Band Structure of Noble Metal Alloys: Optical Absorption in Cu-Ge Alloys at 4.2°K

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Calorimetric optical absorption measurements at 4.2°K have been made on a representative series of copper-germanium alloys, over the wavelength range 0.23 to 4 microns, using electropolished bulk specimens. The variation of the infrared absorptivity with residual resistance for the dilute alloys confirms that the impurity relaxation time for copper is anisotropic. Changes in the absorption spectrum below 6000 A are inconsistent with the rigid band model, but may be reconciled with the theory of Cohen and Heine. The shift in the main absorption edge is analyzed to give information about the screening of the solute atoms in these alloys.

I. INTRODUCTION

S a result of recent work¹ on the α phase of the copper-zinc system, it was considered of interest to extend optical absorption measurements to related alloy systems. According to the theory of Cohen and Heine² the band gap in the $\langle 111 \rangle$ directions for such alloys depends on the nature of the solute as well as the electron concentration. This behavior is to be contrasted with that of the rigid band model, which supposes the energy gap to remain fixed upon alloying. The rigid band model would thus predict that the absorption structure of all α -phase alloys involving copper as solvent should be essentially identical for the same value of electron concentration. In the Cohen and Heine model, on the other hand, the optical properties would depend markedly on the nature of the solute.

Again, measurements of the shift of the main absorption edge as a function of solute concentration for various alloying elements should give valuable information about the solute screening in such systems. If the *d* band, being relatively low lying, is supposed to be unaffected by the alloving process, then the shift in the main absorption edge should give the associated shift in the Fermi level. Assuming the Friedel theory³ of screening to be correct, at least in its qualitative aspects, then the displacement of the Fermi level and hence of the absorption edge should be a function only of the electron concentration. It was to check this conclusion, as well as to obtain a crucial test of the rigid band model of alloy behavior, that a study of the optical properties of the α phase of the copper-germanium system was initiated.

II. EXPERIMENTAL DETAILS

Measurements were made at liquid helium temperatures using the calorimetric technique described in the previous paper.¹ Both the optical and residual resistance specimens were prepared, in the same manner as before,

p. 395. ^a J. Friedel, in Advances in Physics, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 461.

from ingots formed by the induction melting of highpurity copper and germanium. The optical specimens were electropolished in an 80% orthophosphoric acid solution. This bath proved to be somewhat erratic in its behavior for the more concentrated alloys, but by suitably adjusting the current and voltage on the cell, good surfaces were obtained up to a germanium concentration of seven percent. Beyond this value, no satisfactory electropolishing bath could be found and hence the experiments do not extend to the limits of the α phase. After polishing, the optical specimens were washed and mounted in the usual manner.

III. RESULTS

Absorptivity data for the various alloys in the visible and ultraviolet regions of the spectrum are given in Fig. 1. The main absorption edges are shown in more detail in Fig. 2. For the dilute alloys, with germanium concentrations less than one percent, the infrared data are shown in Fig. 3. It should be noted that this figure is drawn on a much enlarged scale compared with Figs. 1 and 2. As in the case of the Cu-Zn alloys, the infrared absorptivity in the region 1.75-4.0 microns is substantially constant, but rises quite sharply in the vicinity of 1 micron. It is of interest that the residual resistivities



FIG. 1. Absorption spectra for copper-germanium alloys in visible and ultraviolet.

¹ M. A. Biondi and J. A. Rayne, Phys. Rev. **115**, 1522 (1959). ² M. H. Cohen and V. Heine, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 7,

of the dilute alloys agree well with the data of Linde,⁴ thus giving a measure of confidence in the metallurgical procedures used in preparing the samples.

IV. DISCUSSION

A. Absorptivity in the Visible and Ultraviolet

Reference to Fig. 2 shows that alloying with germanium moves the main absorption edge to shorter wavelengths. Owing to the high resistivity of the specimens, the residual absorption on the long wavelength side of the edge is quite high. Consequently an accurate determination of λ_0 , the wavelength corresponding to the onset of interband transitions, is not possible. If, however, we adopt a procedure similar to that used for the copper-zinc system, approximate values of λ_0 for the copper-germanium alloys may be found. These values are given in Table I, from which the full curve of Fig. 4 is obtained. Comparing the behavior of the copper-germanium system with that of the copper-zinc



FIG. 2. Details of main absorption edge for copper-germanium alloys.

system, given by the dashed curve in Fig. 4, it is seen that in both cases the initial displacement of the edge for small solute concentrations is essentially zero. This result is in definite contradiction to the original theory of Mott and confirms Friedel's hypothesis³ that there must be a substantial effect on the displacement of the Fermi level, due to screening of the solute atoms by the conduction electrons. Now according to Friedel, the displacement of the Fermi level δE , for a concentration c of solute having a valence Z relative to the solvent, is given by equation

$$\delta E = \frac{Zq}{qR\cosh qR - \sinh qR}.$$
 (1)

In this equation the screening parameter q is related to the density of states, $N(E_0)$ by the relation

$$q^2 = 4\pi N(E_0).$$
 (2)



FIG. 3. Absorption spectra for dilute copper-germanium alloys in infrared.

The screening radius R is given by the equation

$$1/R^3 = c/r_s^3,$$
 (3)

 r_s being the radius of the atomic sphere for the solvent. From Eq. (1) it is readily seen that

$$\delta E/Z = f(qR), \tag{4}$$

where the right hand is a function only of the solute concentration R and of the properties of the *solvent*. Now it was demonstrated previously¹ that the Thomas-Fermi model, on which Eq. (1) was derived, does not adequately describe the solute screening for Cu-Zn alloys. It does not seem unreasonable, however, to suppose that the relation (4) still holds and that $\delta E/Z$ plotted against solute concentration gives a universal function. If this is so, the close agreement between the two curves in Fig. 4 suggests quite definitely that the behavior of germanium in these alloys is not consistent with the idea that it is quadruply ionized. Rather, the present results strongly suggest that only one additional electron is contributed to the alloy by each germanium atom. In view of the large ionization energies that corre-



FIG. 4. Shift in main absorption edge for copper-germanium alloys as a function of solute concentration.

⁴ J. O. Linde, Ann. Physik 10, 52 (1931).

TABLE I. Values of λ_0 , the wavelength corresponding to the onset of the main absorption edge, for Cu-Ge alloys.

Solute concentration (at. %)	λ_0 (A)	<i>E</i> ₀ (ev)	δ <i>E</i> (ev)
0	5790	2.150	0
1	5790	2.150	0
2	5780	2.153	0.003
3	5760	2.161	0.011
5	5730	2.173	0.023
7	5700	2.184	0.034

spond to the quadruply ionized states of Ge, this conclusion is perhaps not so unusual as might at first seem.

The behavior of the absorption curves for the Cu-Ge alloys in the visible and ultraviolet regions of the spectrum is quite different from the corresponding curves for the Cu-Zn system. In the latter case, the absorption peak corresponding to transitions from the valence band into the next zone, moves to longer wavelengths with increasing zinc concentration. For the Cu-Ge system, however, there is definite evidence, as may be seen from the doubly humped curves D, E, that this same peak moves towards shorter wavelengths with increasing germanium concentration. Such behavior is not at all consistent with the rigid band model, which would predict that the absorption structure would be essentially only a function of the electron concentration. On the other hand, the model of Cohen and Heine may be reconciled with the behavior of both alloy systems.

As noted in the previous paper, the onset of absorption into the next zone corresponds to a photon energy equal to the energy gap in the $\langle 111 \rangle$ directions. According to Cohen and Heine, the change in the gap upon alloying is given approximately by the formula

$$\overline{\Delta}_{sp} - (\Delta_{sp})_{\text{solvent}} = \frac{(e/a) - 1}{e/a} \left(1 + \frac{1}{Z} \right) \\ \times \{ (\Delta_{sp})_{\text{solute}} - (\Delta_{sp})_{\text{solvent}} \}, \quad (5)$$

where $\overline{\Delta}_{sp}$ corresponds to the mean gap for the alloy, $(\Delta_{sp})_{\text{solute}}$ and $(\Delta_{sp})_{\text{solvent}}$ correspond to the gaps for the solute and solvent, respectively, and e/a is the electron/atom ratio for the alloy. Now from the Cu-Zn absorption data, $E_s - E_p$ for c = 0.3 is approximately 2.6 ev. From the soft ray absorption spectrum of copper,⁵ it is known that $E_s - E_p$ is approximately 3.5 ev. Hence experimentally, for c = 0.3 in the copper-zinc system, we have⁶

$$\overline{\Delta}_{sp} - (\Delta_{sp})_{\text{solvent}} = 3.5 - 2.6 = 0.9 \text{ ev.}$$
 (6)

Using the theoretical values of s-p splittings given by

Cohen and Heine, we find from (5)

$$\overline{\Delta}_{sp} - (\Delta_{sp})_{\text{solvent}} = 0.9 \text{ ev}, \tag{7}$$

in exact agreement with experiment. In the case of germanium as a solute, however, the theoretical *s-p* splittings predict a similar shift of the absorption curve towards larger wavelengths. This disagreement is, nevertheless, not too significant since an accurate estimate of Δ_{sp} for germanium is difficult to obtain on theoretical grounds. If, in fact, Δ_{sp} for germanium is *less* than that for copper or is negative, then the Cohen and Heine model would be consistent with experiment, since $\overline{\Delta}_{sp} - (\Delta_{sp})_{\text{solvent}}$ would then be negative. At the moment, there does not appear to be any way of giving any theoretical justification to such a hypothesis. It is possible, however, that the abnormal value of Δ_{sp} for germanium is connected with the fact that it is not quadruply ionized in such alloys.

If the present interpretation of the absorption structure on copper-germanium alloys is correct, then it must be concluded that the band gap in the $\langle 111 \rangle$ directions increases slightly with increasing germanium concentration, i.e., the Fermi surface becomes slightly more distorted on alloying. Since it is now known quite definitely⁷ that the Fermi surface in copper touches the zone boundary along the $\langle 111 \rangle$ directions, one would thus expect that the density of states in the coppergermanium system would decrease with increasing solute concentration. Low-temperature heat capacity studies on Cu-Ge alloys⁸ have shown, however, that this is not true. A possible explanation of this discrepancy is to ascribe it to a neglect of the contribution to the density of states curve from regions of the Fermi surface remote from the {111} faces. This contribution is a monotonically increasing function of energy and it may offset the effects of the overlap across the {111} faces. A detailed explanation of the shape of the density of states curve for the Cu-Ge system, based on such a hypothesis, is not possible in view of our rather sparse knowledge concerning the band shape of copper. Further experiments on other alloys systems are clearly needed to determine whether, in fact, the Cohen and Heine model is adequate to give a complete description of the α -phase alloys of the noble metals.

B. Absorptivity in the Infrared

As may be seen from Fig. 3, the absorption data beyond the main edge exhibit considerable tailing out to approximately 1.75 microns. It is now believed that this tailing *does* in fact result from indirect transitions between the *d* band and the Fermi surface, as was originally suggested by Biondi.¹ In order for such transitions to extend over such a wide range of energy, however, there must be considerable warping of the *d*

⁵ Y. Cauchois, Phil. Mag. 44, 173 (1953).

⁶ The Cohen and Heine theory gives the approximate relation $E_s - E_p = -\Delta_{sp} - \frac{1}{2}(BC)_s + (5/4)k_F^2$. In the present work we assume that the last two terms are unchanged on alloying, so that $E_s - E_p \sim -\Delta_{sp}$.

⁷ J. D. Gavenda and R. W. Morse, Bull. Am. Phys. Soc. 4, 463 (1959).

⁸ J. A. Rayne, Phys. Rev. 108, 649 (1958).

band. This feature of the d band has not been revealed by any band calculation⁹ but in view of the rather primitive state of such computations, the absence of warping is perhaps not significant. In this connection, it should be mentioned that the effects of s-d hybridization mentioned by Cohen and Heine may be responsible for the unusual character of the d band.

Beyond 1.75 micron, the absorptivity is essentially constant with increasing wavelength, to within experimental error, for the dilute alloys studied here. As discussed in the previous paper,¹ the absorptivity can be expressed as the sum of three contributions

$$A = A_{\text{surface}} + A_{\text{volume}} + A_{\text{impurity}}.$$
 (8)

The first term results from the scattering of electrons by the surface of the metal, while the second term arises from the interaction of the electrons with the zero point motion of the lattice. An expression for the impurity absorptivity, A_{impurity} , was previously derived by solving the Boltzmann equation without taking into account the spacial variation of the electromagnetic field within the metal. A more rigorous treatment, following the work of Kaganov and Slezov,¹⁰ is given in the Appendix, where it is shown explicitly that it is precisely the effects of this field variation which result in the surface absorption. For $\omega \tau \gg 1$, $\omega \delta / v \gg 1$ the more exact treatment yields an identical expression for $A_{impurity}$ as that obtained previously, viz.,

$$A_{\rm impurity} = \langle \tau \rangle \langle 1/\tau \rangle (Ne^2/\pi m)^{\frac{1}{2}} \rho_{\rm impurity}. \tag{9}$$

In this equation m is the usual average inverse effective mass, N the density of conduction electrons and ρ_{impurity} the resistivity due to the presence of impurities. The quantities $\langle \tau \rangle$ and $\langle 1/\tau \rangle$ are averages of the impurity relaxation time defined by the following integrals:

$$\langle \tau \rangle = \int \tau v dS / \int v dS; \quad \left\langle \frac{1}{\tau} \right\rangle = \int \frac{1}{\tau} v dS / \int v dS. \quad (10)$$

From the Schwarz inequality it may be shown that

$$\langle \tau \rangle \langle 1/\tau \rangle \geqslant 1,$$
 (11)

the equality holding only for isotropic impurity scattering. Thus $\langle \tau \rangle \langle 1/\tau \rangle$ is a measure of the anisotropy of impurity scattering.

In the region of interest, therefore, the absorptivity of the alloys may be expressed in the form

where

(12) $A = A_{\text{surface}} + A_{\text{volume}} + \beta \rho_{\text{impurity}},$

$$\beta = \langle \tau \rangle \langle 1/\tau \rangle (Ne^2/\pi m)^{\frac{1}{2}}.$$
 (13)

Now for the dilute alloys used in this work, A_{surface} and A_{volume} are essentially constant and hence a plot of



FIG. 5. Variation of infrared absorptivity as a function of residual resistance for dilute copper-germanium alloys.

absorptivity versus the residual resistivity should yield a straight line of slope β_0 , the value of β for pure copper. As shown in Fig. 5, this plot is indeed linear. Using the value $m = 1.45m_0$ derived by Schulz¹¹ from his infrared transmission measurements, we find from (13) that the anisotropy factor for impurity scattering in pure copper is given by

$$\langle \tau \rangle \langle 1/\tau \rangle = 1.30 \pm 0.05. \tag{14}$$

This value is in very good agreement with the figure obtained from the initial slope of absorptivity versus residual resistivity for the copper-zinc alloys. In this latter instance, however, there is a greater uncertainty in analyzing the data, since the validity of assuming that A_{surface} and A_{volume} are only slowly varying functions of solute concentration is somewhat questionable. It is believed that the present estimate is much more reliable.

The result expressed by (14) is of considerable interest, since most theoretical treatments of impurity scattering have assumed it to be isotropic. As demonstrated here, this assumption is far from being correct. A satisfactory explanation of the reason for this anisotropy seems hardly possible at the moment. It is believed, however, that in some way it must be connected with the nonspherical nature of the Fermi surface in copper.

V. CONCLUSIONS

From the results of optical absorption measurements on Cu-Ge alloys at 4.2°K, it is concluded that the rigid band model is not capable of describing the effect of alloying on the band structure of copper. The shift in the main absorption edge gives support to the general notions concerning the screening of solute atoms in such alloys, but does not appear to be consistent with the idea that germanium is quadruply ionized. Although the Cohen and Heine model can be reconciled with the present experiments, there still appears to be some doubt that it is capable of providing a unified description of the α phase of the noble metal alloys. The varia-

⁹ See for example D. J. Howarth, Proc. Roy. Soc. (London)

A220, 513 (1953). ¹⁰ M. I. Kaganov and V. Slezov, J. Exptl. Theoret. Phys. (U.S.S.R.) Soviet Phys.-JETP 5, 1216 (1957).

¹¹ L. G. Schulz, J. Opt. Soc. Am. 44, 540 (1954).

tion of infrared absorptivity with residual resistivity for dilute copper-germanium alloys confirms that impurity scattering in copper is anisotropic.

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APPENDIX

Following Kaganov and Slezov,¹⁰ let us consider a plane electromagnetic wave of frequency ω incident normally upon a cubic single crystal whose surface coincides with the plane z=0.

The relevant Boltzmann equation is

$$i\omega f + v_z \frac{\partial f}{\partial z} + \frac{f}{\tau} = -\frac{\partial f_0}{\partial E} \boldsymbol{\epsilon} \cdot \mathbf{v},$$
 (A1)

where the field $\boldsymbol{\varepsilon}$ is given by the Maxwell equations

$$\operatorname{curl} \mathbf{H} = 4\pi J/c; \quad \operatorname{curl} \mathbf{\varepsilon} = -(i\omega/c)\mathbf{H}, \quad (A2)$$

and the current density \mathbf{J} is related to the distribution function f by the relation

$$\mathbf{J} = \frac{2e}{(2\pi)^3} \int \mathbf{v} f d^3 \mathbf{k}.$$
 (A3)

The zeroth order solution of (A1) may be used to solve (A2) and (A3) for the electric field. In particular, for a plane wave polarized along the x axis, these equations yield

$$\mathcal{E}_x = \mathcal{E}_x(0)e^{-z/\delta}, \quad \mathcal{E}_y = 0, \quad \mathcal{E}_z = 0.$$
 (A4)

The skin depth δ is given by the relation

$$\delta = \left(\frac{mc^2}{4\pi Ne^2}\right)^{\frac{1}{2}} \left(1 - \frac{i}{2\omega\tau}\right) = \delta_0 \left(1 - \frac{i}{2\omega\tau}\right), \quad (A5)$$

where m is the usual average inverse effective mass, viz.

$$\frac{1}{m} = \frac{1}{12\pi^3 N\hbar} \int v dS.$$
 (A6)

If (A4) is then used to obtain a better solution for the distribution function, we find from (A1) assuming that f=0 at z=0, i.e., diffuse reflection at the boundary,

$$f = -\frac{\partial f_0}{\partial E} e \mathcal{S}_x(0) \frac{v_x}{(i\omega + 1/\tau) - v_z/\delta} \times \left\{ \exp\left(-\frac{z}{\delta}\right) - A \exp\left(-\frac{i\omega + 1/\tau}{v_z}z\right) \right\}, \quad (A7)$$

where

$$A = 0 \quad \text{if} \quad v_z < 0$$
$$A = 1 \quad \text{if} \quad v_z > 0.$$

Using (A7) and the central symmetry of the Fermi surface, Eq. (A3) may be used to obtain the current. Thus

$$J_{x} = \int_{0}^{\omega} J_{x}(z) dz$$

$$= \frac{2e^{2}}{(2\pi)^{3}\hbar} \mathcal{E}_{x}(0) \oint \left\{ \frac{\delta}{i\omega + 1/\tau} + \frac{\delta}{i\omega + 1/\tau + v_{z}/\delta} \right\} v_{x}^{2} \frac{dS}{v},$$
(A8)

where the integration is carried out over that part of the Fermi surface for which $v_z > 0$. Expressing this equation in terms of the surface resistance R and surface reactance X, we have since $\omega \tau \gg 1$, $\omega \delta / v \gg 1$,

$$R-iX$$

$$R^2 + X^2$$

$$=\frac{2e^{2}}{(2\pi)^{3}\hbar\omega^{2}} \oint' \left\{ 2\delta_{0} \left(1-\frac{i}{2\omega\tau}\right) \left(\frac{1}{\tau}-i\omega\right)+v_{z} \right\} v_{z}^{2} \frac{dS}{v}$$
$$=\frac{2e^{2}}{(2\pi)^{3}\hbar\omega^{2}} \oint' \left\{ \left(\frac{\delta_{0}}{\tau}+v_{z}\right)-2i\delta_{0}\omega \right\} v_{z}^{2} \frac{dS}{v}. \tag{A9}$$

Thus equating real and imaginary parts, we have since $R \ll X$

$$\frac{R}{X^2} = \frac{2e^2}{(2\pi)^3\hbar\omega^2} \left[\oint' v_x^2 v_z \frac{dS}{v} + \frac{\delta_0}{2} \int \frac{v_x^2}{\tau v} dS \right],$$

$$\frac{1}{X} = \frac{2e^2}{(2\pi)^3\hbar\omega^2} \delta_0 \omega \left[\int v_x^2 \frac{dS}{v} \right].$$
(A10)

Hence from (A10) and (A6) we find that the absorptivity A is given by the equation

$$A = \frac{cR}{\pi} = \frac{3}{4} \frac{\tilde{v}}{c} + \left(\frac{m}{\pi N e^2}\right)^{\frac{1}{2}} \langle 1/\tau \rangle, \qquad (A11)$$

where \tilde{v} is an effective velocity given by the expression

$$\bar{v} = 16 \oint v_x^2 v_z \frac{dS}{v} / \int v dS.$$
 (A12)

For a spherical energy surface $\tilde{v} = v_F$, the velocity at the Fermi surface. The average inverse relaxation time $\langle 1/\tau \rangle$ is given by the equation

$$\langle 1/\tau \rangle = \int_{-\tau}^{1} \frac{1}{\tau} dS / \int v dS.$$
 (A13)

If we take into account scattering of the electrons by phonons as well as by impurities, we have

$$\langle 1/\tau \rangle = \langle 1/\tau \rangle_{\text{phonon}} + \langle 1/\tau \rangle_{\text{impurity}}.$$
 (A14)

For spherical energy surfaces and acoustic anisotropy, Holstein¹² has obtained an expression for $\langle 1/\tau \rangle_{\text{phonon}}$, viz.

> $\langle 1/\tau \rangle_{\text{phonon}} = \frac{2}{5} \frac{\theta}{T} \frac{1}{\tau}.$ (A15)

In any case, we can use (A13) and (A11) to write the total absorptivity in the form

$$A = A_{\text{surface}} + A_{\text{volume}} + \left(\frac{m}{\pi N e^2}\right)^{\frac{1}{2}} \langle 1/\tau \rangle, \quad (A16)$$

where $\langle 1/\tau \rangle$ is now understood to refer to the *impurity* relaxation time.

¹² T. Holstein, Phys. Rev. 96, 535 (1954).

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Now the impurity resistance $\rho_{impurity}$ is given by the equation

$$\rho_{\rm impurity} = m/Ne^2 \langle \tau \rangle, \qquad (A17)$$

where

$$\langle \tau \rangle = \int \tau v dS / \int v dS.$$
 (A18)

Using these equations, (A15) may be written in the form

$$A = A_{\text{surface}} + A_{\text{volume}}$$

 $+\langle \tau \rangle \langle 1/\tau \rangle (Ne^2/\pi m)^{\frac{1}{2}} \rho_{\text{impurity}},$ (A19)

which is the same equation as derived previously. From the Schwarz inequality, it may be shown that

$$\langle \tau \rangle \langle 1/\tau \rangle \geqslant 1,$$
 (A20)

the equality only holding for isotropic impurity scattering.

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Electron Scattering by Thin Foils for Energies Below 10 key

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The transmission (η_T) of electrons through thin films of C, Al₂O₃, Al, Ni, Ag, and Au, together with their distribution in angle and energy, were measured in a spherical retarding-potential analyzer. The distributions were characterized by average and most probable scattering angle, average and most probable fractional energy loss, etc. The dependence of these variables on initial energy (E_p) , film thickness, and material was investigated. For sufficient film thickness, the transmitted energies, the scattering angles and η_T can be represented as universal functions of the reduced energy, E_p/E_c , where E_c is the critical E_p for the onset of transmission. Direct relations exist between η_T , scattering angles, and energy losses for the complete range of scattering from small-angle scattering to total diffusion. The dependence of η_T and average fractional energy loss on Z is consistent with published results on backscattering coefficient and energy loss for thick layers. An estimate of the mean free path for inelastic collisions proves to be in good agreement with the predictions of the Bohr-Bethe theory. Range-energy relations are almost independent of Z when the range is measured in mass per unit area.

INTRODUCTION

TPON passing through relatively thick layers of solid matter, electrons generally undergo a considerable number of collision processes in which they gradually lose their energy and change their direction. Although the individual collision processes are rather well understood in terms of elastic nuclear scattering, inelastic scattering on atomic electrons and collisions with the conduction electron plasma, a complete theoretical description of the plural and multiple scattering process, including elastic and inelastic collisions, is at present not possible.¹ Only for certain limiting cases does a successful theoretical treatment of the multiple scattering process exist. Molière² described multiple scattering for small individual deflections, not including any energy loss. The diffusion of high-energy electrons as a result of elastic collisions was treated by Bothe,3 Bethe, Rose, and Smith4 and more recently by Molière.⁵ The energy-loss distribution of electrons passing through solids due to inelastic scattering without appreciable deflection has been calculated by Landau, Blunk, and Leisegang, and others.6 The average rate of energy loss of electrons along their path is well described by Bethe's stopping

¹ See for instance: R. D. Birkhoff, *Handbuch der Physik* (Springer-Verlag, Berlin, 1958), Vol. 34, p. 53. ² G. Molière, Z. Naturforsch **3a**, 78 (1948).

⁸ W. Bothe, Z. Physik **54**, 161 (1928). ⁴ H. A. Bethe, M. E. Rose, and L. P. Smith, Proc. Am. Phil.

Soc. 78, 573 (1938).
 ⁶ G. Molière, Z. Physik 156, 318 (1959).
 ⁶ L. Landau, J. Phys. U.S.S.R. 8, 201 (1944); I. Blunck and S. Leisegang, Ann. Phys. 128, 500 (1950); K. C. Hines, Phys. Rev. 97, 1725 (1955); R. M. Sternheimer, Phys. Rev. 103, 511 (1956). (1956).