TABLE I. Observed and calculated data. The values of γ are taken from reference 3. ΔC_{obs} are calculated from the formula $V_A T_c(\partial H/\partial T)^2/4\pi$.

Metal	$-(\partial H/\partial T)$ gauss/°K	γ 10^{-4} cal/mole °K	γT_c 10^{-4} cal/mole	$2\gamma T_c$ 10^{-4} cal/mole	ΔC_{obs} 10^{-4} cal/mole	$\frac{V_A(\partial H/\partial T)^2}{4\pi\gamma}$
Al	136	2.59	2.98	5.96	4.07	1.36
V	400				116.27	
Zn	98	1.36	1.29	2.58	1.58	1.22
Ta	320	14.11	62.08	124.16	93.05	1.49
Hg	190	4.5	18.86	37.35	38.04	2.04
Pb	196	7.1	51.12	102.24	96.6	1.84

turbation procedure, we have treated the problem at arbitrary temperatures from the same viewpoint. It is found that this interaction can be approximately cast in a form which the author[2] had assumed previously from a formal point of view.

Using the usual Fermi-Dirac statistics, we get for the distribution function $f(\mathbf{k}_j)$ in the one-electron picture as

$$f(\mathbf{k}_j)=1/\{1+\exp[(\hbar^2/2m)+W_j-\zeta]/kT\}, \quad (1)$$

where W_j is the above-mentioned interaction energy, which depends on $f(\mathbf{k}_j)$ and the other $f(\mathbf{k}_i)$'s as in Fröhlich's paper; ζ is the free energy (Gibbs) per electron; and m, $\hbar$, k, have their usual meanings. We assume that the ordinary Fermi distribution suffers a modification in the narrow shell-like region near the Fermi surface, owing to the special character of the interaction. Then the free energy of our system takes the form,

$$G=N\left(\mu_0-\frac{\pi^2}{12}\frac{(kT)^2}{\mu_0}-\xi\right)\Big/\text{cc}, \quad (2)$$

where N is the number of the conduction electron in unit volume, μ_0 is the Fermi energy and ξ is determined by the following equation.

$$\xi=\mu_0(kT/\mu_0)^{\frac{1}{2}}\alpha^{\frac{1}{2}}\left\{\int_c^\infty x^{\frac{1}{2}}dx/(1+\exp[x-(\zeta_f+(\tau-1)\xi)/kT])-\int_c^\infty x^{\frac{1}{2}}dx/(1+\exp[x-(\zeta_f-\xi)/kT])\right\} \quad (3)$$

where $\zeta_f=\mu_0-\pi^2(kT)^2/12\mu_0$, α is the ratio of the effective mass of the electrons in our special state to that which appears in μ_0, and c is the parameter which shows the width of the shell region. Further, τ is given by

$$\tau=16\cdot 2^{-\frac{1}{2}}\eta\nu^{\frac{1}{2}}C^2/3Ms^2, \quad (4)$$

in which ν is the number of electrons per atom, M is the mass of the atom, s is the sound velocity in the metal, C^2 is a quantity which appears in the conductivity formula at high temperatures, and η is a numerical constant of the order of unity introduced in the course of the simplifying assumptions. Equation (3) always has the solution $\xi=0$, and the nonzero $\xi(>0)$ solution appears from a certain critical temperature. So it can be said that a phase transition occurs in our system at that temperature. We consider this nonzero ξ-state as the superconducting state. Unfortunately, we cannot calculate the transition temperature theoretically, due to the ambiguities in η. However, imposing the condition of the second-order phase change, $(\partial\xi/\partial T)_{T_c}=0$, we can derive the formula for the discontinuity of the specific heat at the transition temperature T_c:

$$\Delta C=C_s-C_n=V_A N T_c(\partial^2\xi/\partial T^2)T_c=V_A N\pi^2k^2T_c/[3(\tau-2)\mu_0]. \quad (5)$$

If we take arbitrarily the value of $\tau-2$ to lie between 1 and 2, we can calculate the observed values, and it is found that these values for τ do not contradict those which are estimated from Eq. (4).

For the effect of the magnetic field H, we assume semiphenomenologically that the ζ of the superconducting state has an additional term $+H^2/8\pi N$ owing to the perfect diamagnetic susceptibility, and the electronic energy is not influenced by the field because of its perfect cancelation. We obtain the threshold field relation

$$H=[(\pi^2k^2/12\mu_0)8\pi N]^{\frac{1}{2}}(T_c-T). \quad (6)$$

This will represent the experimental situation in a weak field. From Eq. (6), we can say further that there should be the following relation between the observed $(\partial H/\partial T)_{T_c}$, the electronic specific heat coefficient γ, and the atomic volume V_A:

$$V_A(\partial H/\partial T)^2/4\pi\gamma=1. \quad (7)$$

This is approximately fulfilled as is shown in Table I. In our opinion, the problem of the criterion for the superconducting metals and the isotopic mass dependency of the transition temperature is too difficult to be treated in the present stage of our knowledge concerning the theory of the metal.

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Ferromagnetism in Heusler's Alloys

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THE ferromagnetism of the Heusler alloys is usually attributed to the positive exchange interaction of the Mn atoms (Heisenberg's theory). However, the magnetic properties of these alloys can also be explained by Zener's theory of ferromagnetism.[1] Using known data on the Heusler alloys, it is possible to make some semiquantitative calculations on the basis of the two models.

We note the following data:[2]

	Cu_2MnIn	Cu_2MnAl
Bohr magneton/Mn atom	4.04	4.04
Curie point (°K)	506	603
Internuclear separation of Mn atoms (A)	4.38	4.17

Let us assume that the change in Curie point is due solely to the change in separation of the Mn atoms (the fact that the Bohr magneton number does not change makes this seem reasonable). On the Heisenberg theory the interaction energy is due to direct exchange. Since this energy is proportional to the product of the two overlapping charge distributions, we may say that the coupling is proportional to $|\psi|^4$ evaluated at the midpoint of the two interacting atoms. If we assume that the Hartree calculation for iron can be reasonably well applied to Mn, we find that $\psi\sim\exp(-3.5r/r_0)$ where r_0 is half the equilibrium lattice constant of the Mn superlattice in the alloy and r is the distance as measured from the center of the Mn atom. (This expression is not valid for $r\ll r_0$.) Therefore, the coupling varies as $\exp(-14r/r_0)$. Since the Curie point varies directly as the interaction energy we may calculate the theoretical ratio of the Curie points from the above data. We note that there is a 5 percent change in Mn separation:

$$T_c(\text{Al})/T_c(\text{In})=\exp[-14(r_{\text{Al}}/r_0)]/\exp[-14(r_{\text{In}}/r_0)]=2;$$

where $2r_{\text{Al}}$ = lattice constant of Mn superlattice in Cu_2MnAl, and $2r_{\text{In}}$ = lattice constant of Mn superlattice in Cu_2MnIn.

The exponents in the above expression may be slightly underestimated because the wave functions used did not consider exchange interaction. However, any increase in the exponent would only tend to make agreement with experiment worse. It is to be noted that $T_c(\text{Al})/T_c(\text{In})$ is not overly sensitive to the numerical coefficient in the exponent. (A 10 percent change causes only a 7 percent change in the value of the final expression.)

On Zener's model we assume that direct interaction is negligible and that the coupling is due to the interaction between the conduction electrons and the incomplete d shells. Zener shows that the Curie point is proportional to β^2/γ (β and γ are defined by $E_{\text{coupling}}=\frac{1}{2}\alpha S_d^2-\beta S_c S_d+\frac{1}{2}\gamma S_c^2$); β varies as $1/V$ while γ is made up of the kinetic energy of the electrons plus the exchange energy. Zener[3] shows that

$$\gamma=(10/9)(21.82/n_0)(n/V)^{\frac{1}{3}}-(4/9)10.81/n_0(n/V)^{\frac{1}{3}}$$

where n_0 is the number of conduction electrons per atom and n/V

is the number of conduction electrons/A.[3] For the Heusler alloys $n/V=0.088$. (The final result is very insensitive to the value n/V in this region.) Using the fact that there is a 16 percent change in volume we find

$$T_c(\text{Al})/T_c(\text{In})=1.2.$$

We see that the experimental value is also 1.2. The exact correlation is, of course, fortuitous, but it does indicate that the Zener model is more appropriate than Heisenberg's in this case.

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Use of the Scattering-Matrix Method in the Determination of the Electronic Properties of a Three-Dimensional Crystal

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SAXON and Hutner[1] in their extensive discussion of the electronic properties of the Kronig-Penney model of a one-dimensional crystal utilized the scattering-matrix concept in deducing both the energy-band structure of the fully periodic lattice, and also the effect of imperfections in that lattice. It is the purpose of the present note to point out that the natural generalization of this scattering-matrix method to the three-dimensional case is essentially contained in the paper by Korringa[2] on the application of the dynamical theory of lattice interferences to electron waves.

In the scattering-matrix method, the wave function ψ is characterized by the amplitudes of the waves incident upon and emerging from a given lattice point. $\psi=\psi_{\text{in}}+\psi_{\text{out}}$. The potential within the unit cell containing the lattice point determines one relationship between these amplitudes. This is described by the scattering-matrix $\mathbf{S}_V(E)$, whose elements are functions of the energy E, as well as the potential V. We have

$$\mathbf{S}_V\psi_{\text{in}}=\psi_{\text{out}}. \tag{1}$$

A second relationship arises from the fact that the amplitudes of the waves incident upon one lattice point are determined by the amplitudes of the waves emerging from the other lattice points. The expression of this relationship for the perfectly periodic lattice is equivalent to a statement of Bloch's theorem. It can also be described by a matrix $\mathbf{S}_B(\mathbf{k}, E)$ where $\mathbf{k}$ is the wave vector of the Bloch wave $\psi_{\mathbf{k}}=\exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{k}}(\mathbf{r})$.

$$\mathbf{S}_B\psi_{\text{in}}=\psi_{\text{out}}. \tag{2}$$

In order that (1) and (2) be consistent, we must have

$$\mathbf{S}_B(\mathbf{k}, E)\psi_{\text{in}}=\mathbf{S}_V(E)\psi_{\text{in}}. \tag{3}$$

Equation (3) determines $E(\mathbf{k})$, the energy as a function of wave vector.

The above formalism holds in both the one- and the three-dimensional cases. In the one-dimensional crystal model $\mathbf{S}_B$ and $\mathbf{S}_V$ are 2-by-2 matrices and ψ_{in} has two components corresponding to the two possible directions in the lattice. In the corresponding three-dimensional case ψ_{in} has infinitely many components, corresponding to the different l, m indices of the spherical harmonic expansion.

The Bloch matrix $\mathbf{S}_B$ may be computed as a function of $\mathbf{k}$ and E for any given lattice geometry. For the one-dimensional lattice the computation is trivial, $\mathbf{k}$ entering only in the constant factor $\exp(i\mathbf{k}\cdot\mathbf{r})$. In the general three-dimensional case the elements of $\mathbf{S}_B$ are expressible in terms of derivatives of the function $S(xyz)$ as described by Korringa.[2]

In making use of this formalism, one of course has to find approximations suitable to each particular case. One will generally work with finite matrices, for example, by neglecting terms with $l>l_0$. Simplifications in the form of $\mathbf{S}_V$ will also be possible for special problems.

One additional point may be mentioned relating to approximate calculations. In general, different methods for calculating $E(\mathbf{k})$ involve two steps: one step consists in satisfying the wave equation for the potential with each cell, the other is satisfying the periodicity conditions for the lattice. In the above presentation of the formalism, both steps appear on equal footing, and one can more easily judge the consistency of approximations involved in the separate parts of the problem.

The formalism may also be extended to discuss impurity scattering if one defines an appropriate scattering matrix for the impurity.

In conclusion, it seems likely that if the elements of $\mathbf{S}_B$ can be tabulated for the various crystalline types, a large number of problems involving the motion of electrons within crystalline lattices will become amenable to numerical treatment by the above method. We hope to discuss this later in a more detailed paper.

The author wishes to express his appreciation to Professor Korringa for many valuable discussions.

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Capture and Collision Processes for Excitons in Alkali Halides*

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THE recent elegant experiments of Apker and Taft[1] on the external photoelectric effect in evaporated layers of KI and RbI have given new evidence regarding the properties of excitons and their interactions with vacancies and F-centers. As discussed in reference 1, it seems conclusive that excitons, produced by absorption of light in the first fundamental band, can both create and destroy F-centers. The primary purpose of the present note is to investigate semi-quantitatively some specific mechanisms for these processes, and thus to give a plausible explanation of their high degrees of efficiency as indicated by the experimental results.

For the discussion of these processes we shall have to know the density of F-centers, which can be obtained in two ways from the experimental data, as Apker and Taft[1] have shown. First, the initial slope of the yield *versus* time curve indicates that effective saturation is reached after the production of about 3×10^{19} F-centers/cm^3 in the surface layers. Second, the ordinate of the plateau in the curve of yield *versus* incident photon energy is 10^{-4} electron/photon; this plateau is interpreted as arising largely from direct photoelectric ejection of the electrons from F-centers near the surface, and depends on the density of F-centers, the absorption cross section, and the probability that an electron, once released, will escape the crystal.Taking this probability to be $\frac{1}{10}$, we obtain a density of 10^{20}/cm^3. In view of their crudeness, these two estimates are in satisfactory agreement.

There are two reasons why such high densities should be possible. First, one might expect that in an evaporated layer the number of vacancies initially present should be higher than in an annealed single crystal. Second, as Seitz has pointed out,[2] an incipient negative ion vacancy at a jog in a dislocation line has an effective charge of $+e/2$ and hence may trap an electron. The electron and incipient vacancy may then diffuse away as an F-center and the jog move over, ready to act again. (This process of lengthening the dislocation line of course can result in a decrease in crystal density as observed by Estermann, Leivo, and Stern.[3]) It is interesting to note that Hilsch[4] has measured F-center densities even higher than the above estimate in similar evaporated films by optical absorption measurements.