(1966). This paper contains references to other previous work of the authors.

[3]K. L. Shaklee, F. H. Pollak, and M. Cardona, Phys. Rev. Letters 15, 883 (1965); M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. (to be published); J. Feinleib, Phys. Rev. Letters 16, 200 (1966).

[4]M. Garfinkel, J. J. Tiemann, and W. E. Engeler, Phys. Rev. 148, 695 (1966).

[5]See for example, H. Ehrenreich, in Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965 (North-Holland Publishing Company, Amsterdam, 1966), p. 109; C. N. Berglund, ibid., p. 285; W. E. Spicer, ibid., p. 296.

[6]J. Feinleib, Phys. Rev. Letters 16, 200 (1966).

[7]B. R. Cooper, H. Ehrenreich, and H. R. Philipp, Phys. Rev. 138, A494 (1965), and other references cited therein.

[8]It should be noted that their derivation is not strictly valid, since they used as a parameter the pressure dependence of the dc conductivity, while in fact the conductivity has a frequency dependence which could alter the results. One should use instead the pressure dependence of the optical conductivity which is not presently available. However, for our discussion, we also will use Eq. (4) which gives the contribution of the dilatation effect to $\Delta\epsilon_2^f$.

[9]A detailed study of ϵ_2 versus temperature for the noble metals from reflectance measurements is planned.

[10]S. Roberts, Phys. Rev. 118, 1509 (1960).

EXCITONS IN METALS

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It is shown that exciton states exist in metals, occurring near the interband threshold in optical absorption and substantially altering the shape and strength of the absorption edge. Their relation to the corresponding donor states is discussed.

Theoretical calculations of interband optical absorption in metals have met with mixed success.[1] Band-structure calculations predict sucessfully many of the energy thresholds,[2] but miss by factors of 3 to 5 on predicting the strength of the absorption. This Letter points out that exciton states exist in metals, and that the inclusion of these exciton states in optical absorption calculations should resolve many of the above discrepancies. As in the semiconductor case,[3] these exciton states arise from the final-state Coulomb scattering between the electrons and holes. However, quite unlike the semiconductor excitons, an exciton state in the absorption spectra does not require that the corresponding donor state exist. Discrete exciton bound states only occur in special cases. Yet, in many types of transitions, metallic excitons will cause large resonances which enchance the interband absorption.

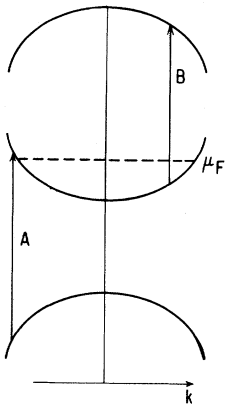

FIG. 1. Two types of interband transitions discussed in the text.

It has already been shown[4] that large exciton resonances occur in the interband transition A of Fig. 1. The optical spectra can be evaluated by treating the absorption as the photon creation of an electron-hole pair.[3] The absorption spectra is found by evaluating the electron-hole correlation function[5]

$$\pi(i\omega_n)=\frac{\alpha_0}{V}\sum_{\vec{p}\vec{p}'}\int_0^\beta d\tau\exp[i\omega_n(\tau-\tau')]\times\langle T_\tau c_{\vec{p}}(\tau)d_{\vec{p}}(\tau)d_{\vec{p}}(\tau)d_{\vec{p}}^{\dagger}(\tau')c_{\vec{p}'}^{\dagger}(\tau')\rangle, \quad (1)$$

where c_p refers to electrons in the conduction band and d_p to holes in the valence band. This form assumes that the band-to-band dipole transition is allowed. After evaluating $\pi(i\omega_n)$, the retarded function $\pi_{\mathrm{ret}}(\omega)$ is obtained by letting $i\omega_n \to \omega - E_G - \mu_e - \mu_h + i\delta$, where E_G is the en-

ergy gap. The absorption is

$$A(\omega) = 2\,\mathrm{Im}\pi_{\mathrm{ret}}(\omega).$$

Assuming that both bands are parabolic, in the absence of any final-state interactions and any damping, the absorption is just the density-of-states result

$$A_0(\omega) = (\alpha_0/2\pi)(2\nu)^{3/2}(\omega - E_G)^{1/2}\theta(\omega - E_G - \epsilon_{F'}),$$

where ν is the electron-hole reduced mass, and $\epsilon_{F'} = p_{F'}^2/2\nu$, where p_F is the electron Fermi momentum.

The metallic excitons are caused by the final-state Coulomb interactions between the electron and hole. The most important terms in the correlation function, Eq. (1), are the ladder diagrams. A consideration of these scattering terms shows that the correlation function has the form[4]

$$\pi(i\omega_n) = -\alpha_0 \int \frac{d^3p}{(2\pi)^3} \frac{[1 - n_F(p)]\Gamma(\vec{p}, i\omega_n)}{i\omega_n + \mu_e + \mu_h - p^2/2\nu},$$

$$\Gamma(\vec{p}, i\omega_n) = 1 + \int \frac{d^3p'}{(2\pi)^3} \times \frac{V(\vec{p} - \vec{p}')[1 - n_F(p')]\Gamma(\vec{p}, i\omega_n)}{i\omega_n + \mu_e + \mu_h - p'^2/2\nu}, \qquad (2)$$

where $V(q) = -4\pi e^2/(q^2 + k_s^2)$ is the attractive Coulomb potential. The vertex function Γ has a logarithmic singularity at the absorption edge. A detailed solution of these equations is given in Ref. 4. There it is shown that the logarithmic singularity greatly enhances the interband optical absorption. There is also an exciton bound state. This state occurs at binding energy E_B below the absorption edge. An approximate expression for this binding energy is

$$E_B = 4\epsilon_{F'} \exp(-1/\Delta),$$

$$\Delta = \left(\frac{\nu}{m}\right)\left(\frac{1}{2\pi p_F a_B}\right) \ln(1 + 4p_F^2/k_s^2). \qquad (3)$$

In most cases the discrete absorption line associated with the bound state will not be observed because of the lifetime broadening of the valence band states. The nonsphericity of real bands may also act as an effective broadening mechanism. The exciton state is metastable when the hole mass is finite, since there is a lower energy configuration for the electron and hole—i.e., when the hole is at $p = 0$. In the case where the valence band is flat (hole mass equal to infinity), a real exciton-bound-state absorption line may occur. Even when broadening smears out the exciton-bound-state absorption line, the logarithmic nature of the exciton resonance greatly enhances the absorption at the interband edge.

A calculation has also been performed for an interband transition of the type B of Fig. 1. Here the final-state Coulomb scattering occurs between the electron in the upper band and hole left in the Fermi sea. Calculations show that exciton resonances enhance the direct transitions. Phonon-assisted transition, perhaps to indirect exciton states at the zone edge, are also important in transition B of Fig. 1. Metals whose lowest interband transition is type B, such as the alkalis, will have a more complicated absorption edge. When the lowest transition is of type A, such as in the noble metals,[2] one gets the exciton resonances of Fig. 5 in Ref. 4.

It is possible to give semiclassical arguments to show the existence of these logarithmic singularities. Treating optical absorption as an inelastic scattering of photons by electrons, Hopfield[6] has noted that a sharp threshold in the inelastic scattering amplitude at $\omega = \omega_1$ necessarily leads to a term $\ln(\omega - \omega_1)$ in the elastic scattering. The exciton resonances are just manifestations of this logarithmic behavior near the interband thresholds.

The exciton states exist near the interband thresholds because the exclusion principle limits the electron's scattering during the final-state interactions. It is well known that the Fermi factors n_F cancel out when one considers the scattering of an electron from an ionized impurity. This self-energy is[7]

$$\Sigma(p) = n_i \int \frac{d^3p'}{(2\pi)^3} V(\vec{p} - \vec{p}')\mathcal{G}(\vec{p}', ip_n)\Gamma(\vec{p}, \vec{p}', ip_n),$$

such that

$$\Gamma(\vec{p}, \vec{p}', ip_n) = V(\vec{p} - \vec{p}') + \int \frac{d^3p''}{(2\pi)^3} V(\vec{p}' - \vec{p}'')\mathcal{G}(\vec{p}'', ip_n)\Gamma(\vec{p}, \vec{p}'', ip_n), \qquad (4)$$

where n_i is the impurity concentration. This form ignores vertex corrections which just include the electron's propagator.

We now show why the exclusion principle factors do enter the exciton problem, Eq. (2), and do not enter the ionized impurity scattering, Eq. (4). In order to make it resemble the exciton case, treat the impurity as a particle and assign it a propagator $\mathcal{G}_i(k) = (ik_n - \xi_i)^{-1}$. The infinite mass impurity is given a k eigenvector although its energy ξ_i is independent of k. Then the electron's self-energy from impurity scattering can be written as

$$\Sigma(p) = \frac{1}{\beta V^2} \sum_{ik_n, \vec{p}} \frac{\mathcal{G}_i(k) V(\vec{p}-\vec{p}') [1 - n_F(p')] \Gamma(\vec{p}, \vec{p}', ik_n, ip_n)}{ik_n + ip_n - \xi_{p'} - \xi_i} . \tag{5}$$

Typical diagrams for this self-energy are shown in Fig. 2. The vertex function in Eq. (5) is similar to that of Eq. (2), in that it contains n_F factors, and it has a pole corresponding to an impurity-electron bound state, where the binding energy is given by Eq. (3). On the other hand, at any finite order in the perturbation expansion, this self-energy, Eq. (5), reduces to Eq. (4) when the thermodynamic average is taken over the impurity distribution. By taking the sum over ik_n and then the classical limit $\beta\xi_i \to \infty$ [$n_i = V^{-1} \exp(-\beta\xi_i)$], then Eq. (5) reduces identically to Eq. (4), with all the n_F terms cancelling out. Thus it is the thermodynamic averaging over the impurity states which eliminates the n_F factors.

In the exciton case, the holes are created optically, so one never takes this last thermodynamic average (sum over ik_n, $\beta\xi_i \to \infty$). The n_F factors remain in the vertex and cause the exciton-bound-state pole in the scattering amplitude. Our conclusion is that there is an exciton state regardless of whether there is the corresponding donor state.

As for whether the donor state does exist, many-body theory provides both a yes and a no answer. The bound-state pole in the particle scattering amplitude of Eq. (5) does not appear in the potential scattering formalism of Eq. (4). These two formalisms differ because, in the particle case, one can sum the diagrams before averaging over the impurity distribution. Since the two methods differ only in infinite order perturbation theory, it is not clear which result is correct.

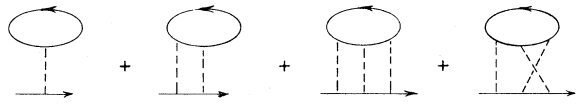

FIG. 2. The type of self-energy diagrams in Eq. (5) which give results equivalent to Eq. (4). The closed loops are impurity propagators.

It should be remarked that photoemission processes will also involve exciton states. The optical (soft-X ray) emission spectra is like the donor case in that one has to average thermodynamically over the distribution of holes in the initial state. I wish to thank Professor J. J. Hopfield for several clarifying discussions.

[1]Colloquium on the Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965, edited by F. Abelès (North-Holland Publishing Company, Amsterdam, 1966).

[2]B. R. Cooper, H. Ehrenreich, and H. R. Philipp, Phys. Rev. 138, A494 (1965).

[3]R. J. Elliott, Phys. Rev. 108, 1384 (1957).

[4]G. D. Mahan, Phys. Rev. 153, 983 (1967). In this reference, it is stated that the exciton effects should go away as the hole mass becomes large. This conclusion is incorrect, as is discussed above.

[5]A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, Quantum Field Theory in Statistical Physics (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[6]J. J. Hopfield, "Elastic Scattering at Inelastic Thresholds—Application to Solids," Proceedings of the Tokyo Summer Institute for Theoretical Physics, 1965 (to be published).

[7]R. H. Parmenter, Phys. Rev. 104, 22 (1956).