PHYSICAL REVIEW VOLUME 111, NUMBER 2 JULY 15, 1958

Influence of Electron Interactions on Metallic Properties

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(Received February 27, 1958)

The influence of electron interactions on the one-electron energy in metals is calculated. The calculation is based on the Bohm-Pines collective description of electron interactions and has for its principal approximation the treatment of the screened interaction H_{sr} by perturbation theory. Results are given for the band width, specific heat, relaxation time, conductivity, thermoelectric power, and diamagnetic susceptibility. Comparison with experimental values of band width and specific heat for the alkali metals shows satisfactory agreement. Density-of-states plots for the alkalis are given.

1. INTRODUCTION

THE independent-particle model of solids has always been regarded as invaluable for interpretation of experimental results. Recent theoretical developments[1-5] have shown how this model can be understood in terms of particle-like elementary excitations when the long-range Coulomb force is properly treated. In particular, a recent detailed investigation[2] has shown that it is now sensible to attempt a numerical calculation of the influence of the effective electron interaction on several properties of experimental interest.

Basing our work on the collective description of Bohm and Pines,[1] we have carried through such a program for some of the best-understood metals—the alkalis, Be, Mg, and Al—and have found in general that the over-all corrections to the free-electron values are frequently not inappreciable. When electron interactions are taken into account, it is found that the agreement between theory and experiment for the band width and specific heat is markedly improved over that obtained on the basis of the free-electron theory.

2. DERIVATION OF THE ONE-ELECTRON ENERGY

Bohm and Pines[1] have shown that, by introducing extra variables to describe the collective oscillations, one can bring the Hamiltonian for the valence electrons in a metal into the form

$$H=\sum_i\left(\frac{p_i^2}{2m}+V(\mathbf{r}_i)\right)+\tfrac{1}{2}\sum_{k<k_c}(P_k{}^*P_k+\omega_p{}^2Q_k{}^*Q_k)-\sum_{k<k_c}\frac{2\pi ne^2}{k^2}+H_{\mathrm{int}}+H_{\mathrm{sr}}+U. \quad (1)$$

The first term describes a set of independent electrons moving in the periodic field of the ion cores; the second, a set of field oscillators whose quanta are the plasmons; the third is the self-energy term. H_{int} is the electron-plasmon coupling:

$$H_{\mathrm{int}}=i\sum_{ik<k_c}\left(\frac{4\pi e^2}{m^2}\right)^{\frac{1}{2}}e^{-i\mathbf{k}\cdot\mathbf{r}_i}\mathbf{k}\cdot\left(\mathbf{p}_i-\frac{\hbar}{2}\mathbf{k}\right)Q_k; \quad (2)$$

H_{sr} is a screened electron-electron interaction of range $k_c{}^{-1}$:

$$H_{\mathrm{sr}}=\sum_{i\neq j}\sum_{k>k_c}\frac{2\pi e^2}{k^2}e^{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)}. \quad (3)$$

U is a coupling the terms of which involve an electron and two different field oscillators:

$$U=-\frac{2\pi e^2}{m}\sum_{k,l<k_c;\ k\neq -l}(\boldsymbol{\varepsilon}_k\cdot\boldsymbol{\varepsilon}_l)Q_kQ_l\sum_i e^{-i(\mathbf{k}+\mathbf{l})\cdot\mathbf{r}_i}. \quad (4)$$

Finally the admissible solutions must satisfy the subsidiary conditions

$$\left[P_k-\left(\frac{4\pi e^2}{k^2}\right)^{\frac{1}{2}}\sum_i e^{-i\mathbf{k}\cdot\mathbf{r}_i}\right]\psi=0. \quad (5)$$

In accordance with the usual terminology, we have taken n for the electron density and $\omega_p=(4\pi ne^2/m)^{\frac{1}{2}}$ for the plasma frequency.

The coupling H_{int} can be treated by a suitable canonical transformation[1,2]; it gives rise to a shift in the plasmon frequency and a weak long-range electron-electron interaction H_{rp}. Since the total contribution to the system energy from these two sources is at most 0.019 ry per electron,[6] we shall neglect H_{int}.

The "random phase approximation" in which U is considered to be negligible has been justified in detail.[1] A similar remark can be made regarding the subsidiary conditions; they have no importance for the low-lying elementary excitations, as has been thoroughly discussed.[7]

Strictly speaking, we should now go on to a perturbation treatment of H_{sr} using Slater determinants of Bloch functions ψ_{kn} for our basis set. However, *for the*

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* National Science Foundation Predoctoral Fellows, 1955–1958.

† Mr. Larson died in a traffic accident on June 21, 1958.

[1] D. Pines, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 367.

[2] P. Nozières and D. Pines, Phys. Rev. **109**, 741 (1958).

[3] P. Nozières and D. Pines, Phys. Rev. **109**, 1062 (1958).

[4] M. Gell-Mann and K. Brueckner, Phys. Rev. **106**, 364 (1957).

[5] M. Gell-Mann, Phys. Rev. **106**, 369 (1957).

[6] P. Nozières and D. Pines, Phys. Rev. **110**, 442 (1958), preceding paper.

[7] Bohm, Huang, and Pines, Phys. Rev. **107**, 71 (1957).

purposes of obtaining exchange and correlation corrections, especially for the alkali metals where the wave functions have a plane-wave character over a great majority of the crystal volume, we may be justified in a plane-wave calculation of H_{sr}. The limitations of this procedure are essentially measured by the strength of the interband transitions

There remains to be discussed the cutoff momentum k_c. Pines has calculated the ratio $\beta = k_c/k_0$ (k_0 is the Fermi wave number) by a variational argument and obtained $\beta = \gamma r_s^{\frac{1}{2}}$ with $\gamma = 0.353$. The usual dimensionless parameter r_s gives the electron density through $n = (\frac{4}{3}\pi r_s^3 a_0^3)^{-1}$, where a_0 is the Bohr radius. A recalculation by Nozières and Pines which included the effect of H_{int} gave the value $\gamma = 0.4$. We shall also consider $\gamma = 0.471$ in the following, this value corresponding physically to the maximum momentum at which a plasmon can be considered a well-defined elementary excitation.[6–8] Another possible approach to the cutoff k_c is to regard it as a parameter which is to be fixed by experimental observations; we shall discuss the consequences of this approach later.

With the above approximations our Hamiltonian reduces to the following:

$$H = \sum_i \frac{p_i^2}{2m^*} + \sum_{i\neq j} \sum_{k>k_c} \frac{2\pi e^2}{k^2} e^{i\mathbf{k}\cdot(\mathbf{r}_i - \mathbf{r}_j)} + \tfrac{1}{2} \sum_{k<k_c} (P_k^* P_k + \omega_p^2 Q_k^* Q_k) - \sum_{k<k_c} \frac{2\pi n e^2}{k^2}. \tag{6}$$

Calculation of the system energy to second order in H_{sr} now yields, per electron (leaving aside the plasmon and self-energy contribution),

$$E = E^{(0)} + E^{(1)} + E_a^{(2)} + E_p^{(2)}. \tag{7a}$$

The zero-order part is

$$E^{(0)} = \frac{3}{4\pi} \frac{m}{m^*} (\alpha r_s)^{-2} \int d^3k\, f_{\mathbf{k}} k^2 = \frac{3}{5} \frac{m}{m^*} (\alpha r_s)^{-2}. \tag{7b}$$

We measure energies in units of the Rydberg and wave numbers in units of the Fermi wave number k_0; m^* is the effective mass; α is a constant given by

$$\alpha = (4/9\pi)^{\frac{1}{3}} = 0.521,$$

and $f_{\mathbf{k}} = 1$, $k \leq 1$; $f_{\mathbf{k}} = 0$, $k > 1$. In first order we have the screened exchange energy:

$$E^{(1)} = -\frac{3}{8\pi^3} \frac{1}{\alpha r_s} \int d^3k \int_{p>\beta} d^3p\, f_{\mathbf{k}} f_{\mathbf{k}+\mathbf{p}} p^{-2} = -\frac{3}{2\pi \alpha r_s} \left(1 - \frac{4}{3}\beta + \frac{1}{2}\beta^2 - \frac{1}{48}\beta^4\right). \tag{7c}$$

In second order we get a part which comes from the excitation of electrons with antiparallel spins:

$$E_a^{(2)} = -\frac{3}{16\pi^5} \int_{p>\beta} \frac{d^3p}{p^4} \int d^3k \int d^3k' \frac{f_{\mathbf{k}} f_{\mathbf{k}'} (1 - f_{\mathbf{k}+\mathbf{p}})(1 - f_{\mathbf{k}'-\mathbf{p}})}{\mathbf{p}\cdot(\mathbf{p}+\mathbf{k}-\mathbf{k}')}, \tag{7d}$$

and a part coming from parallel spins:

$$E_p^{(2)} = E_a^{(2)} + \frac{3}{16\pi^5} \int_{p>\beta} \frac{d^3p}{p^2} \int d^3k \int_{|\mathbf{k}-\mathbf{k}'+\mathbf{p}|>\beta} d^3k' \frac{f_{\mathbf{k}} f_{\mathbf{k}'} (1 - f_{\mathbf{k}+\mathbf{p}})(1 - f_{\mathbf{k}'-\mathbf{p}})}{(\mathbf{k}-\mathbf{k}'+\mathbf{p})^2 \mathbf{p}\cdot(\mathbf{p}+\mathbf{k}-\mathbf{k}')}. \tag{7e}$$

To obtain the energy of an "effective electron" of wave number k, we now calculate the change in the system when an electron is annihilated at k in the ground state. This we obtain most simply by taking the functional derivative:

$$E(k) = \frac{\delta E}{\delta f_k} = E^{(0)}(k) + E^{(1)}(k) + E_a^{(2)}(k) + E_p^{(2)}(k); \tag{8a}$$

$$E^{(0)}(k) = \left(\frac{k}{\alpha r_s}\right)^2 \frac{m}{m^*}; \tag{8b}$$

$$E^{(1)}(k) = -\frac{1}{\pi^2 \alpha r_s} \int_{p>\beta} d^3p\, f_{\mathbf{k}+\mathbf{p}} p^{-2}; \tag{8c}$$

$$E_a^{(2)}(k) = -\frac{1}{2\pi^4} \int_{p>\beta} \frac{d^3p}{p^4} \int d^3q \frac{f_{\mathbf{q}} (1 - f_{\mathbf{q}-\mathbf{p}})(1 - f_{\mathbf{k}+\mathbf{p}})}{\mathbf{p}\cdot(\mathbf{k}-\mathbf{q}+\mathbf{p})} + \frac{1}{2\pi^4} \int_{p>\beta} \frac{d^3p}{p^4} \int d^3q \frac{f_{\mathbf{q}} f_{\mathbf{k}-\mathbf{p}} (1 - f_{\mathbf{q}-\mathbf{p}})}{\mathbf{p}\cdot(\mathbf{k}-\mathbf{q})}; \tag{8d}$$

$$E_p^{(2)}(k) = E_a^{(2)}(k) + \frac{1}{2\pi^4} \int_{p>\beta} \frac{d^3p}{p^2} \int_{|\mathbf{k}-\mathbf{q}+\mathbf{p}|>\beta} d^3q \frac{f_{\mathbf{q}} (1 - f_{\mathbf{k}+\mathbf{p}})(1 - f_{\mathbf{q}-\mathbf{p}})}{(\mathbf{k}-\mathbf{q}+\mathbf{p})^2 \mathbf{p}\cdot(\mathbf{k}-\mathbf{q}+\mathbf{p})} - \frac{1}{2\pi^4} \int_{p>\beta} \frac{d^3p}{p^2} \int_{|\mathbf{k}-\mathbf{q}|>\beta} d^3q \frac{f_{\mathbf{q}} f_{\mathbf{k}-\mathbf{p}} (1 - f_{\mathbf{q}-\mathbf{p}})}{(\mathbf{k}-\mathbf{q})^2 \mathbf{p}\cdot(\mathbf{k}-\mathbf{q})}. \tag{8e}$$

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[8] R. Ferrell, Phys. Rev. **107**, 450 (1957).

The energy in first order, $E^{(0)}(k)+E^{(1)}(k)$, has been evaluated and discussed by Pines.[1] We give the second-order expression for antiparallel spins $E_a^{(2)}(k)$, together with the first-order result, in the appendix. We neglect the parallel-spin contribution $E_p^{(2)}(k)$ since $E_p^{(2)}$ is small compared to $E_a^{(2)}$ for actual densities. It should be stressed that this approximation is *well justified* for actual metallic densities ($2<r_s<5$), but is invalid for the high-density limit ($r_s\rightarrow 0$); in fact, for $r_s\rightarrow 0$, we have

$$E_p^{(2)}=E_a^{(2)}+\text{const}+(\text{terms that vanish as } r_s\rightarrow 0).$$

In Sec. 3A we consequently take $E_p^{(2)}(k)=E_a^{(2)}(k)$ for our examination of the high-density limit of the specific heat. Similarly, the higher order terms in the H_{sr} perturbation series are negligible for $2<r_s<5.5$, but become important for $r_s\rightarrow 0$. For a justification of this procedure we follow in the regime of actual metallic densities, we refer the interested reader to a forthcoming paper on the correlation energy by Nozières and Pines.[6]

We will be interested in the first and second energy derivatives at the Fermi surface as well as the total band width, $E(1)-E(0)$. The contribution to the band width from $E_a^{(2)}$ is[9]

$$\Delta^{(2)}\equiv E_a^{(2)}(1)-E_a^{(2)}(0)=\frac{1}{\pi^2}\biggl[\frac{\pi^2}{4}+\frac{35}{6}+(\ln 2)^2-\ln 2-(\ln\beta)^2+2\ln\beta-\frac{3}{\beta}-2f(\beta)$$
$$+\frac{4}{3}\frac{\ln 2}{\beta^2}+\frac{1-\beta^2}{\beta^2}\ln(1-\beta)+\left(\frac{\beta}{12}-\frac{1}{2}+\frac{1}{\beta}-\frac{2}{3\beta^2}\right)\ln(2-\beta)-\left(\frac{\beta}{12}+\frac{1}{2}+\frac{1}{\beta}+\frac{2}{3\beta^2}\right)\ln(2+\beta)\biggr],\quad (0\leq\beta\leq 1);\qquad\text{(9a)}$$

$$\Delta^{(2)}=\frac{1}{\pi^2}\biggl[\frac{\pi^2}{12}+(\ln 2)^2-\ln 2-\frac{1}{6}+\frac{4}{3}\frac{\ln 2}{\beta^2}+\frac{3}{\beta}+2f\left(-\frac{1}{\beta}\right)+2\ln\beta+\frac{1-\beta^2}{\beta^2}\ln(1+\beta)$$
$$+\left(\frac{\beta}{12}-\frac{1}{2}+\frac{1}{\beta}-\frac{2}{3\beta^2}\right)\ln(2-\beta)-\left(\frac{\beta}{12}+\frac{1}{2}+\frac{1}{\beta}+\frac{2}{3\beta^2}\right)\ln(2+\beta)\biggr],\quad (1\leq\beta\leq 2).\qquad\text{(9b)}$$

For reference we repeat the first-order result calculated by Pines[1]:

$$\Delta^{(1)}\equiv E^{(0)}(1)+E^{(1)}(1)-E^{(1)}(0)=\frac{1}{(\alpha r_s)^2}\frac{m}{m^*}+\frac{1}{\pi\alpha r_s}(2-2\beta-\tfrac{1}{2}\beta^2).\qquad\text{(9c)}$$

The energy derivatives are conveniently expressed in terms of ratios to the corresponding expressions in the free-electron theory with an effective mass. For $0\leq\beta\leq 2$ we have

$$\lambda\equiv\frac{E'(1)}{E_{\text{free}}'(1)}=1+\tfrac{1}{2}(\alpha r_s)^2\frac{m^*}{m}\biggl\{\frac{1}{\pi\alpha r_s}\left(\frac{\beta^2}{2}-2+2\ln\frac{2}{\beta}\right)+\frac{1}{\pi^2}\biggl[\frac{5}{3}\ln 2-\frac{4}{3}\ln\beta-2$$
$$-\frac{4}{3\beta^2}-\frac{4}{3}\frac{\ln 2}{\beta^2}+\left(\frac{\beta}{12}+\frac{2}{3}+\frac{3}{2\beta}+\frac{2}{3\beta^2}-\frac{2}{3\beta^3}\right)\ln(2+\beta)+\left(-\frac{\beta}{12}+\frac{2}{3}-\frac{3}{2\beta}+\frac{2}{3\beta^2}+\frac{2}{3\beta^3}\right)\ln(2-\beta)\biggr]\biggr\}.\qquad\text{(10a)}$$

$$\mu\equiv\frac{E''(1)}{E_{\text{free}}''(1)}=1+\tfrac{1}{2}(\alpha r_s)^2\frac{m^*}{m}\biggl\{\frac{1}{\pi\alpha r_s}\left(3-\beta^2+2\ln\frac{\beta}{2}\right)+\frac{1}{\pi^2}\biggl[\frac{37}{12}-\frac{5}{3}\ln 2+\frac{17}{6}\ln\beta$$
$$+\frac{2}{3}\frac{\ln 2}{\beta^2}+\frac{4}{3\beta^2}-\frac{1}{30\beta^4}+\left(\frac{\beta}{6}-\frac{17}{12}+\frac{5}{2\beta}-\frac{1}{3\beta^2}-\frac{2}{3\beta^3}\right)\ln(2-\beta)-\left(\frac{\beta}{6}+\frac{17}{12}+\frac{5}{2\beta}+\frac{1}{3\beta^2}-\frac{2}{3\beta^3}\right)\ln(2+\beta)\biggr]\biggr\}.\qquad\text{(10b)}$$

Evaluation of the integral (7d) for the contribution of $E_a^{(2)}$ to the correlation energy gives the following expression ($0\leq\beta\leq 2$):

$$E_a^{(2)}=\frac{1}{\pi^2}\biggl[\frac{\pi^2}{4}-\frac{71}{60}-\frac{5}{3}\ln 2+2(\ln 2)^2+2(1-\ln 2)\ln\beta+\frac{4}{5}\frac{\ln 2}{\beta^2}-\frac{\beta^2}{80}$$
$$+\left(\frac{\beta^3}{320}-\frac{\beta}{8}-\frac{1}{2}-\frac{3}{4\beta}-\frac{2}{5\beta^2}\right)\ln(2+\beta)-\left(\frac{\beta^3}{320}-\frac{\beta}{8}+\frac{1}{2}-\frac{3}{4\beta}+\frac{2}{5\beta^2}\right)\ln(2-\beta)\biggr].\qquad\text{(11)}$$

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[9] The function $f(z)\equiv-\int_0^z[(\ln|1-x|)/x]dx$ has been tabulated and discussed extensively by K. Mitchell, Phil. Mag. **40**, 351 (1949). See also G. Källén and A. Sabry, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. **29**, 17 (1955).

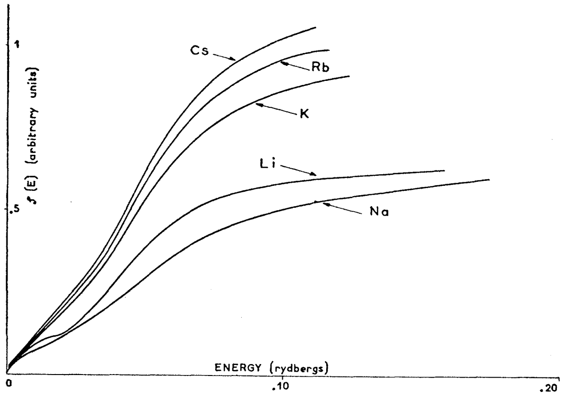

FIG. 1. Density of states for alkali metals with $\gamma=0.400$.

3. APPLICATION TO METALLIC PROPERTIES

A. Specific Heat

We have evaluated the ratio of the specific heat to that in the free-electron model for the three above-mentioned choices of γ and present these values, together with several recent experimental results[10] for comparison, in Table I. The experimental values have been referred to the free-electron model with Brooks' value of the effective mass by division by the effective mass ratio. We see that the situation is satisfactory: the "theoretical" point of view in which we choose $\gamma=0.4$ gives a 10% agreement (which is roughly the accuracy of our calculation); on the other hand, the "experimental" point of view shows that a value of γ close to 0.4 can be chosen to give exact agreement for Li and Na; although this is not so for K, the experimental error was larger there. It is to be noted that the previous calculation of Pines,[1] based on the treatment of H_{sr} in first order, indicated that the exchange and correlation corrections to the specific heat were in the other direction.

TABLE I. Ratio of specific heat to that in the free-electron model, for three choices of γ. The experimental values were taken from reference 10 and corrected for effective mass (see text).

Metal	m^*/m	C/C_0 ($\gamma=0.4$)	C/C_0 ($\gamma=0.353$)	C/C_0 ($\gamma=0.471$)	C/C_0 (expt.)
Li	1.45	1.450	1.756	1.281	1.60
Na	0.98	1.357	1.560	1.232	1.25
K	0.93	1.437	1.706	1.279	1.18
Rb	0.89	1.443	1.718	1.282	
Cs	0.83	1.436	1.704	1.276	
Be	1.0	1.113	1.177	1.069	
Al	1.0	1.133	1.207	1.083	
Mg	1.0	1.200	1.307	1.130	

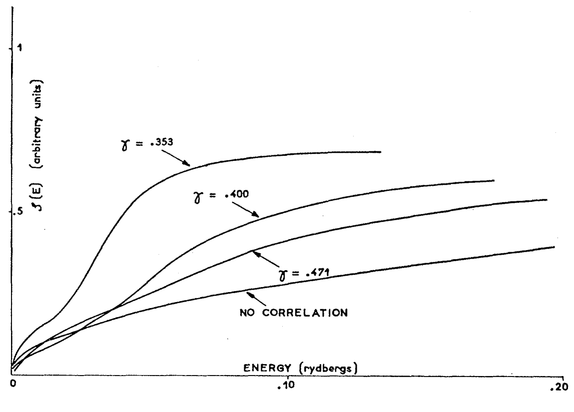

FIG. 2. Density of states for sodium.

Gell-Mann[5] has recently calculated the high-density limit of the specific heat. For comparison, we may evaluate the high-density limit of our result by noting that the exchange contribution does not enter $E_p^{(2)}$ in the first few orders. Hence we take

$$E(k)=E^{(0)}(k)+E^{(1)}(k)+2E_a^{(2)}(k),$$

which gives, for $m^*=m$,

$$\frac{C}{C_0}=\left[1+\frac{\alpha r_s}{2\pi}(-\ln r_s+D_1+D_2 r_s+\cdots)\right]^{-1},$$

where

$$D_1=2\ln\frac{2}{\gamma}-2-\frac{4\alpha}{\pi\gamma^2},$$

$$D_2=\frac{\gamma^2}{2}+\frac{2\alpha}{\pi}\left(3\ln 2-\frac{13}{18}-\frac{4}{3}\ln\gamma\right).$$

Evaluation for the different choices of γ gives the results in Table II. The result of Gell-Mann was $D_1=-0.203$. The disagreement is hardly surprising, for the higher order terms in the perturbation series expansion of H_{sr} all contribute to D_1 and D_2; in fact this comparison gives us a measure of their importance in the high-density region.

B. X-Ray Band Widths

The interpretation of the soft x-ray emission data for various metals has been discussed by Landsberg,[11] Raimes,[12] and Pines.[1] There are two effects of importance in the calculation: the density of states is modified by correlation and exchange, and there is a line broadening due to an Auger effect. Landsberg has discussed the Auger effect and has found that the observed low-energy tail can be reproduced rather well. For a satis-

TABLE II. High-density expansion coefficients.

γ	D_1	D_2
0.353	−3.855	0.976
0.400	−2.928	0.937
0.471	−2.099	0.895

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[10] L. M. Roberts, Proc. Phys. Soc. (London) **B70**, 744 (1957).

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

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

TABLE III. Band widths. All results in Rydbergs; experimental values from Skinner.[a]

Metal	$\Delta^{(1)}$	$\Delta^{(2)}$ ($\gamma=0.400$)	Δ	$\Delta^{(1)}$	$\Delta^{(2)}$ ($\gamma=0.353$)	Δ	$\Delta^{(1)}$	$\Delta^{(2)}$ ($\gamma=0.471$)	Δ	Δ_{free}	Δ_{expt}
Li	0.30	−0.15	0.16	0.35	−0.24	0.11	0.24	−0.05	0.19	0.25	0.27±0.04
Na	0.25	−0.08	0.17	0.29	−0.16	0.13	0.19	0.00	0.19	0.24	0.18±0.02
K	0.15	−0.02	0.12	0.18	−0.09	0.09	0.09	0.02	0.11	0.17	
Rb	0.13	−0.01	0.12	0.16	−0.07	0.09	0.07	0.02	0.09	0.15	
Cs	0.11	+0.01	0.11	0.14	−0.05	0.09	0.05	0.02	0.07	0.14	
Be	1.31	−0.37	0.94	1.37	−0.50	0.87	1.23	−0.23	1.00	1.06	1.02±0.07
Al	1.08	−0.33	0.76	1.13	−0.45	0.68	1.00	−0.19	0.81	0.88	0.87±0.04
Mg	0.65	−0.22	0.43	0.69	−0.33	0.37	0.57	−0.10	0.47	0.53	0.47±0.02

[a] H. B. Skinner, Trans. Roy. Soc. (London) **A239**, 95 (1940).

factory comparison with experiment, the two effects must be combined and the resulting curve matched against the observed data. We discuss here only the exchange and correlation corrections. In Fig. 1 we give the density of states, $\rho(E)=k^2/[\pi^2(dE/dk)]$, *versus* energy for the alkalis with $\gamma=0.4$; in Fig. 2 we give the corresponding curves for Na for the three choices of γ as an indication of the γ dependence of the results. For comparison the curve without exchange and correlation corrections is also given. For reference we have calculated $E(1)-E(0)$ and give the results in Table III. Our results here for the modified density of states furnish the groundwork for a final calculation of the Landsberg type. A preliminary comparison with experiment may be made, and again we find encouraging results.

C. Transport Properties

Barrie[13] and Blatt[14] have previously considered the relaxation time, conductivity and thermoelectric power, basing their results on the first-order one-electron energy obtained by Pines.[1] The relevant formulas are as follows:

relaxation time	$\tau/\tau_0=\lambda^2$,
conductivity	$\sigma/\sigma_0=\lambda^3$,
thermoelectric power	$s/s_0=(\lambda+\mu)/2\lambda^2$;

the resulting values are given in Tables IV, V, and VI, respectively. We see that the changes produced by our corrections are rather large and reverse the first-order corrections. We do not attempt a comparison with experimental results here.

TABLE IV. Relaxation time.

Metal	τ/τ_0 ($\gamma=0.400$)	τ/τ_0 ($\gamma=0.353$)	τ/τ_0($\gamma=0.471$)
Li	0.476	0.324	0.610
Na	0.543	0.411	0.659
K	0.485	0.344	0.612
Rb	0.480	0.339	0.609
Cs	0.485	0.344	0.614
Be	0.808	0.722	0.876
Al	0.779	0.687	0.853
Mg	0.695	0.586	0.784

TABLE V. Conductivity.

Metal	σ/σ_0 ($\gamma=0.400$)	σ/σ_0 ($\gamma=0.353$)	σ/σ_0 ($\gamma=0.471$)
Li	0.328	0.185	0.476
Na	0.400	0.263	0.535
K	0.337	0.201	0.478
Rb	0.333	0.197	0.475
Cs	0.338	0.202	0.481
Be	0.726	0.614	0.820
Al	0.687	0.569	0.787
Mg	0.579	0.448	0.694

D. Diamagnetic Susceptibility

The dominant contribution to the diamagnetic susceptibility is

$$\chi_d=-\frac{e^2k_0}{3h^2c^2}\left(\frac{2}{3}\frac{d^2E}{dk^2}+\frac{1}{3k}\frac{dE}{dk}\right)_{k=k_0}. \tag{12}$$

TABLE VI. Thermoelectric power.

Metal	s/s_0 ($\gamma=0.400$)	s/s_0 ($\gamma=0.353$)	s/s_0 ($\gamma=0.471$)
Li	2.044	2.945	1.616
Na	1.760	2.292	1.468
K	1.902	2.630	1.529
Rb	1.899	2.635	1.521
Cs	1.857	2.561	1.493
Be	1.251	1.389	1.160
Al	1.258	1.456	1.189
Mg	1.436	1.687	1.282

TABLE VII. Diamagnetic susceptibility.

Metal	χ/χ_0 ($\gamma=0.400$)	χ/χ_0 ($\gamma=0.353$)	χ/χ_0 ($\gamma=0.471$)
Li	1.067	1.084	1.053
Na	1.029	1.042	1.018
K	0.997	1.009	0.986
Rb	0.985	0.996	0.975
Cs	0.970	0.980	0.961
Be	1.048	1.054	1.043
Al	1.012	1.057	1.044
Mg	1.052	1.063	1.044

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[13] R. Barrie, Phys. Rev. **103**, 1581 (1956).
[14] F. J. Blatt, Phys. Rev. **99**, 1735 (1955).

Thus the ratio to the free-electron value is

$$\chi/\chi_0=(\lambda+2\mu)/3. \tag{13}$$

Pines[1] has previously discussed the diamagnetic susceptibility and found the comparison with experiment unsatisfactory; as can be seen from Table VII, our corrections do not alter this conclusion.

APPENDIX

We give here the one-electron energy for $0\leq\beta\leq 2$ only; larger values will not occur.

A. First-order energy

$$E^{(0)}(k)=\frac{k^2}{\alpha^2 r_s^2}\frac{m}{m^*}; \tag{A1}$$

$$E^{(1)}(k)=-\frac{1}{\pi\alpha r_s}\left[2-4\beta+\frac{1-k^2}{k}\ln\frac{1+k}{1-k}\right], \qquad 0\leq k\leq 1-\beta,\ 0\leq\beta\leq 1; \tag{A2}$$

$$=-\frac{1}{\pi\alpha r_s}\left[1-2\beta+\frac{\beta^2+3k^2-1}{2k}+\frac{1-k^2}{k}\ln\frac{1+k}{\beta}\right], \qquad 1-\beta\leq k\leq 1,\ 0\leq\beta\leq 1; \tag{A3}$$

$$=0, \qquad 0\leq k\leq\beta-1,\ 1\leq\beta\leq 2; \tag{A4}$$

$$=-\frac{1}{\pi\alpha r_s}\left[1-2\beta+\frac{\beta^2+3k^2-1}{2k}+\frac{1-k^2}{k}\ln\frac{1+k}{\beta}\right], \qquad \beta-1\leq k\leq 1,\ 1\leq\beta\leq 2. \tag{A5}$$

B. Second-order result $E_\alpha^{(2)}(k)$ $(0\leq\beta\leq 1)$ $[\zeta\equiv(2-k^2)^{\frac{1}{2}}]$

$$\begin{aligned}
0\leq k\leq 1-\beta:\quad \pi^2E_\alpha^{(2)}(k)=&\left[\frac{\beta}{3k}+\frac{k-2}{2k}+\frac{1-k^2}{k\beta}+\frac{(1+k)^2(k-2)}{6k\beta^2}\right]\ln(1+k-\beta)\\
&+\left[-\frac{\beta}{3k}+\frac{k+2}{2k}+\frac{k^2-1}{k\beta}+\frac{(1-k)^2(2+k)}{6k\beta^2}\right]\ln(1-k-\beta)+\left(\frac{k}{\beta}-\frac{\beta}{4k}\right)\ln\left|\frac{\beta-2k}{\beta+2k}\right|\\
&+\frac{5}{3\beta}-\ln\beta\ln(1-k^2)+\left(\ln\frac{\beta}{2}\right)^2+\frac{1}{6k\beta^2}[(1+k)^2(2-k)\ln(1+k)-(1-k)^2(2+k)\ln(1-k)]\\
&+f\left(\frac{\beta}{1+k}\right)+f\left(\frac{\beta}{1-k}\right)+\tfrac{1}{2}f\left(\frac{4k^2}{\beta^2}\right)+\frac{8k^4\ln k}{15(1-k^2)^2}+\frac{4\zeta^5}{15k(1-k^2)^2}\ln\frac{1-k\zeta}{1+k\zeta}+\frac{25k^2-93}{30(1-k^2)}\\
&+\ln 2\ln(1-k^2)+\left[\ln\frac{1+k}{1-k}\right]^2-\tfrac{1}{2}f(k^2)+\frac{23k^4+98k^3+68k^2-22k-7}{30k(1-k)(1+k)^2}\ln(1+k)\\
&+\frac{7-22k-68k^2+98k^3-23k^4}{30k(1+k)(1-k)^2}\ln(1-k).
\end{aligned} \tag{B1}$$

$$\begin{aligned}
1-\beta\leq k\leq 1:\quad \pi^2E_\alpha^{(2)}(k)=&\frac{\pi^2}{3}-\tfrac{1}{2}f(k^2)+\tfrac{1}{2}f\left(\frac{4k^2}{\beta^2}\right)-\tfrac{1}{2}f\left[\left(\frac{1+k}{\beta}\right)^2\right]-f\left(\frac{k-1}{k+1}\right)\\
&+\ln 2\ln\frac{2(1-k^2)}{\beta^2}-\ln(1+k)\ln(1-k)-\frac{25k^2+67k+8}{30k(1+k)}+\frac{4}{15}\frac{1-k^2}{k\beta^2}-\frac{2}{3}\frac{1+3k^2}{k(1-k^2)}\ln\beta\\
&+\frac{2}{15}\frac{15k^4-15k^2+2}{k(1-k^2)^2}\ln 2+\left[\frac{-16k^5+15k^4+20k^3-10k^2-13}{30k(1-k^2)^2}\right]\ln(1-k)\\
&-\left[\frac{22k^5+75k^4-40k^3-110k^2+30k+35}{30k(1-k^2)^2}\right]\ln(1+k)+\frac{(1+k)^2(2-k)}{3k\beta^2}\ln(1+k)
\end{aligned}$$

$$+\frac{4k^4\ln k}{15(1-k^2)^2}+\left(\frac{k}{\beta}-\frac{\beta}{4k}\right)\ln\left|\frac{\beta-2k}{\beta+2k}\right|+\frac{2\zeta^5}{15k(1-k^2)^2}\ln\left[\frac{\beta^2-(1-\zeta)^2}{(1+\zeta)^2-\beta^2}\right]$$

$$+\frac{2\zeta^5}{15k(1-k^2)^2}\ln\frac{\zeta+1-k-k^2}{\zeta-1+k+k^2}+\left[-\frac{\beta}{24k}+\frac{k^2-5}{8k\beta}+\frac{(1-k^2)(5-k^2)}{24k\beta^3}-\frac{(1-k^2)^3}{120k\beta^5}\right]\ln\frac{\beta^2+2\beta+k^2-1}{1+2\beta-\beta^2-k^2}$$

$$+\left[\frac{7-5k^2}{15k(1-k^2)^2}-\frac{1}{3k\beta^2}\right]\ln[4\beta^2-(\beta^2+k^2-1)^2]+\left[\frac{7\beta}{24k}+\frac{5-9k^2}{8k\beta}-\frac{(1-k^2)(k^2+3)}{24k\beta^3}+\frac{(1-k^2)^3}{120k\beta^5}\right]\ln\frac{1+k-\beta}{1+k+\beta}$$

$$+\left[\frac{19k^3+8k^2-33k-24}{30k(1+k)^2}+\frac{k^2-3}{6\beta^2}\right]\ln[(1+k)^2-\beta^2]+\left[-\frac{\beta}{24k}-\frac{k^2+3}{8k\beta}-\frac{(1-k^2)(k^2+3)}{24k\beta^3}+\frac{(1-k^2)^3}{120k\beta^5}\right]\ln\frac{k-1+\beta}{1+\beta-k}$$

$$+\left[\frac{-2k^3+4k^2-6k+3}{15k(1-k)^2}+\frac{1}{3k\beta^2}\right]\ln[\beta^2-(1-k)^2]. \quad \text{(B2)}$$

C. Second-order energy $(1\leq\beta\leq 2)$

$$0\leq k\leq\beta-1:\quad \pi^2E_a{}^{(2)}(k)=\left[\frac{\beta}{3k}+\frac{2+k}{2k}+\frac{1-k^2}{k\beta}+\frac{(1-k)^2(2+k)}{6k\beta^2}\right]\ln(\beta+1-k)$$

$$+\left[-\frac{\beta}{3k}-\frac{2-k}{2k}-\frac{1-k^2}{k\beta}-\frac{(1+k)^2(2-k)}{6k\beta^2}\right]\ln(\beta+1+k)+\left(\frac{k}{\beta}-\frac{\beta}{4k}\right)\ln\left|\frac{\beta-2k}{\beta+2k}\right|$$

$$-f\left(\frac{k-1}{\beta}\right)-f\left(-\frac{1+k}{\beta}\right)+\tfrac{1}{2}f\left(\frac{4k^2}{\beta^2}\right)+\frac{1}{6k\beta^2}[(1+k)^2(2-k)\ln(1+k)-(1-k)^2(2+k)\ln(1-k)]$$

$$-2\ln 2\ln\beta-\frac{5}{3\beta}-\frac{1+k}{2k}\ln(1+k)+\frac{1-k}{2k}\ln(1-k)-\tfrac{1}{2}f(k^2)+2(\ln 2)^2-\frac{5}{6}+\frac{\pi^2}{6}-\ln\left(\frac{1+k}{2}\right)\ln\left(\frac{1-k}{2}\right). \quad \text{(C1)}$$

$\beta-1\leq k\leq 1$: The same expression as that given in (B2) is obtained for $E_a{}^{(2)}(k)$.

D. Band gap and derivatives at Fermi surface

It is an interesting check on the calculation to see that the second-order energy satisfies the Seitz identity[15]:

$$E_a{}^{(2)}(1)=E_a{}^{(2)}-\frac{1}{3}\beta\frac{d}{d\beta}E_a{}^{(2)}, \quad \text{(D1)}$$

$$\pi^2E_a{}^{(2)}(1)=\frac{\pi^2}{4}+2(\ln 2)^2-\ln 2-\frac{5}{3}+\frac{4}{3}\frac{\ln 2}{\beta^2}+2(1-\ln 2)\ln\beta$$

$$+\left(\frac{\beta}{12}-\frac{1}{2}+\frac{1}{\beta}-\frac{2}{3\beta^2}\right)\ln(2-\beta)-\left(\frac{\beta}{12}+\frac{1}{2}+\frac{1}{\beta}+\frac{2}{3\beta^2}\right)\ln(2+\beta), \quad \text{(D2)}$$

$$\pi^2\frac{dE_a{}^{(2)}}{dk}(1)=\frac{5}{3}\ln 2-2-\frac{4}{3}\ln\beta-\frac{4}{3\beta^2}-\frac{4}{3}\frac{\ln 2}{\beta^2}+\left(\frac{\beta}{12}+\frac{2}{3}+\frac{3}{2\beta}+\frac{2}{3\beta^2}-\frac{2}{3\beta^3}\right)\ln(2+\beta)$$

$$+\left(-\frac{\beta}{12}+\frac{2}{3}-\frac{3}{2\beta}+\frac{2}{3\beta^2}+\frac{2}{3\beta^3}\right)\ln(2-\beta), \quad \text{(D3)}$$

$$\pi^2\frac{d^2E_a{}^{(2)}}{dk^2}(1)=\frac{37}{12}-\frac{5}{3}\ln 2+\frac{17}{6}\ln\beta+\frac{2}{3}\frac{\ln 2}{\beta^2}+\frac{4}{3\beta^2}-\frac{1}{30\beta^4}$$

$$+\left(\frac{\beta}{6}-\frac{17}{12}+\frac{5}{2\beta}-\frac{1}{3\beta^2}-\frac{2}{3\beta^3}\right)\ln(2-\beta)-\left(\frac{\beta}{6}+\frac{17}{12}+\frac{5}{2\beta}+\frac{1}{3\beta^2}-\frac{2}{3\beta^3}\right)\ln(2+\beta), \quad \text{(D4)}$$

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[15] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 343.

$$0\leq\beta\leq 1:\quad \pi^2E_a{}^{(2)}(0)=2f(\beta)+\frac{3}{\beta}-\frac{15}{2}+\left(\ln\frac{\beta}{2}\right)^2+\frac{\beta^2-1}{\beta^2}\ln(1-\beta), \tag{D5}$$

$$1\leq\beta\leq 2:\quad \pi^2E_a{}^{(2)}(0)=-2f\left(-\frac{1}{\beta}\right)+(\ln 2)^2+\frac{\pi^2}{6}-\frac{3}{2}-\frac{3}{\beta}-2\ln 2\ln\beta+\frac{\beta^2-1}{\beta^2}\ln(\beta+1). \tag{D6}$$

ACKNOWLEDGMENTS

We wish, first and foremost, to express our gratitude to Professor David Pines, who has guided and inspired us throughout this calculation. We wish to thank the National Science Foundation for its generous support during the work. One of us (D. L.) wishes to thank the Ford Motor Company Scientific Laboratory and the General Electric Research Laboratory for their kind hospitality and guidance as well as the generous allowance of their digital computing facilities.

PHYSICAL REVIEW VOLUME 111, NUMBER 2 JULY 15, 1958

Transient Photoconductivity in Silver Chloride at Low Temperatures*

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(Received March 24, 1958)

Primary photoconductivity has been investigated down to 6.5°K in single crystals of pure AgCl using low intensity, monochromatic light pulses and a sensitive electrometer. Results are presented which are in agreement with a theory of the transient response taking into account light absorption and electron trapping. The electron yield per absorbed photon (quantum efficiency) is found to be high, somewhat less than one, in the long-wavelength tail and through the first peak of optical absorption for all crystals and temperatures down to 6.5°K. These results agree with the proposed band scheme if one allows for direct and indirect transitions as discussed in Sec. V. Electron trappping properties are strongly dependent on sample preparation, but certain features are believed characteristic of the silver halides. Whereas the density of deep (0.5 ev) traps may be very low in well-annealed AgCl, a high density of very shallow (<0.1 ev) traps exists in the crystals prepared so far. Prominent electrical glow peaks have been observed at 15°K, 35°K, and 178°K. No evidence for hole mobility has been found and upper limits on possible hole ranges are given.

I. INTRODUCTION

At low temperatures silver chloride is a sensitive photoconductor which has vanishingly small dark conductivity. Primary photocurrents, characterized by a saturation behavior with increasing collection voltage, were observed in crystals of this material by Lehfeldt[1] many years ago. He showed that experiments carried out with a sensitive electrometer and low-intensity flash illumination lend themselves to a relatively simple interpretation in terms of electron range (*Schubweg*) governed by a volume distribution of traps. When range can be determined, it is possible to compute the quantum efficiency defined as the ratio of the number of electron-hole pairs created to the number of photons absorbed.

In order to understand the optical excitation process, it is of importance to know how the quantum efficiency depends on impurity content and temperature in the region of fundamental absorption, which begins in the vicinity of 400 mμ and extends into the far ultraviolet. In particular, one would like to compare the spectral dependence of quantum efficiency with optical absorption over a wide range of absorption coefficients. Whether or not holes as well as electrons contribute to the photoresponse of the silver halides is a problem of considerable interest,[2–5] and certain other results of the earlier work remain unexplained. For example, the striking decrease in photoconductivity that has been observed at temperatures below 50°K[1,6] might be explained either by a drop in quantum efficiency or by a reduced range at low temperatures due to shallow traps. The present experiment extends quantum

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* Supported in part by the U. S. Air Force.

† Now at Research Laboratories, Eastman Kodak Company. Work performed in partial fulfillment of the requirements for the Ph.D. degree at the University of Illinois.

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