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Further Evidence for Collective Resonances in Monovalent Metals*

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Photoemission data from the alkali metals Na and K and the noble metals Cu and Ag are examined for evidence of collective resonances. In all cases the vacuum level is more than 1.5 eV above E_F, the Fermi energy. The photoemissive energy distributions taken with photon energies above 2.5 eV and up to 5 eV exhibit structure which can be interpreted in terms of an s-wave resonance 0.3 eV or less below E_F and several p-wave resonances above E_F. Circumstantial reasoning based on the trends from Na to K, or from Cu to Ag, supports the assignment of the structure to collective resonances rather than to excitons or one-electron band structure.

1. INTRODUCTION

FOR many years the conventional theory of normal metals, based on the Hartree or independent-particle model, has given a good account of the low-frequency properties of metals. Also, high-energy plasma oscillations can be treated semiclassically using the Hartree model.[1] With the advent of precise Fermi surface experiments electron-electron interactions are sometimes included through a Landau-Fermi liquid model. Even this model, however, basically treats the particles as weakly interacting and introduces collective modes (such as zero sound) semiclassically. The Hartree or Landau theories cannot be used to derive collective pairing of the kind used to explain superconductivity, or other possible many-particle quantum correlations.

In the limit of high-electron densities ($r_s<1$) the Hartree model is extremely plausible, as one can show by perturbation theory.[2,3] For low densities ($r_s>40$) the model breaks down; the free-electron gas forms a crystal.[4] The situation at intermediate densities is unclear. At and near E_F, Fermi surface experiments suggest that electron-electron correlation effects are small. When the excitation energy $\hbar\omega$ is of order E_F, however, one may have correlations which lie outside the Hartree-Landau model.

We have recently discussed[5] optical data[6] in K and Cs which indicate that between 0.5- and 1.5-eV resonances are present. The collective character of the resonances is manifested by the line shape and in particular by the interference with the Drude background, which results in an antiresonance on the low-energy side.[5] In the antiresonance region $\mathcal{E}_2$ drops below the Drude value, especially at low temperatures. The stability of the resonance is reflected by its persistence into the liquid state.[6]

In Sec. 3 of this paper we discuss photoemissive evidence for resonances in the alkali metals Na and K, and in Sec. 4 evidence for Cu and Ag. At present no rigorous theory of the collective resonances is available, but Cohen has proposed[7] a model which contains attractive features. We review these in Sec. 2 in order to set the stage for circumstantial arguments based on trends from Na to K (Sec. 3) or from Cu to Ag (Sec. 4). Finally in Sec. 5 we discuss other possible explanations for the resonances, and compare them with the experimental evidence thus far surveyed.

2. RESONANCE MODEL FOR COLLECTIVE STRUCTURE

According to our analysis of the Mayer–El Naby data, collective resonances are present in the optical spectra of Na and K near 1 eV. There are two possible candidates for this resonance: electron-hole pairs (excitons) which can be described within the quasiparticle framework, and electron-electron s-wave pair amplitudes which exist macroscopically in the ground state. Cohen has proposed[7] to describe such resonances in terms of "coherent pairing" of the second kind (CP II). Because of the complexity of electron-electron interactions at large excitation energies, the question of the mathematical consistency and completeness of such a description is entirely open at present. Nevertheless, from a phenomenological viewpoint the "resonance model" represents a useful alternative to excitons. The two models are qualitatively different, because one refers to wave packets derived from the electron-hole states that would contribute to direct interband absorption, while the other depends on properties of the electron gas such as the dielectric function which, in the monovalent metals, are comparatively unaffected by the conduction band structure.

The predictions of the two models are the following:

Excitons. The energy E_0 of the lowest resonance is determined primarily by the position E_0 of the direct

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[1] H. Frohlich and H. Pelzer, Proc. Phys. Soc. (London) **A68**, 525 (1955).

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

[3] B. W. Ninham, Ann. Phys. (N.Y.) **28**, 220 (1964).

[4] E. P. Wigner, Phys. Rev. **46**, 1002 (1934); Trans. Faraday Soc. **34**, 678 (1938); F. W. deWette, Phys. Rev. **135**, A287 (1946).

[5] M. H. Cohen and J. C. Phillips, Phys. Rev. Letters **12**, 662 (1964).

[6] H. Mayer and M. H. El Naby, Z. Physik **174**, 289 (1963).

[7] M. H. Cohen, Phys. Rev. Letters **12**, 664 (1964).

TABLE I. The interelectronic spacing and threshold energies in monovalent metals (see Ref. 10).

Element	r_s/a_0	E_t (eV)	Element	r_s/a_0	E_t (eV)
Li	3.2	3.6	Cu	2.8	4–5
Na	4.0	2.0	Ag	3.2	4–5
K	4.9	1.2	Au	3.4	4–5
Rb	5.2	1.3			
Cs	5.6	1.3			

interband threshold. The exciton binding energy

$$B=E_t-E_0$$

should vary at most as $r_s^{-1/2}$ when screening is taken into account. The threshold energies E_t and the interelectronic spacing r_s are given for the alkalies and the noble metals in Table I.

Higher resonances may be found between E_t and E_0. Coulomb effects may be important up to E_t+B, but not above.

Pair resonances. The energy E_0 of the lowest resonance depends on the energy difference between the s-wave resonance below E_F and the lowest p-wave resonance above E_F. Both of these are determined primarily by r_s. Schematically, the trajectories of the lowest s wave and the p-wave resonances as a function of r_s for E_F fixed are shown in Fig. 1(a). Allowing for the dependence of E_F on r_s gives Fig. 1(b). We have assumed that the resonances are all above E_F for $r_s<1$ because quasiparticle perturbation theory seems to work well in this region.[2,3] Cohen has suggested[7] that the s-wave crossover point may lie near $r_s=3$. For r_s above the lowest p-wave crossover, the electron liquid would presumably form domains. No anisotropy of this kind has been observed in the alkalies, so that the lowest p-wave crossover presumably occurs for $r_s\geq 6$.

Higher short-range p-wave resonances P_N may also be present; in contrast to the long-range higher excitons the spacing between P_{I} and P_{II} should be greater than that between S_{I} and P_{I}. The higher resonances should be quite broad.

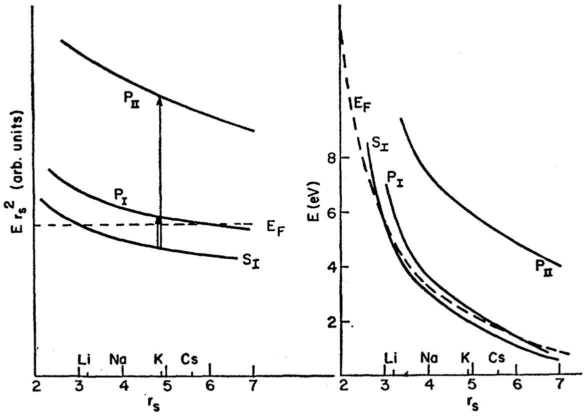

FIG. 1. A sketch of pair resonance trajectories as a function of r_s in a free-electron gas. The sketch is based on perturbation calculations for $r_s<1$ and on the analysis of experimental data given here and in Refs. 5 and 7.

3. Na and K

The photoemission data here come from the early work of Dickey.[8] Her energy distributions, which are shown in Figs. 2 and 3, deviated strikingly from the predictions of a one-electron model. Berglund and Spicer[9] have suggested that direct and indirect one-electron transitions would give roughly rectangular energy distributions from $E=0$ (vacuum level) to $E=E_m$ (photon energy less work function). For the nearly free-electron alkali metals this assumption seems adequate. Superposed on the rectangular distribution are a low-energy peak, which Berglund and Spicer attribute (and we believe correctly) to electrons that have scattered inelastically to produce electron-hole pairs. The most striking feature of the distributions, however, is the very large peak centered at

$$E=E_m-0.3\text{ eV} \tag{3.1}$$

for photon energies between 3.4 and 6.7 eV in both crystals. The peak is so striking (and unexpected) that Dickey emphasized it by plotting $N(E)$ against E_m-E.

Berglund and Spicer attribute this peak to a large peak in the density of states 0.3 eV below E_F. We believe this explanation is correct in a general way. Specifically, however, it is not present in a one-electron model. Both theory[10] and experiment[11,12] indicate that no peak is present in the one-electron density of states of Na and K that would even be resolved experimentally,

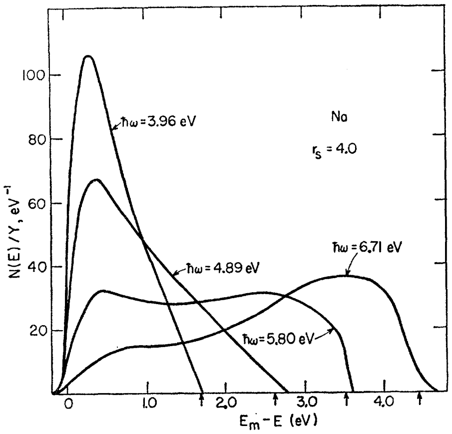

FIG 2

FIG. 2. Photoemissive energy distributions for fixed photon energies $\hbar\omega$ in Na (see Ref. 8). Note that the abscissa is $E(\max)-E$.

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[8] J. Dickey, Phys. Rev. **81**, 612 (1951).

[9] C. N. Berglund and W. E. Spicer, Phys. Rev. **136**, A1030, A1044 (1964).

[10] F. Ham, Phys. Rev. **128**, 82, 2524 (1962); V. Heine and I. Abarenkov, Phil. Mag. **9**, 451 (1964).

[11] C. C. Grimes and A. F. Kip, Phys. Rev. **132**, 1991 (1963).

[12] D. Schoenberg and P. J. Stiles (to be published).

much less dominate the energy distributions for $\hbar\omega<5$ eV. We believe the peak represents the density of states of the s-wave resonance.

The first point to note is that the peak is very strong at photon energies much larger than those involved in the resonance $S_{\rm I}-P_{\rm I}$ previously discussed near 1 eV. From the positions of the peaks we would guess the energies of the resonances in K occur approximately at

$$\begin{aligned} S_{\rm I}&:\ E_F-0.3\text{ eV},\\ P_{\rm I}&:\ E_F+[0.3\text{ to }1.5\text{ eV}],\\ P_{\rm II}&:\ E_F+[3.0\text{ to }4.5\text{ eV}]. \end{aligned}\tag{3.2}$$

Similar, and equally rough, estimates may apply to the other alkalies. Unpublished data of Mayer show a second peak in $\omega\mathcal{E}_2$ near 4.5 eV in Cs, which is presumably the $S_{\rm I}-P_{\rm II}$ resonance.

Both the data and our understanding of it are too crude at present to extract the oscillator strength of the $S_{\rm I}-P_{\rm II}$ resonance as a function of photon energy. However, as stressed by Dickey (see Figs. 2 and 3), the resonance peak is stronger in K than in Na and it clearly persists to $\hbar\omega=6.7$ eV in K. This qualitative point also favors resonances against excitons. Because r_s is larger in K than in Na (see Table I), the resonances should be stronger there. A one-electron model must predict the opposite trend because the energy scale for one-electron bands is determined by E_F, which is smaller for K than for Na. Finally, at energies so far above $E_t\simeq1.3$ eV, no exciton effects should be present in any case.

4. Cu and Ag

Energy distributions for cesiated Cu and Ag crystals have been obtained over a wide range of photon energies (1.5 to 11.5 eV) by Berglund and Spicer.[9] They find peaks in the energy distributions (see Figs. 4 and 5) corresponding to a peak in the density of states 0.3 eV below E_F. The peaks are assigned to direct transitions from the neighborhood of $L_{2'}$ to L_1.

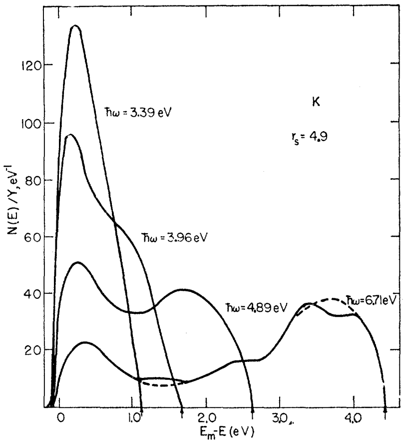

FIG. 3. Photoemissive energy distributions in K (see Ref. 8).

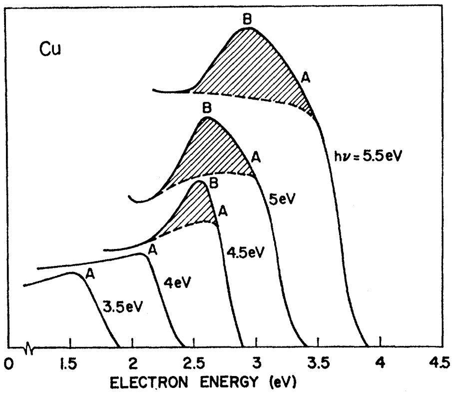

FIG. 4. Photoemissive energy distributions in Cu (see Ref. 9). The shaded regions are believed to represent electrons excited from the $S_{\rm I}$ resonance centered 0.3 eV or less below E_F.

At first glance this assignment is quite plausible. However, the transverse masses and diameters of the Fermi surface necks in these crystals are known quite accurately from de Haas–van Alphen studies.[13,14] From these values one can calculate $E_F-E(L_{2'})$. One obtains 0.3 eV in Ag, but 0.7 eV in Cu. *Both* peaks in the photoemission are centered 0.3 eV below E_F.

The resonance peaks are strongest near 4.5 eV in both crystals. This suggests that we are again observing an $S_{\rm I}-P_{\rm II}$ resonance which is quantitatively similar to the one seen in the alkalies. Moreover, as we can see

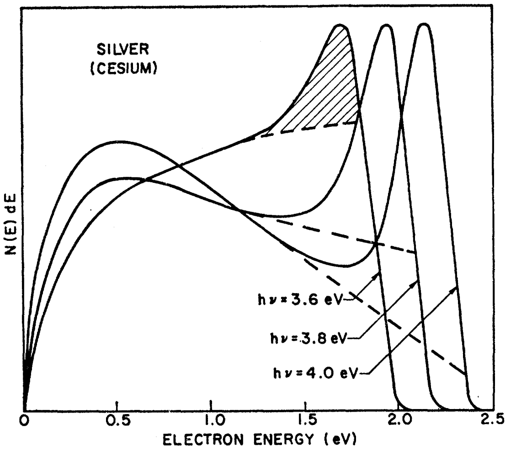

FIG. 5. Photoemissive energy distributions in Ag (see Ref. 9). Electrons excited from the $S_{\rm I}$ resonance to the $P_{\rm II}$ resonance are marked off by the dashed lines and by the shaded region for $\hbar\omega=3.6$ eV.

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[13] A. S. Joseph and A. C. Thorsen, Phys. Rev. Letters **13**, 9 (1964).

[14] We disregard the long period in Ag ascribed to a (111) cap associated with an L_1 band edge in Ref. 13. Professor A. B. Pippard (private communication) explains the long period as a beating between two belly periods.

from Figs. 4 and 5, the resonance is much stronger in Ag ($r_s=3.2$) than in Cu($r_s=2.8$). The band-structure explanation would lead to the opposite conclusion because the occupied neck region in **k** space in Ag is significantly smaller than in Cu.[13]

The similarity of the resonance peaks in dN/dE for photon energies near 4 eV in the alkali and noble metals raises the question of whether an $S_\text{I}-P_\text{I}$ optical resonance is to be expected in the noble metals as well as the alkalies. The photon energy would be near 1 eV, which is much smaller than the average band gap energy in the noble metals. The anisotropy of the band gaps might easily broaden the P_I resonance too much. At present there is no optical evidence for resonances in this region, but the reflectivity is so close to 100% that very careful experiments would be required to find the resonance if it were present at all.

5. CONCLUSIONS

Before summarizing our results we mention several other explanations of the Mayer–El Naby data of a more conventional kind. One may argue that the direct edge has been broadened by indirect transitions. It is difficult to see, however, how Lorentzian broadening of a linear threshold at 1.2 eV could produce a very sharp edge at 0.6 eV, even if the electron-phonon coupling were 10 to 100 times stronger than it is believed to be for these metals.

Overhauser has suggested[15] that the alkali metals are antiferromagnetic. If they are, it is surprising that domain effects have never been observed in low-field magnetoresistance studies. His suggestion can be tested directly by studying the optical resonance in the presence of a magnetic field.

The photoemission data reviewed here describe effects at large photon energies $\gtrsim 4$ eV where resonances are much broader than below 1 eV. That strong effects are still found may not be too surprising in view of the persistence of the Mayer–El Naby resonance in the liquid state.[6]

We have shown that the qualitative trends in both alkali and noble metals favor short-range pair resonances in both the ground and excited states, rather than long-range electron-hole resonances (excitons) in the excited state. We do not pretend to have a formal theory of these pair states. It is probable that they cannot be obtained by perturbation theory from a Hartree or Hartree-Fock ground state. While Cohen's analogy[7] with superconductivity is suggestive, we must bear in mind that here the excitation energies are comparable to the Fermi energy. Thus we cannot work only in a narrow ($\sim k\theta_D$, the Debye energy) energy shell about E_F. This makes the dynamical problem into a truly strong-coupling one. Our essential point is that the available evidence strongly suggests that the ground state of the electron gas at intermediate densities $r_s>2$ or 3 is not derivable from a Landau quasiparticle model, except for elementary excitations very close to E_F.

It would be interesting to test this point by studying the optical spectrum of Li. With luck this metal might show no (or only weak) resonances in the liquid state. One could then vary r_s between 3.2 and 4 in alkali metal alloys to study the oscillator strength at or near the crossover region.

The experimental data reviewed in this paper have been brought to the author's attention by Professor W. E. Spicer, whom I also thank for copies of his data on Cu and Ag prior to publication.

Note added in proof. W. E. Spicer has pointed out that the trend from Cu to Ag can also be explained by assigning the high-energy peak in dN/dE in Cu to $L_{2'} \rightarrow L_1$ transitions and in Ag to an $s_\text{I} \rightarrow p_\text{II}$ resonance. This interpretation seems more natural because in Ref. 9 it is shown that in Cu the dependence of the peak energy on photon energy agrees well with what one would anticipate from $L_{2'} \rightarrow L_1$ transitions.

Why does the resonance, absent in Cu, appear in Ag? In accordance with a remark by Cohen,[7] this could be caused by increasing r_s from 2.8 in Cu to 3.2 in Ag, if $r_s^c \simeq 3.0$ is the critical value for resonance behavior. Then it is surprising that the resonance is so strong in Ag.

Another important factor is the screening of *s-s* interactions by virtual *d-s* excitations. The minimum energy E_{mi} for such *d-s* excitations in Cu is 2 eV, while in Ag it is 4 eV. Thus the screening is much weaker in Ag than in Cu, which may enhance Coulomb interactions enough to create resonance behavior in the conduction band.

A photoemission experiment to determine which of these factors is dominant can be carried out on Au, for which $r_s=3.2$ as in Ag, and $E_{mi}=2$ eV, as in Cu. Our guess is that dN/dE in Au will resemble dN/dE in Cu. This would mean that the critical factor determining the presence or absence of resonances in the conduction bands of the noble metals is virtual *d-s* excitation.

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[15] A. W. Overhauser, Phys. Rev. Letters **13**, 190 (1964).