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On *d*-Resonant Levels in Heavy Alkali Metals*

V. BORTOLANI
Istituto di Fisica dell' Università di Modena, Modena, Italy,
and
Gruppo Struttura della Materia di Modena, Modena, Italy,
and
Istituto di Fisica Nucleare Sezione di Bologna, Bologna, Italy

AND

C. CALANDRA
Istituto di Fisica dell' Università di Modena, Modena, Italy
and
Gruppo Struttura della Materia di Modena, Modena, Italy

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An electron-ion scattering amplitude that takes into account the effects due to the *d* excited bands in heavy alkali metals is proposed. The *d* bands are treated as resonant levels, and the scattering amplitude is constructed via an effective-range approximation. The cross section is given in terms of two resonance parameters and of the Born approximation for the pseudopotential. We use a modified form of the nonlocal and energy-dependent Heine-Abarenkov model potential, where the high-angular-momentum components of the potential are properly treated. We test our model by calculating the resistivity and thermoelectric power for the solid phase of K, Rb, Cs. The results give satisfactory agreement with experiment. In particular, for *K* we find that the strong *d* nonlocality obtained by Lee and Falicov is equivalent to a *d* resonance built into the electron-ion scattering amplitude.

I. INTRODUCTION

THE aim of this work is to investigate the effects of the *d* bands on the electron-ion cross section in the heavy alkali metals.

Until now, all the "first-principles" calculations of the macroscopic properties of alkali metals give the least satisfactory agreement with experiment for the heavy alkali metals.[1-3] In a previous paper,[4] we pointed out that for Rb and Cs the excited *d* bands are important in calculating transport properties, so that, in some sense, these elements look like transition metals. Further evidence of this resemblance is given by the energy-band structure. The calculations performed by Ham[5] and Kenney[6] show that, through the sequence K, Rb, Cs, the mixing between the *s* and *d* bands increases, and the *d* bands approach the Fermi surface and their width decreases. Through the sequence, the energy difference between the position of the H_{15}, N_1', T_{25}' levels, with respect to H_{25}', N_2, T_{12}', becomes smaller and smaller: For instance, in the case of K we have[5] $H_{25}'-H_{15}=0.232$ Ry, in the case of Rb[5] $H_{25}'-H_{15}=0.181$ Ry, and for Cs[5] $H_{25}'-H_{15}=0.080$ Ry. Even if these levels do not have the reverse order due to the hybridization, as in bcc iron,[7] the resemblance to transition metals is clear in passing from K to Cs.

In view of these facts, we postulate that the excited *d* bands can be described by resonant states, as various authors have already suggested for the noble and transition metals.[8-10]

In the model we propose, we describe the total scattering amplitude as the sum of a resonant term, which accounts for the *d* state ($l=2$), and of the partial scattering amplitude, calculated in Born approximation, for all the other angular momenta. The resonant term is obtained by using an effective-range approximation, as described in Sec. II. The Born approximation of the partial scattering amplitudes for $l\neq 2$ is calculated by using the model potential of Heine and Abarenkov[11] (HA) for $l=0$, 1. For the higher angular momentum components of the form factor, in Sec. III we show how, by virtue of the centrifugal term, the potential can be approximated, inside the model radius R_M, by Z/R_M, when Z is the ionic valence. In this way, we are able to improve on the approximation introduced by HA in their model potential for $l\geqslant 2$. To test our model, we calculate the transport properties of K, Rb, and Cs. The formulas for the resistivity and thermoelectric power, for the case of a nonlocal and energy-dependent form factor, such as the one we use, are given in Sec. IV. Since for solid alkali metals it is possible to obtain with accuracy the structure factor from elastic constants or neutron data,[3,4] we performed the calculations for the solid phase.

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In Sec. V our results for the resistivity and thermopower are displayed. The results were obtained by taking the position and the width of the resonance in the range of values suggested by the energy-band calculations.

The introduction of the resonant d level gives a substantial improvement, with respect to previous calculations, for the transport coefficients of Rb and Cs, while for K the resonance contribution is less remarkable. This is in agreement with the band structure information, i.e., with the influence of the d states on the sequence K, Rb, Cs.

II. TOTAL SCATTERING AMPLITUDE

The total scattering amplitude can be written in the form

$$f(k,\theta)=\sum_{l}(2l+1)f_l(k)P_l(\cos\theta)\,, \tag{2.1}$$

where k is the incident momentum, θ is the scattering angle, and $f_l(k)$ is the partial wave amplitude of angular momentum l, given by

$$f_l(k)=1/[k\cot\delta_l(k)-ik]; \tag{2.2}$$

here δ_l is the scattering phase shift.

We assume that for $l\neq 2$, $f_l(k)$ can be approximated by the corresponding Born term:

$$f_l(k)=\delta_l{}^B(k)/k\,,\quad \text{for } l\neq 2 \tag{2.3}$$

where $\delta_l{}^B$ is the lth phase shift in Born approximation. To introduce the $l=2$ resonant term, we rewrite (2.2) as

$$f_2(k)=\Gamma(E)/[k\Gamma(E)\cot\delta_2(k)-ik\Gamma(E)]\,, \tag{2.4}$$

where the function $\Gamma(E)$ is chosen to satisfy the relation

$$\Gamma(E)k\cot\delta_2(k)=E_d-E\,, \tag{2.5}$$

with E_d equal to the energy of the resonance and $E=k^2$. We shall assume that, as k goes to zero, the real part of (2.4) goes to the Born approximation given by (2.3). This approximation is reasonable, because we are far away from the resonance. We than have

$$\lim_{E\to 0}\Gamma(E)=(E_d/k)\delta_l{}^B(k)\,. \tag{2.6}$$

Since $\delta_2{}^B(k)$ behaves as k^5 for small k, the function $\Gamma(E)$ goes to zero like E^2. Then, for small k, (2.5) becomes

$$(R^5/45)E_dk^5\cot\delta_2(k)=E_d-E\,, \tag{2.7}$$

where R is the range of the potential. This shows that our approximation for $l=2$ is the usual effective-range approximation.

In order to extend (2.6) to the range of k of interest, we shall in the rest of the paper assume $\Gamma(E)$ to be of the form

$$\Gamma(E)=(E_d/k)\delta_2{}^B(k)(1+\beta E)\,. \tag{2.8}$$

The parameter β is fixed by the condition that $k_D\Gamma(E_D)$ is equal to the width of the d band.[5,6]

In this way, the limit (2.6) is preserved, and we can introduce in (2.8) the position and the width of the resonant d level from band-structure calculations. The total scattering amplitude becomes

$$\begin{aligned}f(k,\theta)=\sum_{l\neq 2}(2l+1)f_2{}^B(k)P_l(\cos\theta)+5P_2(\cos\theta)&\\ \times(1/k)E_d\delta_2{}^B(k)(1+\beta E)/&\\ [(E_d-E)-iE_d\delta_2{}^B(k)(1+\beta E)]&\,. \end{aligned}\tag{2.9}$$

This expression can be written as

$$\begin{aligned}f(k,\theta)=f^B(k,\theta)+5P_2(\cos\theta)&\\ \times\left[\frac{1}{k}\,\frac{E_d\delta_2{}^B(1+\beta E)}{(E_d-E)-iE_d\delta_2{}^B(k)(1+\beta E)}\right.&\\ \left.-f_2{}^B(k)\right]&\,. \end{aligned}\tag{2.10}$$

This formula gives the total scattering amplitude from the knowledge of the two resonant parameters E_d, $k_d\Gamma(E_d)$ and of the scattering amplitude in Born approximation.

III. BORN APPROXIMATION OF SCATTERING AMPLITUDE

The term $f^B(k,\theta)$, which we need in order to calculate (2.9), is the Fourier transform of the screened electron-ion pseudopotential. We will consider the model potential proposed by Heine and Abarenkov[11]

$$v(r)=-(Z/r)\theta(r-R_M)-\sum_{0}^{\infty}{}_l\,\theta(R_M-r)A_l(E)P_l\,. \tag{3.1}$$

The function $\theta(r)$ is the usual step function, P_l is an operator that picks out the lth component of the wave function, and the depths of the wells $A_l(E)$ are chosen to reproduce the correct eigenvalues of the free ion. In the original version of the HA model potential, the $A_l(E)$ parameters were taken to be $A_l(E)=A_2(E)$ for $l\geqslant 2$. Since previous calculations[12] show that this choice is not accurate, we shall investigate this point in detail.

As is well known, for large values of l the centrifugal potential prevents the electron from approaching the nucleus, so that, for these l components of the potential, one can replace the true potential with a Coulombic one. To see quantitatively the value of l_0 beyond which this replacement is valid, we rewrite (3.1) as

$$\begin{aligned}v(r)=-\frac{Z}{r}-\sum_{0}^{l_0}\left(A_l(E)-\frac{Z}{r}\right)\theta(R_M-r)P_l&\\ +\sum_{l_0+1}^{\infty}\left(v_a+\frac{Z}{r}\right)\theta(R_M-r)P_l&\,, \end{aligned}\tag{3.2}$$

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TABLE I. Screened form factors and depletion holes of the model potential for K, Rb, Cs at the Fermi surface. The values are in rydbergs.

$q/2k_F$	K	Rb	Cs
0	−0.10386	−0.09090	−0.07761
0.05	−0.10234	−0.08801	−0.07541
0.1	−0.09845	−0.08659	−0.07352
0.15	−0.09549	−0.08400	−0.07135
0.2	−0.09142	−0.08041	−0.06834
0.25	−0.08635	−0.07595	−0.06458
0.3	−0.08043	−0.07072	−0.06016
0.35	−0.07381	−0.06490	−0.05522
0.4	−0.06669	−0.05863	−0.04990
0.45	−0.05924	−0.05209	−0.04431
0.5	−0.05164	−0.04546	−0.03863
0.55	−0.04409	−0.03890	−0.03301
0.6	−0.03675	−0.03260	−0.02762
0.65	−0.02979	−0.02671	−0.02259
0.7	−0.02335	−0.02141	−0.01810
0.75	−0.01758	−0.01684	−0.01429
0.8	−0.01263	−0.01317	−0.01132
0.85	−0.00861	−0.01055	−0.00934
0.9	−0.00568	−0.00915	−0.00855
0.95	−0.00397	−0.00916	−0.00913
0.1	−0.00473	−0.01199	−0.01257
α	0.28111	0.33319	0.38090

where v_a is the atomic potential calculated self-consistently.[13] Formula (3.2) is obtained by replacing in (3.1) $A_l(E)$ for $l>l_0$ by the true potential v_a and assuming that for $r>R_M$, $v_a=-Z/r$.

Equation (3.2) gives us a criterion to fix l_0.

The order of magnitude of the form factor is typically 10^{-3} Ry, around the first reciprocal-lattice vectors, so that we fix l_0 by requiring that the last term of (3.2) is at least one order of magnitude less than 10^{-3} Ry. We calculated the matrix element of (3.2) with the initial momentum k_F on the Fermi surface and for various values of the momentum transfer q. The values of l_0, for which the last term gives a contribution $<10^{-3}$ Ry, are given below the alkali metals:

	Li	Na	K	Rb	Cs
l_0	1	1	1	2	2

For $l>l_0$, the true potential can be replaced by a Coulombic one. We also found that for $l>l_0$, the matrix elements

$$(k_F|(Z/r-Z/R_M)P_l|k_F+q)\equiv v_l(q)$$

are smaller than 10^{-3} Ry and that the series $\sum_{l_0+1}^{\infty} v_l(q)$ is rapidly convergent.

This shows that, for high l, the Coulombic potential acts as a weak potential and can be substituted by Z/R_M. In this way it is possible to eliminate the unjustified approximation of the HA model potential, i.e., the assumption $A_l(E)=A_2(E)$ for $l>2$.

TABLE II. Values of the *d* scattering amplitudes in Born approximation at the Fermi energy.

K	Rb	Cs
0.14549	0.17984	0.21439

TABLE III. Calculated resistivities and thermopowers of Cs at 273°K (in units of μΩ cm) for different values of E_d.

E_d	ρ	ξ
0.23642	11.05	3.6
0.21642	13.43	2.2
0.200	17.81	0.4
⋯	19.0[a]	0.2[a]
⋯	7.5[b]	6.4[b]

[a] Experimental values.
[b] Results in Born approximation.

Our formulation of the nonlocal and energy-dependent HA potential becomes

$$v(r)=-\sum_{0}^{l_o}\theta(R_M-r)(A_l(E)-Z/R_M)P_l$$
$$-(Z/R_M)\theta(R_M-r)-Z/r\theta(r-R_M). \quad (3.3)$$

The screened form factor $f(k,\theta)$ is obtainable by a linear self-consistent screening of (3.3). We follow exactly the procedure of Shaw and Harrison,[14] which takes into account both the nonlocality and energy dependence of the model potential and treats correctly the depletion hole α.

The screened form factor in units of $q/2k_F$ and the depletion hole[14] α are given in Table I. The parameters that enter the calculation are taken from Animalu.[15]

IV. RESISTIVITY AND THERMOELECTRIC POWER

It is well known that the resistivity and thermoelectric power depend sensitively on the scattering amplitude. We have therefore calculated these quantities, in order to test the correctness of our model scattering amplitude of Eq. (2.10).

This test is possible for the solid phase, because the structure factor $S(q)$ can be constructed very accurately from experimental phonon frequencies or from elastic constants data,[3] so that any error is due almost exclusively to the computed cross section.

TABLE IV. Calculated resistivities and thermopowers of Rb at 273°K (in units of μΩ cm) for different values of E_d.

E_d	ρ	ξ
0.270	9.59	3.8
0.260	10.33	3.3
0.250	11.38	2.6
⋯	11.6[a]	2.3[a]
⋯	6.6[b]	6.3[b]

[a] Experimental values.
[b] Results in Born approximation.

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TABLE V. Calculated resistivities and thermopowers of K at 273°K (in units of $\mu\Omega$ cm) for different values of E_d.

E_d	ρ	ξ
0.315	3.96	5.3
0.300	4.33	4.5
0.290	4.72	3.7
···	6.1[a]	3.8[a]
···	3.15[b]	7.3[b]

[a] Experimental values.

[b] Results in Born approximation.

In the relaxation time approximation of the Boltzmann equation, the resistivity of the metal in the solid phase can be written as

$$\rho=\sum_{\hat{k}} l(\hat{k})\rho(\hat{k})/\sum_{\hat{k}} l(\hat{k}). \tag{4.1}$$

Here the average is performed as in Ref. (3), and the symbols have the following meaning: $\hat{k}$ is the unit vector in the direction of the incident momentum; $l(\hat{k})$ is the electron mean free path in the direction $\hat{k}$ and is given by

$$1/l(\hat{k})=\frac{4\Omega_0 m^2}{9\pi^3 h^4 k_F{}^2}\int_0^{2k_F} q^3|f(k,q)|^2 S(\hat{k},q)dq. \tag{4.2}$$

$\rho(\hat{k})$ is the partial resistivity coefficient:

$$\rho(\hat{k})=(hk_F/ne^2)(1/l(\hat{k})). \tag{4.3}$$

Similarly, the thermoelectric power coefficient ξ is given by

$$\xi=\sum_{k} l(\hat{k})\xi(\hat{k})/\sum_{\hat{k}} l(\hat{k}), \tag{4.4}$$

with the partial thermopower coefficients given by

$$\xi(\hat{k})=1+[d\ \ln l(\hat{k})\,|\,d\ \ln E(\hat{k})]_{k=k_F}. \tag{4.5}$$

$S(\hat{k},q)$ is the structure factor with the initial momentum in the $\hat{k}$ direction.

V. RESULTS AND DISCUSSION

To evaluate the transport coefficients of the solid phase, we use the structure factor $S_k(q)$, obtained from elastic constant data,[3] with **k** along the principal symmetry directions $\langle 100\rangle$, $\langle 110\rangle$, $\langle 111\rangle$.

The partial scattering amplitude $f_2{}^B(k,\theta)$ is calculated by projecting the screened form factor on the $l=2$ subspace of the angular momenta. The results are given in Table II.

We found that the calculated transport coefficients are more critically dependent on the position of the resonance than on its width. We have therefore taken the width of the resonance to be equal to 0.1 rydbergs, for all the elements, in agreement with band calculations,[4,5] and we have evaluated the transport properties for various values of E_d, in the range suggested by the band structures.

In Tables III–V are collected our calculated values for resistivity and thermopower, together with experimental data[16,17] and the values calculated in Born approximation. On the whole, the results indicate the importance of the resonant d levels. From Tables III–V, it is evident that the resonant contribution gives a considerable improvement with respect to the results of the Born approximation for Rb and Cs. For k, even if the d bands are more distant from the Fermi surface than for Rb and Cs, the resonance contribution is still noticeable. This is in agreement with the strong d nonlocality of the potential found by Lee and Falicov[18] from Fermi-surface analysis. These authors introduce a deep square well for the d component of the potential, to account for this strong nonlocality. Using their parameters, we find that the condition that gives a resonance[11] for a square-well potential of a range R and depth V_0, i.e., $J_{l-1}((k^2+V_0)^{1/2}R)\simeq 0$ is satisfied in the range of energy suggested by the band structure calculations. Hence a strong d nonlocality seems equivalent to a d resonance in the electron-ion scattering.

From Tables III–V it appears that in the Born approximation the computed resistivity is lower than the experimental value, while the computed thermoelectric power is higher than the experimental one. The introduction of the d resonance in the theory enhances the resistivity and lowers the thermopower, giving a reasonable agreement with experiments for both quantities. This fact strongly supports our hypothesis that the d levels of heavy alkali metals can be treated as resonant levels in the electron-ion scattering.

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