

well beneath both curves except at the low-temperature extreme. In other words there appears to be a trend toward the $b(T)$ curve with decreasing Mn concentration. It should be mentioned that the transition temperatures derived from our data, and shown in Table II, are much smaller than those predicted by Overhauser from specific heat results. For example, T_c indicated from the latter for a 1 atomic per cent alloy is 27°K, as contrasted with our result of 7°K.

Concerning the magnitude of the effective field, it may be remarked that H_0 is about an order of magnitude larger than the *magnetic* field available from complete alignment of the Mn atoms. (The latter is given by $4\pi M_{\max}$, with M_{\max} equal to $n_v g \mu_B$, n_v being the num-

ber of Mn atoms per unit volume.) This inequality is consistent with the idea that the magnetization in these alloys has its origin in exchange interactions. The possibility that these interactions take the form of a conduction-electron field tending to align the Mn atoms appears to be strengthened by the paramagnetic character of the remanent magnetization.

ACKNOWLEDGMENTS

We wish to acknowledge the cooperation of the mechanical group of the Research Center in construction of the apparatus, and to thank members of the solid-state physics group for many helpful discussions during the course of this work.

PHYSICAL REVIEW

VOLUME 125, NUMBER 2

JANUARY 15, 1962

Impurity States in Metals

A. M. CLOGSTON

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received August 11, 1961)

A treatment of impurity states in metals due to Slater and Koster is extended to show the connection with the phase shift analysis of Friedel. In a simple case this allows the impurity potential to be made self-consistent. Application is made to the susceptibility and Knight shift of dilute alloys of transition metal compounds.

I. INTRODUCTION

IN a set of three papers,¹⁻³ Slater and Koster have discussed the theory of impurity states in crystals employing a Wannier function representation and using a Green's function to solve the resulting difference equations. If very restrictive conditions are placed on the problem, assuming (1) that the perturbations of only one band are important and, (2) that the perturbations caused by the impurity center are highly localized, the Green's function method gives extremely simple results. Assuming that the Wannier functions of the unperturbed problem are known, the wave functions of the electrons scattered from the impurity center can be obtained in closed form as a function of distance and energy of the incident wave.

In this particular case, the results obtained by Slater and Koster can be extended in a simple way to show the connection with the phase shift analysis of Friedel.⁴ It is possible thereby to make the scattering potential self-consistent and to obtain some simple results for charge impurities in metals. These results are particularly striking for the narrow bands and high densities of states encountered in transition element metals and

intermetallic compounds. Some clarification is also obtained of the nature of virtual states in metals and it can be seen that there is no real distinction between virtual states and bound states.

II. CONDITION OF SELF-CONSISTENCY

Following Slater and Koster, we suppose that the unperturbed lattice has a Hamiltonian H and a set of Bloch waves ψ_{nk} belonging to the n th band and \mathbf{k} th wave vector such that

$$H\psi_{nk} = E_{nk}\psi_{nk}. \quad (1)$$

We define a set of Wannier functions by the equations

$$W_n(\mathbf{r}-\mathbf{r}_i) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}_i} \psi_{nk}, \quad (2)$$

where N is the number of lattice sites in the crystal. It is easy to show that

$$HW_n(\mathbf{r}-\mathbf{r}_i) = \sum_j \epsilon_n(\mathbf{r}_j-\mathbf{r}_i) W_n(\mathbf{r}-\mathbf{r}_j), \quad (3)$$

if

$$\epsilon_n(\mathbf{r}_i) = \frac{1}{N} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}_i} E_{nk}. \quad (4)$$

Let us suppose now that a perturbation V is intro-

¹ G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954).

² G. F. Koster, Phys. Rev. **95**, 1436 (1954).

³ G. F. Koster and J. C. Slater, Phys. Rev. **96**, 1208 (1954).

⁴ J. Friedel, Suppl. Nuovo cimento **7**, 287 (1958).

duced so that the new Schrödinger problem becomes $(H+V)\psi=E\psi$. We expand the new wave functions in terms of the Wannier functions so that

$$\psi = \sum_{nj} U_n(\mathbf{r}_j) W_n(\mathbf{r} - \mathbf{r}_j). \quad (5)$$

The coefficients $U_n(\mathbf{r}_i)$ are then shown by Slater and Koster to satisfy the set of difference equations,

$$\sum_j U_m(\mathbf{r}_j) E_m(\mathbf{r}_i - \mathbf{r}_j) - E U_m(\mathbf{r}_i) = - \sum_{nj} U_n(\mathbf{r}_j) (W_m(\mathbf{r} - \mathbf{r}_i) | V | W_n(\mathbf{r} - \mathbf{r}_j)). \quad (6)$$

A set of Green's functions for Eq. (6) are given by

$$G_{mE}(\mathbf{r}_i - \mathbf{r}_0) = \frac{1}{N} \sum_{\mathbf{k}} \frac{e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_0)}}{E_{m\mathbf{k}} - E}, \quad (7)$$

since it may be easily shown that

$$\sum_j G_{mE}(\mathbf{r}_j - \mathbf{r}_0) \epsilon_m(\mathbf{r}_i - \mathbf{r}_j) - E G_{mE}(\mathbf{r}_i - \mathbf{r}_0) = \delta(\mathbf{r}_i - \mathbf{r}_0). \quad (8)$$

If the problem is specialized to the case of one band, and if we assume that the perturbation V is so localized that only the matrix component $(W(\mathbf{r} - \mathbf{r}_0) | V | W(\mathbf{r} - \mathbf{r}_0)) = V_0$ exists, Eqs. (6) and (7) become

$$\sum_j U(\mathbf{r}_j) \epsilon(\mathbf{r}_i - \mathbf{r}_j) - E U(\mathbf{r}_i) = - U(\mathbf{r}_0) V_0 \delta(\mathbf{r}_i - \mathbf{r}_0), \quad (9)$$

$$G_E(\mathbf{r}_i - \mathbf{r}_0) = \frac{1}{N} \sum_{\mathbf{k}} \frac{e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_0)}}{E_{\mathbf{k}} - E}. \quad (10)$$

If V_0 is zero, it is easily seen that a solution of Eq. (9) corresponding to the unperturbed lattice is

$$U(\mathbf{r}_j) = e^{i\mathbf{k} \cdot \mathbf{r}_j}, \quad E = E_{\mathbf{k}}. \quad (11)$$

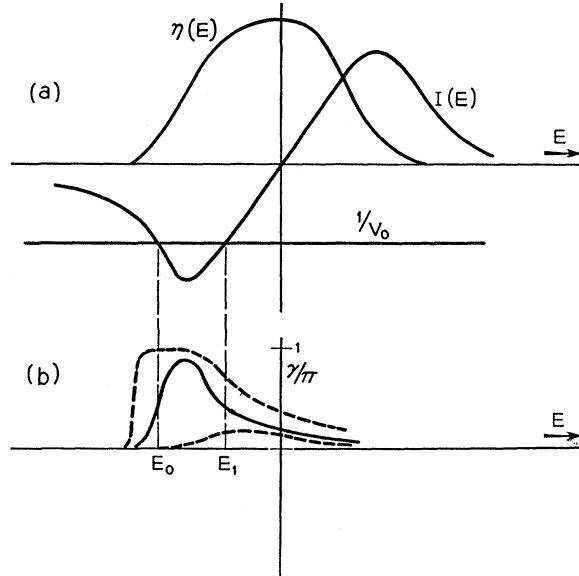


FIG. 1. (a) The density of states, $\eta(E)$, and the principal part, $I(E)$, of the Green's function defined in Eq. (16). (b) Change in number of states below energy E , γ/π , for three different values of the perturbing potential V .

We may expand $e^{i\mathbf{k} \cdot \mathbf{r}_i}$ in spherical harmonics in the usual way to obtain

$$e^{i\mathbf{k} \cdot \mathbf{r}_i} = 4\pi \sum_{l,m} i^l j_l(kr_j) Y_l^m(\theta_j, \varphi_j) Y_l^{-m}(\theta_k, \varphi_k). \quad (12)$$

By inverting this expansion we see that, for a spherical band, solutions of the unperturbed equation for energy $E = E_{\mathbf{k}}$ are also $j_l(kr_j) Y_l^m(\theta_j, \varphi_j)$.

Let us consider now the perturbed Eq. (9). Using the properties of the Green's function given by Eq. (8) it is clear that a spherically symmetric solution for $E = E_{\mathbf{k}}$ is

$$j_0(kr_i) - \frac{V_0}{1 + V_0 G_E(0)} G_E(\mathbf{r}_i - \mathbf{r}_0). \quad (13)$$

The other elementary solutions for $l \neq 0$ remain unaltered since $j_l(0) = 0$ for $l \neq 0$.

Next we shall consider the form taken by (13) for r_i very large. In reference (2) Koster obtains an asymptotic expression for the Green's function. If this result is specialized to the case of a spherical band, the asymptotic form of (13) may be written

$$\frac{1}{kr_i} \cos(kr_i - \pi/2) - \frac{\pi \Omega \eta(E) V_0}{1 + V_0 G_E(0)} \frac{e^{ikr_i}}{kr_i}, \quad (14)$$

where Ω is the atomic volume and $\eta(E)$ the density of states per unit volume. This result may be written more simply as follows. From Eq. (10), $G_E(0)$ can be expressed as an integral over all states in the band

$$G_E(0) = \Omega \int \frac{\eta(E_{\mathbf{k}}) dE_{\mathbf{k}}}{E_{\mathbf{k}} - E} \quad (15)$$

$$= -I(E) + i\pi \Omega \eta(E), \quad (16)$$

if $-I(E)$ is defined as the principal part of the integral. Using Eq. (16), (14) may be brought into the form

$$\frac{1}{kr_i} e^{i\gamma} \cos[kr_i - \frac{1}{2}\pi + \gamma(E)], \quad (17)$$

with the phase shift $\gamma(E)$ being given by

$$\gamma(E) = \tan^{-1} \left(\frac{\pi \Omega \eta(E)}{I(E) - 1/V_0} \right). \quad (18)$$

This is a very simple result and a very useful one because of the physical significance that can be given to γ . Let us suppose, following the lines laid down by Friedel,⁴ that the metallic crystal is in the form of a large sphere of radius R , and that all the wave functions are quantized within this sphere by requiring that they undergo total reflection at the surface. For the spherically symmetric wave we must have, for example

$$kR + \gamma(E) = m\pi, \quad (19)$$

with m an integer. The change in k between two successive wave functions of this type is clearly given by

$$\Delta k(R + d\gamma/dk) = \pi. \quad (20)$$

The number of states per unit increment of k is $(1/\pi)(R + d\gamma/dk)$, and the change of number of states due to the perturbation is just $(1/\pi)(d\gamma/dk)$ per unit of k . Consequently, the total change in number of states up to some particular value of k is just $(1/\pi)\gamma(k)$. Suppose that we have introduced at $r=0$ a charge perturbation Ze . In order that this charge may be shielded at infinity, we must bring below the Fermi level $Z/2$ new states, since each state can be occupied by an electron of each spin. We require therefore that at the Fermi surface E_f

$$(1/\pi)\gamma(E_f) = Z/2. \quad (21)$$

Since $\gamma(E_f)$ is related to V_0 through Eq. (18), Eq. (21) is the condition for self-consistency of the perturbation.

III. VIRTUAL STATES AND BOUND STATES

Considerable clarification of the nature of virtual and bound states can be obtained from a study of Eq. (18). The quantity $I(E)$ which enters this relation has been calculated for a special model by Slater and Koster in reference 3. An appreciation of the general shape of $I(E)$ can also be obtained by assuming simple forms for $\eta(E)$. For instance, if we assume that the band extends from $E = -\epsilon$ to $E = +\epsilon$ and place

$$\eta(E) = \eta(0)[1 - (E/\epsilon)^2], \quad (22)$$

then $I(E)$ is found to be given by

$$I(E) = \Omega\eta_0 \left[2\left(\frac{E}{\epsilon}\right) + \left(\frac{E^2}{\epsilon^2} - 1\right) \ln \left| \frac{E - \epsilon}{E + \epsilon} \right| \right]. \quad (23)$$

Guided by these models, we have made a sketch in Fig. 1 of how $\eta(E)$ and $I(E)$ might appear in a typical case. Suppose now that V_0 is negative (an attractive potential) and is large enough so that $1/V_0$ cuts $I(E)$ in two points as illustrated in the figure. Then we can determine from Eq. (18) that γ will have the form shown by the solid line in the lower half of the figure. At the extreme left γ rises until it equals $\pi/2$ at the first intersection E_0 , approaches π , falls to the value $\pi/2$ again at the second intersection E_1 , and then approaches zero as E continues to increase. A curve very similar to this may be seen in Fig. 17 of reference 4. We may interpret the behavior of γ as follows. Just to the right of E_0 , γ reaches nearly the value π , which we have seen means that approximately one whole state has been brought below this energy by the perturbation. In other words, a virtual state has been created in the vicinity of E_0 where $d\gamma/dE$ is large. Since γ falls to zero at the upper edge of the band, the total number of states is conserved, and it is clear that

the virtual state has been removed from the vicinity of E_1 .

The width of the virtual state is of interest. This is clearly controlled by the value of $\eta(E)$ at the point of intersection. If $\eta(E)$ is small, the state is very narrow, and vice versa. If we increase V_0 , the intersection moves to the left as shown by one of the dotted curves in Fig. 1(b) and the state will become sharper. If the intersection is below the edge of the band, $\eta(E)$ will be zero, and the state will be infinitely sharp. The distinction between bound states and virtual states is thus largely one of degree. In fact, even if $1/V_0$ does not intersect $I(E)$, $\gamma(E)$ will still exist, as shown in the second dashed curve in Fig. 1(b), and there will be an accumulation of states in a broad energy range.

We may also use Fig. 1(b) to discuss the condition of self-consistency given by Eq. (21). With a charge perturbation Ze in the lattice, $(1/\pi)\gamma$ must equal $Z/2$ at the Fermi energy. With the Fermi energy E_f determined by the bulk of the crystal remote from the perturbation, V_0 must increase until $\gamma(E_f)$ has the proper value. If Z is small enough, this can occur for E_f anywhere within the band. With larger values of Z , however, the model is restricted in its ability to achieve a self-consistent value of V_0 . Since we have limited ourselves to a one-band model and a perturbation localized to one site, we can never displace more than one state below the Fermi level. Furthermore, beyond the point for which $I(E) = 0$, $(1/\pi)\gamma$ cannot be greater than $\frac{1}{2}$. If the band is full, γ can never be anything but zero. These restrictions mean physically that the model cannot supply enough charge to shield a perturbation that is too large, and that the self-consistent potential would be important at sites removed from r_0 , or would cause appreciable distortion of nearby bands.

IV. APPLICATIONS

a. Susceptibility

We can use Eqs. (18) and (21) to derive an expression for the susceptibility of a metal containing a small number of charge impurities. By differentiation we obtain from Eq. (18)

$$\frac{d\gamma}{dE} = -\frac{1}{2} \frac{1}{\eta} \frac{d\eta}{dE} \sin 2\gamma - \frac{1}{\pi\Omega\eta} \frac{dI}{dE} \sin^2\gamma, \quad (24)$$

which becomes, using Eq. (21),

$$\begin{aligned} \frac{1}{\pi} \left(\frac{d\gamma}{dE} \right)_{E_f} &= \frac{1}{2\pi} \left(-\frac{1}{\eta} \frac{d\eta}{dE} \right)_{E_f} \sin \pi Z \\ &\quad - \frac{1}{\pi^2\Omega} \left(\frac{1}{\eta} \frac{dI}{dE} \right)_{E_f} \sin^2(\pi Z/2). \end{aligned} \quad (25)$$

The left-hand side of Eq. (25) is just the change in density of states at the Fermi surface. According to the

rigid-band model, this quantity should be given by $(Z/2)(d\eta/\eta dE)_{E_f}$. Equation (25) correctly reduces to this limit for small Z . In order to obtain the change of susceptibility due to the perturbation, we must multiply (25) by $2\mu_B^2 n$, where n is the density of impurity centers. We have then

$$\Delta\chi = 2\mu_B^2 n \left[\frac{1}{2\pi} \left(\frac{1}{\eta} \frac{d\eta}{dE} \right)_{E_f} \sin \pi Z - \frac{1}{\pi^2 \Omega} \left(\frac{1}{\eta} \frac{dI}{dE} \right)_{E_f} \sin^2(\pi Z/2) \right]. \quad (26)$$

If x is the fractional concentration of impurities equal to $n\Omega$, this can be put into the form

$$\Delta\chi_{\text{mol}} = \frac{2\mu_B^2}{M_0} x \left[\frac{1}{2\pi} \left(\frac{1}{\eta} \frac{d\eta}{dE} \right)_{E_f} \sin \pi Z - \frac{1}{\pi^2 \Omega} \left(\frac{1}{\eta} \frac{dI}{dE} \right)_{E_f} \sin^2(\pi Z/2) \right], \quad (27)$$

where M_0 is the mass of an atom of unit atomic weight.

If Z is large, the predictions of this formula are very different from those of the rigid-band model. For instance, if the impurity is a nucleus differing by one charge unit from the matrix we have $Z=1$, and (27) becomes

$$\Delta\chi_{\text{mol}} = -\frac{2\mu_B^2}{M_0} x \frac{1}{\pi^2 \Omega} \left(\frac{1}{\eta} \frac{dI}{dE} \right)_{E_f}. \quad (28)$$

This result represents a different physical situation depending upon the location of the Fermi energy. If E_f is in the low part of the band where η is small and

dI/dE negative, a large increase in χ_{mol} is predicted because of the presence of a virtual state at the Fermi surface. On the other hand, if E_f is higher in the band where dI/dE is positive, then we should predict a decrease in susceptibility. Using Eq. (23) we can determine that near the center of the band $(dI/\Omega \eta dE)_{E_f}$ equals approximately $8/w$, where w is the width of the band. Equation (28) then becomes approximately

$$\Delta\chi_{\text{mol}} = -(2\mu_B^2/M_0)x(8/\pi^2 w). \quad (29)$$

If the band is narrow, the impurities will cause a large decrease in the molar susceptibility. It is interesting to note that this effect is indifferent to the sign of the impurity charge.

For the intermetallic compound $V_3\text{Ga}$, measurements of Knight shift and susceptibility⁵ seem to require that the Fermi level intersect an extremely narrow peak in density of states. The temperature dependence of the susceptibility fixes the width of the peak at about 0.04 eV, while the maximum susceptibility indicates that the peak contains about 1 state per formula unit.

Some measurements have been made of the susceptibility of alloys of $V_3\text{Ga}$ with small amounts of Ti and Cr.⁶ The results extrapolated to 0°K are shown as the experimental points in Fig. 2. We note first the striking fact that the experimental susceptibility decreases sharply upon alloying with both Ti and Cr. This is in agreement with Eq. (29), but is in marked contrast with the rigid-band model which would predict a monotonic variation of susceptibility with electron concentration. The point is emphasized by the alloy $V_{2.7}\text{Cr}_{0.15}\text{Ti}_{0.15}\text{Ga}$ which has a susceptibility appropriate for $x=0.30$ and not for $x=0$ as would be expected from the rigid-band model.

We also show in Fig. 2 the initial rate of decrease of susceptibility upon alloying with small amounts of Cr or Ti predicted by Eq. (29) using a bandwidth of 0.035 eV, a value which gives an approximate fit to the experimental data. This value of w is close to the value determined from susceptibility measurements. It is remarkable that these two determinations of w , one from an experiment representing a weak, uniform perturbation of the band, and the other a strong local perturbation, should be in such good agreement.

b. Knight Shift

It is of interest to inquire about the Knight shift to be expected at the nucleus of the impurity atom according to this model. This problem has been discussed by Daniel,⁷ using a square well to represent the potential around the impurity. We may proceed here by taking, as a solution of the difference equation (9),

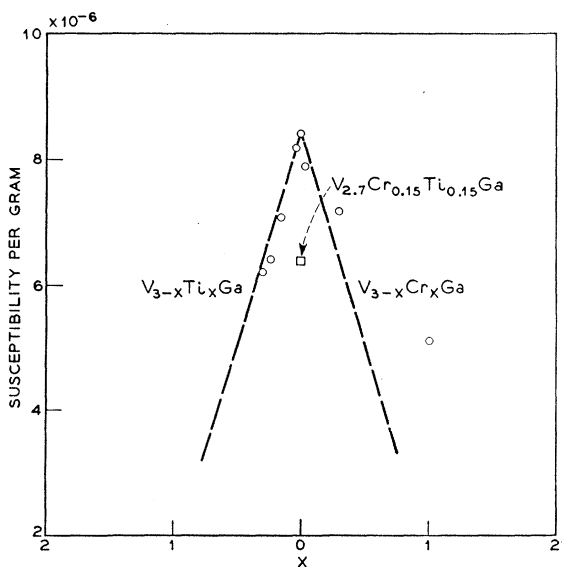


FIG. 2. Susceptibility versus fractional concentration of impurities in doped $V_3\text{Ga}$. The dashed line is predicted by Eq. (29).

⁵ A. M. Clogston and V. Jaccarino, Phys. Rev. **121**, 1357 (1961).

⁶ This work has been done in conjunction with V. Jaccarino, H. J. Williams, A. Gossard, J. H. Wernick, and R. C. Sherwood and will be reported more completely later.

⁷ E. Daniel, J. Phys. Chem. Solids **10**, 174 (1959).

$$U_k(\mathbf{r}_i) = \frac{1}{\sqrt{N}} \left[e^{ik \cdot \mathbf{r}_i} - \frac{V_0}{1 + V_0 G_E(0)} G_E(\mathbf{r}_i - \mathbf{r}_0) \right]. \quad (30)$$

It is possible to show with a little manipulation that the $U_k(\mathbf{r}_i)$ satisfy the condition of orthonormality,

$$\sum_i U_{k'}^*(\mathbf{r}_i) U_k(\mathbf{r}_i) = \delta_{kk'}. \quad (31)$$

It follows that the wave function $\Psi = \sum_i U(\mathbf{r}_i) W(\mathbf{r} - \mathbf{r}_i)$ is normalized. The Knight shift⁸ then will be given by

$$k = (8\pi/3) \chi V [|\Psi(r_0)|^2]_{E=E_f}, \quad (32)$$

where χ is the susceptibility per unit volume of the matrix. χ depends upon the density of states per unit volume and is not affected by a single impurity. We assume that only the Wannier function at the origin will have amplitude at r_0 , and that it will be equal to the atomic wave function $\Phi(0)$ appropriately modified in the crystal. We have then,

$$k = \frac{8\pi}{3} \chi \Omega |\Phi(0)|^2 \left| 1 - \frac{G_E(0)}{1/V_0 + G_E(0)} \right|_{E_f}^2, \quad (33)$$

Consider the factor

$$P = \left| 1 - \frac{G_E(0)}{1/V_0 + G_E(0)} \right|_{E_f}^2.$$

Using Eq. (18) again, this can be put in the form

$$P(E_f) = \left(\cos \gamma - \frac{I}{\pi \Omega \eta} \sin \gamma \right)_{E_f}^2. \quad (34)$$

In the usual discussion, it is assumed that the Knight shift in an alloy will be fixed by the susceptibility of the matrix in conjunction with the hyperfine field appropriate to the impurity atom. P measures the deviation from this rule. If $Z=1$, $\gamma=\pi/2$ and we obtain from

⁸ C. H. Townes, C. Herring, and W. D. Knight, Phys. Rev. **77**, 852 (1950).

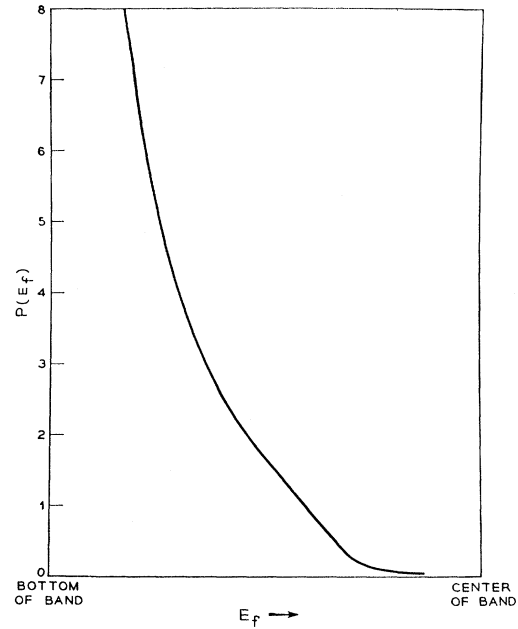


FIG. 3. The factor $P(E_f)$ defined by Eq. (34) as a function of E_f .

Eq. (34), $P = [I(E_f)/\pi \Omega \eta(E_f)]^2$. In Fig. 3 we have made a plot of $P(E_f)$ for $Z=1$, using data for I and η given in reference 3. We see that P is very large near the bottom of the band and drops rapidly as E_f increases, becoming zero at the center of the band. This behavior can be compared with that calculated by Daniel.⁷ He also finds P very large for E_f small. According to his model, however, P decreases rapidly to approximately unity as E_f decreases and never drops below this value. The difference arises from the fact that we are dealing here with a single band of limited width. The present model may have application to the study of Knight shifts in metals and intermetallic compounds with partially filled d bands.