atom with 2p hole. In writing down Eq. (5.11), we ignored the small contribution from the d electrons. We did not compute separately L_2 and L_3 emission spectra because the energy separation between them is only 0.21 eV.

The calculations agree qualitatively with the shape of the L_{23} band, the only difference being the low-energy tail. This feature is common to all the low-energy sides of the spectra of solids, and it is particularly pronounced for L_2 and L_3 bands. Cady and Tomboulian[34] suggested that the tail might be due to partial Auger effect. In this theory the long-wavelength radiation is presumed to arise from a double electron transition in which one electron falls into a vacant inner level while a second electron jumps into the conduction band. Landsberg[35] made a quantitative calculation of sodium. He took into account the broadening of energy levels, assuming a screened Coulomb potential between the pair of interacting electrons. By adjusting the screened lengths, he obtains a curve which possesses a tail in qualitative agreement with the observed tail of the L_{23} spectrum of Na. Raimes[36] has suggested that the tail effect is due to the short-range correlation between the electronic positions.

The L_1 x-ray emission of sodium which occurs when a p electron in the conduction band makes a radiative transition to a 2s hole is not observed. The fact that L_1 emission of Na is unobservable may be due to an Auger effect or to intrashell transition of the type $L_3 \rightarrow L_1$ and $L_2 \rightarrow L_1$, or both processes may be operating at the same time. The L_1 and M_1 spectra of other substances are unobservable and may be due to the above processes. We have, however, also carried on a quantitative calculation of the spectrum of L_1 emission of sodium on the lines adopted for K emission of lithium. The calculations indicate that there is a p-scattering resonance in the conduction band of Na.

In Figs. 5(a) and 5(b) are shown the observed spectra of K and L_3 emissions of Li and Na, respectively. Figure 5(a) was taken from Crisp and Williams,[4] while Fig. 5(b) was taken from Skinner.[1] Compare this with Figs. 6(a), 6(b), and 6(c), which show, respectively, the computed K emission spectra of Li, with $m^*=1$ and 1.5, and the L_{23} emission of Na. In computing Fig. 6(c), we did not take into account the tail effect, for the origin of this effect is due to an entirely different cause. Computation was also made for the K emission

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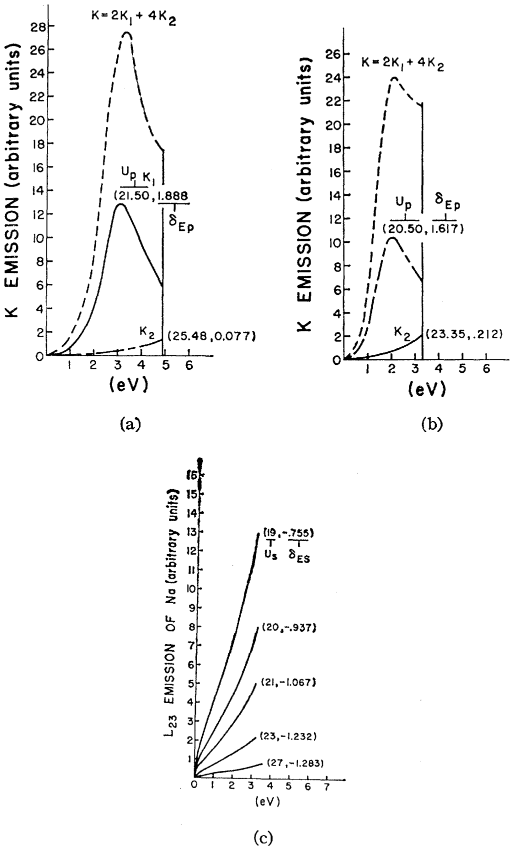
[34] W. M. Cady and D. M. Tomboulian, Phys. Rev. **59**, 38 (1941).

[35] P. T. Landsberg, Proc. Phys. Soc. (London) **A62**, 806 (1949).

[36] S. Raimes, Phil. Mag. **45**, 727 (1954).



(a) (b)

(c)

FIG. 6. (a) K is the total K emission of Li, and $m^*=1.00$ with two resonant p electrons. K_1 and K_2 are, respectively, the partial K emissions of the resonant and the nonresonant p electrons. (b) K is the total K emission of Li, and $m^*=1.50$, with two resonant p electrons. K_1 and K_2 are, respectively, the partial K emissions of the resonant and the nonresonant p electrons. (c) L_{23} emissions of Na with Us a parameter.

spectrum of Li for $m^*=1.37$ and 2. The shapes of the spectra are similar to that shown in Figs. 6(a) and 6(b). Figure 7(a) shows the variation of phase shifts as a function of kinetic energy of the electron in the conduction band for $m^*=1.00$. Calculations for Li with $m^*=1.37$, 1.5, and 2, and for Na, show similar variation. In Fig. 7(b) are shown shapes of partial emission spectrum of p electron. Figures 7(c) and 7(d) show the resultant spectra if only one p electron is resonant. To get the right spectrum, two electrons were assumed to be resonating in the conduction band [Figs. 6(a) and 6(b)]. It is also possible to obtain the right shape of the spectrum if three electrons are resonant. Figure 8 shows the partial L_1 emission spectra of Na, with U_p as a parameter.

6. RECAPITULATION

As shown in Sec. 5, our results give qualitative agreement with the observed x-ray emission spectra of Li and Na. However, our work is partially phenomenological in that we have not been able to derive all the parameters which enter our problem from the first principles. The difficulties lie with the old-time problem of exchange and correlation energies. We remarked in Sec. 2 that the proper potential inside the Wigner-Seitz sphere should read

$$V_{\text{atom}}+V_{\text{Hartree}}+V_{\text{exchange}}+V_{\text{correlation}}. \qquad (6.1)$$

It is known from the Wigner-Seitz[23] calculation of cohesive energy of Na that if we allow only for V_{atom} inside the cell, a good agreement is obtained. This is because V_{exchange} essentially cancels the interactions of parallel spin electrons, while $V_{\text{correlation}}$ keeps out all of the antiparallel spin electrons. Hence, the last three terms of Eq. (6.1) cancel.

In our problem, we have allowed for the exchange term, but the correlation term is absent. We have absorbed it into J, making J effective. From Wigner and Seitz we also know that for the s electrons (which are typical electrons), $J_{\text{effective}}$ turns out to be very close to zero for the atomic problem. However, we do not know the effect that ionic potential (potential with inner hole) makes on $J_{\text{effective}}$.

The s-p exchange, which we neglected, will also have its effect and is the first obvious term ($g=1$) in a better calculation of the Coulomb expansion. It is interesting to note that for the p electrons we have computed J_{pp} with $g=0$, using as our wave function $R_{kp}(r)$, as defined by Eq. (4.15) for the Li atom with $1s$ hole.

$$J_{pp}=(4\pi)^2e^2\int_0^{r_s}\rho(r')\left[\frac{1}{r'}\int_0^{r'}\rho(r)r^2dr+\int_{r'}^{r}\rho(r)rdr\right]r'^2dr'\bigg/\left|\int_0^{r}\rho(r)d^3r\right|^2, \qquad (6.2)$$

$$\rho(r)=|R_{kp}|^2. \qquad (6.3)$$

J_{pp}, calculated from Eqs. (6.2) and (6.3), is of the same order as that we used to fit the Li spectrum. To do J_{pp} properly, we have to include the $g=2$ term in the multiple Coulomb expansion.

We may say that our problem is reminiscent of Heisenberg theory of magnetism, where the theory gives a good agreement but where the exchange parameter has yet to be calculated from the first principle for dense systems. In the Anderson work[13] of localized magnetic states, the J that enters is also $J_{\text{effective}}$, in the sense that it includes the correlation term.

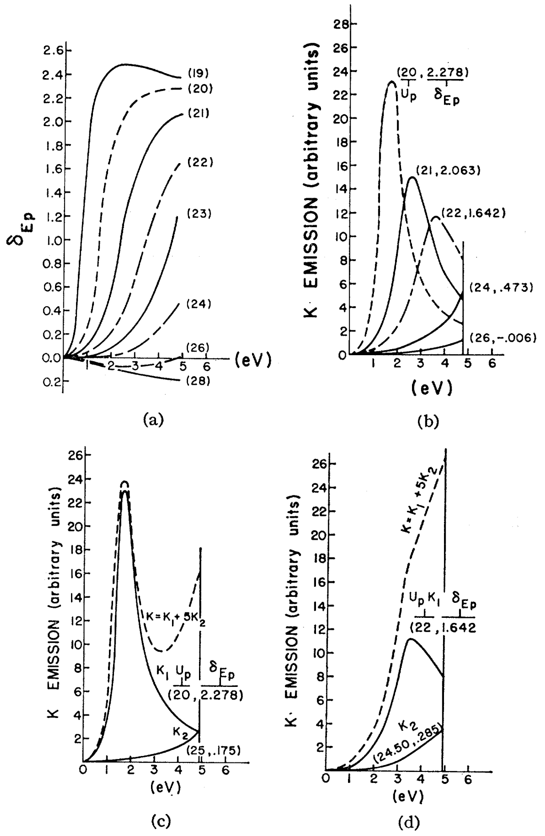


FIG. 7. (a) Phase shifts at r_s as a function of the kinetic energy of the electron, with U_p as a parameter of Li, and $M^*=1.00$. (b) Partial K emissions of Li, and $m^*=1.0$ with U_p as a parameter. (c) and (d) K is the total K emission of Li, and $m^*=1$, with only one resonant p electron. K_1 and K_2 are, respectively, the partial K emissions of the resonant and the nonresonant p electron.

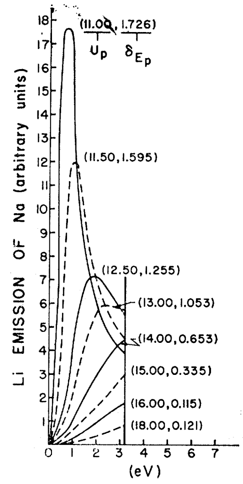


FIG. 8. Partial K emissions of Na with Up as a parameter.

An attractive feature of our model is that it contains few parameters, J_{pp}, J_{ps}, and J_{ss}. Also, at a fixed z_p, the decision of what the best p states are does not depend on either J_{ss} or J_{ps}.

Our work gives a plausible explanation of the peculiar shape of the K x-ray emission spectrum of Li as being due to electron-hole scattering resonance in conduction band. It also shows that the normal shape of the L_{23} emission spectrum of Na may be due to the absence of electron-hole scattering resonance within its conduction band.

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