very wide range of polyvalent alloy systems. A well-marked regularity has emerged which has suggested that a physical distinction exists between two types of scattering in such alloys. If Z and Z_0 are the impurity and solvent valencies, respectively, then for $Z \geqslant Z_0$ there is a large contribution to the scattering arising from differences of potential deep inside the ion cores. However, for $Z < Z_0$, resistance arises primarily from scattering by the long-range Coulomb potential which can be reasonably approximated within the framework of existing simple models.

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Effect of Pressure on the Interstitial Diffusion of Nickel in Lead to 50 kbar*

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The diffusion of nickel in lead has been investigated using radioactive-tracer and sectioning techniques for pressures of up to 50 kbar and for temperatures in the range 208–591 °C. The data were analyzed assuming a single effective mechanism of diffusion with a temperature- and pressure-dependent activation energy and preexponential factor. The activation energy and volume at the melting temperature and atmospheric pressure are, respectively, $\Delta H = 10.6 \pm 0.4$ kcal/mole and $\Delta V/V_0 = 0.13 \pm 0.04$. The pressure and temperature coefficients of the activation volume, although quite uncertain, were also determined. The small activation energy and volume indicate that nickel diffuses in lead primarily by the interstitial mechanism.

I. INTRODUCTION

The diffusion of the near-noble metals (group IIB and VIIIB elements) in lead has been of interest since the early work of Seith, Hofer, and Etzold,[1] who measured the diffusion of Ni, Cd, and Hg in Pb. This interest stems at least in part from the observation that the diffusivity of these impurities in lead tends to be more rapid than for lead self-diffusion,[2,3] yet much less than for the diffusion of the noble metals in lead.[4] This observation is substantiated by the more recent work of Miller[5] for the diffusion of Cd in Pb and by preliminary measurements at this laboratory for Pd in Pb. Furthermore, a number of similar bimetallic systems have been found which also exhibit unusually rapid diffusion. These include Cu, Au, Zn, and Ag in Sn; Au and Ag in In and Tl; Au and Co in Pr; and Cu, Au, Na, Zn, and Ag in Li.[6] The basic question one would like to answer is in regard to the respective mechanisms of diffusion for these rapidly diffusing systems.

Recent high-pressure measurements for self-diffusion[7,8] and for impurity diffusion of the noble metals[9–11] in Pb have helped to establish the respective diffusion mechanisms involved. By applying kinetic theory and equilibrium thermodynamics, an activation volume ΔV is obtained through the pressure dependence of the diffusion coefficient. For interstitial diffusion ΔV involves only the activation volume of motion ΔV_m of the impurity ion, whereas for substitutional diffusion ΔV includes both an activation volume of motion ΔV_m and an activation volume of vacancy formation ΔV_f. Theoretical estimates[12,13] for ΔV_m and ΔV_f are < 0.2 and 0.55 atomic volumes, respectively. These estimates are in good agreement with the experimental values for ΔV_m and ΔV_f of 0.15 and 0.53 atomic volumes as obtained from high-pressure annealing[14] and quenching[15] experiments in Au. One further finds excellent correlation for the measured activation volume $\Delta V_m + \Delta V_f$ of 0.64–0.72 atomic volumes as obtained from measurements of the pressure dependence of Pb self-diffusion.[7,8]

The measured activation volumes for the diffusion of Cu, Au, and Ag in Pb are 0.04, 0.28, and

0.34 atomic volumes, respectively.[9] The activation volume for the diffusion of Cu in Pb is clearly in the range indicative of pure interstitial diffusion. However, the results for Au and Ag in Pb seem only to rule out substitutional or other large-activation-volume mechanism. Such considerations led Decker, Vanfleet, and co-workers,[10,11] Ascoli *et al.*,[16] Kidson,[17] and Dyson *et al.*[18] to postulate a combined interstitial-substitutional double mechanism. Miller,[5,19] making self-diffusion-enhancement measurements on Ag-, Au-, and Cd-Pb alloys, and Miller and Edelstein,[20] making isotope-effect measurements for the diffusion of Cd in Pb, concluded that the noble metals diffuse interstitially while Cd diffuses by the dissociative mechanism in Pb.[21]

Several questions regarding rapid bimetallic diffusion are still the subject of conjecture. For interstitial-dominated diffusion the effect of atom or ion size is not clearly understood nor is the relative importance of solvent and solute valence effects. One further finds a rather wide range of activation energies and volumes for bimetallic couples that diffuse rapidly in comparison to self-diffusion of the host, and only by correlating the results of several experiments can the mechanisms of diffusion be determined with any certainty. As one tabulates the systems which exhibit rapid diffusion one is struck with the fact that the noble metals Cu, Au, and Ag in that order occur over and over again. One also finds the alkali metals, the other periodic series of valence-I metals, along with several of the near-noble metals such as Co, Zn, and Cd, appearing as rapidly diffusing impurities in polyvalent hosts. One aspect of the basic problem of diffusion mechanisms can be answered by measurements of the activation volume through high-pressure diffusion measurements. In this experiment we have investigated the diffusion of Ni in Pb because it was suspected that Ni, because of its similarities to Cu, may be a rapidly diffusing impurity. This seems reasonable since Cu and Ni are miscible in all proportions, because of their similar electronic structures, and because of the large correlation energy discussed by Mott.[22]

II. EXPERIMENTAL PROCEDURE

Following the experimental procedures described by Candland, Decker, and Vanfleet[9] a total of 33 usable diffusion measurements were made for temperatures ranging between 208 and 591 °C at mean pressures of 1 bar and 20, 30, 40 and 50 kbar. One end of each cylindrical Pb crystal was plated with ^{63}Ni from a radioactive nickel-chloride solution prior to the high-pressure anneal. The plating solution was prepared by boiling off the HCl in the original International Chemical and Nuclear Corp. solution and then adding 10 ml of distilled water and 0.15 g of boric acid.

Oxides at the plated surface containing trapped ^{63}Ni were eliminated by our "preanneal" procedure. Each sample was dipped into 320 °C silicone fluid for 20 sec so that free ^{63}Ni diffused just beyond the Pb surface. This surface was then wiped on a Kimwipe until the lines, characteristic of the original microtome cut, were removed. This left the surface bright and polished in appearance.

Samples were then suspended in petroleum ether within a pressure cell similar to that described by Curtin *et al.*[11] These samples were then annealed after being brought to the desired pressure in a tetrahedral anvil press.

Liquid-scintillation-counting techniques made possible the efficient detection of the low-energy β^- particle emitted from the ^{63}Ni tracer. Each lead crystal was sectioned perpendicular to its axis by a microtome. Five successive 20-μ slices were placed in each polyethylene counting vial. The lead in each vial was dissolved in a 4-ml mixture of two parts glacial acetic acid, one part 30% hydrogen peroxide, and 21 parts distilled water. Gel-like fluorescent emulsions were formed by adding 10 ml of Insta-Gel (Packard Instrument Co.) to each vial. A Packard Tri-Carb liquid-scintillation spectrometer model 3320 was used to detect the fluorescent radiation.

III. METHOD OF ANALYSIS

The analysis of diffusion as a function of temperature and pressure has generally been interpreted in terms of kinetic theory. This theory leads to an expression for the measured diffusion coefficient D_m of the form

$$D_m(P, T) = fa^2\nu(P, T)e^{-\Delta G(P,T)/RT}, \tag{1}$$

where f is the product of a geometric and a correlation factor and a is the lattice parameter (a constant for our experiment because all samples were sectioned at 1 bar and 23 °C). ν is the mean vibrational frequency of the diffusing atoms, ΔG is the Gibbs free energy of activation per mole of activated complexes, R is the molar gas constant, P is the pressure, and T is the temperature. Following the analysis of Weyland *et al.*,[10] $\ln\nu(P, T)$ and $\Delta G(P, T)$ were expanded in Taylor series about $P=0$ and $T=T_0$ and the coefficients in the expansions determined by a least-squares fit of Eq. (1) to the diffusion data. In this way, one obtains the preexponential factor

$$D_0 = fa^2\,\nu(O, T_0)e^{\Delta S(O,T_0)/R}, \tag{2}$$

the activation energy or enthalpy $\Delta H(0, T_0)$, the activation volume $\Delta V(O, T_0)$, and the temperature

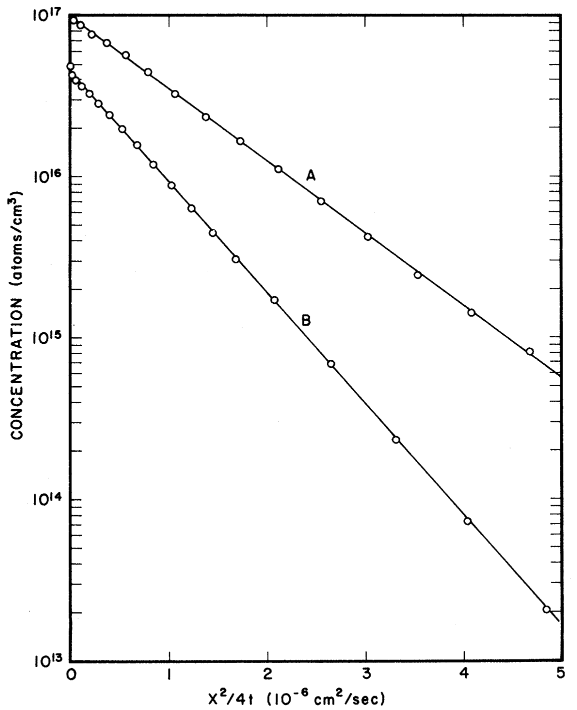

FIG. 1. Solute concentration profiles for the diffusion of Ni in Pb. Sample A was annealed for 28.1 min at 30 kbar and 389 °C, and sample B for 11.2 min at atmospheric pressure and 283 °C.

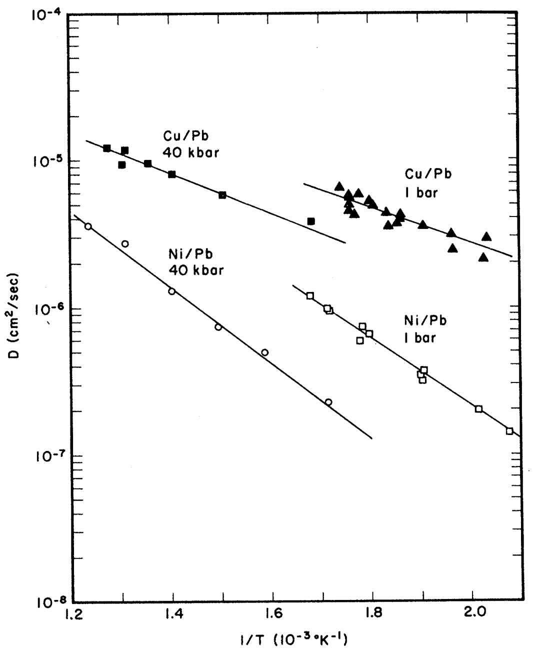

FIG. 2. Variation of the diffusion coefficient with inverse temperature for pressures of 1 bar and 40 kbar. The solid line represents the best fit of Eq. (1) to all of the data.

and pressure derivatives of the activation volume. It is also possible to obtain ΔC_p, the specific heat of activation, if accurate measurements are made over a sufficiently large temperature range.

The calibration of the high-pressure hydrostatic cell, along with the pressure and temperature corrections and uncertainties, is described and discussed by Candland *et al.*[9]

IV. RESULTS

Concentration profiles for two typical samples are shown in Fig. 1. Sample A was annealed at 30 kbar and 389 °C, whereas B was annealed at 1 bar and 283 °C. The concentration profiles for the high-pressure runs generally extended over 2–3 orders of magnitude while those at atmospheric pressure extended over 3–4 orders of magnitude. This difference in range was the result of having to use smaller samples for the high-pressure runs. It should also be noted that all samples that were preannealed and then annealed at temperatures greater than 210 °C were Gaussian in shape, similar to samples A and B.

The diffusion coefficients for Ni in Pb as a function of reciprocal temperature are shown in Fig. 2 for pressures of 1 bar and 40 kbar. Because of the temperature dependence of the pressure calibration no two high-pressure samples were annealed at exactly the same pressure. Hence the 40-kbar data points in Fig. 2 were corrected by as much as 1.3 kbar using the best-fit parameters from all the

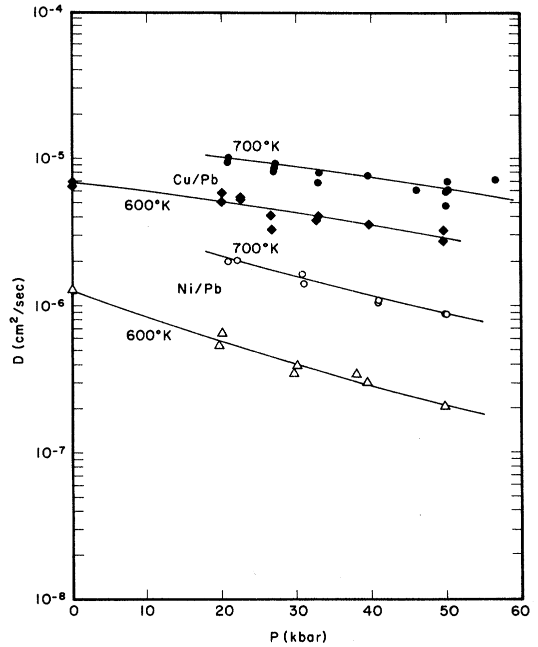

FIG. 3. Variation of the diffusion coefficient with pressure for temperatures of 600 and 700 °K. The solid line represents the best fit of Eq. (1) to all of the data.

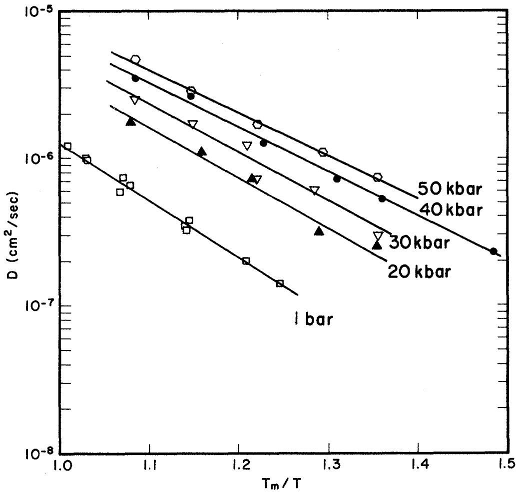

FIG. 4. Variation of the diffusion coefficient as a function of the ratio of the pressure-dependent melting temperature to the annealing temperature. The reciprocal of this ratio is referred to as the reduced temperature.

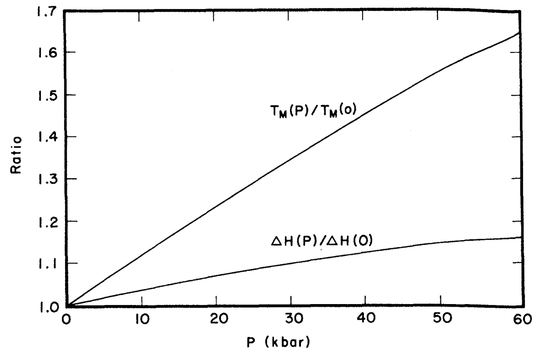

FIG. 5. Variation of the activation energy for the diffusion of Ni in Pb and the melting temperature of Pb with pressure. The melting-temperature data are from Ref. 24.

data and the expansion of Eq. (1).

The diffusion coefficients for Ni in Pb as a function of pressure are shown along the 600 and 700 °K isotherm in Fig. 3. Since no attempt was made to take the data isothermally, the data points as shown in Fig. 3 were corrected by as much as ± 50 °C using the best-fit parameters from all the data and the expansion of Eq. (1). The solid lines are again the best-fit curves of all the data to Eq. (1). For comparison, corresponding data from Ref. 9 for the diffusion of Cu in Pb have been included in Figs. 2 and 3.

Figures 4 and 5 have been included in order to discuss the applicability of Nachtrieb's[23] postulated law of corresponding states for diffusion along the melting curve. Figure 4 shows the diffusion coefficient versus the reciprocal of the reduced temperature $T_m(P)/T$ for all the data where $T_m(P)$ is the melting temperature of Pb as a function of pressure as measured by Millet.[24] The increase in ΔH as a function of pressure is compared with the increase in $T_m(P)$ in Fig. 5.

Table I shows the experimental values for the preexponential factor D_0, the activation energy ΔH, the activation volume per atomic volume $\Delta V/V_0$, and the pressure and temperature derivatives of the activation volume for both Ni and Cu in Pb. Note that D_0, ΔH, and ΔV are functions of temperature and/or pressure and have been calculated for various temperatures and pressures.

V. DISCUSSION

The experimental data with the associated uncertainties were analyzed assuming a single mech-

TABLE I. Measured parameters for the diffusion of Ni in Pb.

Solute	(P, T) (kbar, °K)	D_0 (10^{-3} cm²/sec)	ΔH (kcal/mole)	$\Delta V/V_0$	$\frac{1}{V_0}\left(\frac{\partial \Delta V}{\partial P}\right)_T$ (10^{-3}/kbar)	$\frac{1}{V_0}\left(\frac{\partial \Delta V}{\partial T}\right)_P$ (10^{-4}/°K)
Ni	(0, 298)	10.1 ± 3.4	10.63 ± 0.37	0.111 ± 0.04	−0.8 ± 0.8	0.7 ± 0.5
	(0, 600)	9.4	10.63	0.131		
	(0, 700)	9.1	10.63	0.137		
	(50, 298)	6.0	12.20	0.072		
	(50, 600)	5.7	12.20	0.092		
	(50, 700)	5.7	12.20	0.099		
Cu[a]	(0, 298)	0.83 ± 0.6	5.6 ± 0.5	0.047 ± 0.03	0.2 ± 0.4	0.3 ± 0.4
	(0, 600)	0.77	5.6	0.056		
	(0, 700)	0.75	5.6	0.058		
	(50, 298)	0.75	6.6	0.058		
	(50, 600)	0.72	6.6	0.066		
	(50, 700)	0.71	6.6	0.069		
Cd[b]	(0, • • •)	409 ± 100	21.2 ± 0.2			

[a] Candland, Decker, and Vanfleet, Ref. 9.

[b] Miller (temperature range 150–320 °C), Ref. 5.

anism of diffusion characterized by a pressure- and temperature-dependent activation energy and preexponential factor following the analysis of Weyland *et al.*[10] The specific heat of activation ΔC_p in this analysis was taken equal to zero because it did not appear to be statistically significant from the χ^2 test. However, the fit of the data to the other diffusion parameters, as determined by the χ^2 test, was significantly worsened by taking them outside the uncertainties quoted in Table I.

The diffusion constants as measured in this experiment were larger than the early measurements of Seith, Hofer, and Etzold[1] by a factor of about 4×10^3. In an attempt to determine how such a large discrepancy could occur when similar techniques by both sets of experimenters had yielded accepted values for other couples, we reanalyzed the concentration-profile data as reported in Seith *et al.*'s paper. The first problem we encountered was that their penetration curves were not consistent with the quoted solubilities. This led to an ambiguity as to how the data should be analyzed and what meaning the results might have for the proposed experiment. However, analyzing their data on the assumption of either a constant or semi-infinite source and assuming the relative concentrations to be correct, one finds the diffusion constants for their three measurements to be virtually independent of temperature. Their quoted low-temperature diffusion constant is smaller by a factor of about 10 than we calculated, whereas the other two values were within their uncertainties. Seith *et al.* obviously had misgivings about their Ni-in-Pb data since they failed to calculate an activation energy as they did for other diffusion couples reported in their paper. It seems likely that the early measurement is in error as the result of the severe solubility problem encountered and the current values for the diffusion parameters as reported here are correct within their uncertainties.

The small activation energy for the diffusion of Ni in Pb of 10.6 kcal/mole as measured in this experiment compared to 26.1 kcal/mole for self-diffusion, along with the small activation volume of 0.1 atomic volumes, seems to rule out substitutional diffusion and suggest an interstitial-dominated mechanism. However, on the basis of measurements on the linear enhancement of Pb self-diffusion[5,19] in Ag-, Au-, and Cd-Pb alloys and on the isotope effect[20] for Cd in Pb, Miller has concluded that impurity diffusion of the noble metals in Pb is dominated by pure interstitial diffusion and that Cd in Pb goes by the dissociative mechanism first proposed by Frank and Turnbull.[21] If the impurity ions of both Ni and Cd at Pb interstices are in their most common valence states with an effective charge $Z_{\text{eff}} = +2$ then, following the arguments of Miller, one would expect the diffusion of Ni in Pb to proceed by the dissociative mechanism. On the other hand, since the ionic radius of Ni^{+2} is much smaller than for Cu^{+1}, 0.72 and 0.96 Å, respectively, and because of the other similarities between Ni and Cu, one might expect Ni to diffuse interstitially in Pb as does Cu. On the hypothesis that this is the case and assuming the interactions to be primarily Coulombic in nature, one would expect the activation energy to be proportional to the effective ionic charge and hence for Ni about twice as large as the value measured for Cu in Pb. Furthermore, since the interatomic forces have doubled from Cu to Ni one would expect the activation volume for Ni to be larger than for a Cu impurity in Pb. Comparison of the data for Cu and Ni from Table I shows the conditions to be in agreement with the hypothesis of interstitial diffusion. Additional evidence that suggests that Ni in Pb diffuses by a pure interstitial mechanism is the small activation energy of 10.6 kcal/mole compared to 21.2 kcal/mole for Cd in Pb. If Ni and Cd diffused in Pb by the same mechanism and assuming the Pb lattice to be sufficiently open to accommodate the ions, one would have expected the activation energies to be about the same. It is therefore concluded on the basis of the correlation of the diffusion parameters of Ni in Pb with those for Cu in Pb, as opposed to those for Cd in Pb, that Ni in Pb diffuses by a pure interstitial mechanism and not by the dissociative mechanism.

Comparison of the properties of Pd and Pt with those of Ni, in light of the rapid diffusion of Ni, Cu, Au, and Ag in Pb, suggests that Pd and Pt will diffuse rapidly in Pb, probably by a pure interstitial mechanism.

On the basis of diffusion measurements to 10 kbar Nachtrieb[23] and his collaborators proposed a law of corresponding states for diffusion in solids,

$$D(P,T)=D_0 e^{-bT_m(P)/T}, \tag{3}$$

where D_0 and b are constants. Thus the pressure and temperature dependence of D is described wholly in terms of the reduced temperature $T/T_m(P)$ where $T_m(P)$ is the pressure-dependent melting temperature. From the results of Fig. 4 one can see that a single curve corresponding to Eq. (3) will not represent the data. Nachtrieb's law has also been interpreted to infer a proportionality between the activation energy and the alloy-melting temperature with pressure. This follows from Eq. (1) if the pressure dependence of $\nu(P,T)$ and $\Delta S(P,T)$ is small. One can see in Fig. 5 that $\Delta H(P,T)$ and $T_m(P)$ are not proportional for the diffusion of Ni in Pb and the second interpretation also fails. Nachtrieb's law has been shown to be invalid at relatively low pressures for the diffusion of Ni and Cu in Pb and Li in Ge[25] and in all likelihood fails in general at sufficiently high pressures.

VI. CONCLUSIONS

Comparison of the measured activation energy and volume from this experiment, with the results for Cu and Cd in Pb and with Pb self-diffusion, suggests that Ni diffuses in Pb by an interstitial-dominated mechanism. It also seems apparent that although both Ni and Cd probably diffuse as divalent ions in Pb they diffuse by different mechanisms. This difference is probably the result of the larger ionic radius of Cd.

It seems probable that because of the similarities between Ni, Cu, Ag, and Au with Pd and Pt that these impurities will also diffuse very rapidly in Pb.

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Transmission of Electromagnetic Waves through a Conducting Slab. IV. A Simple Multiple-Reflection Method

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We present a new method for calculating the electric field in the interior of a slab of finite thickness when the electrons suffer diffuse reflection at each surface. The method is a generalization of the multiple-internal-reflection scheme which may be familiar in the corresponding optical problem. As such, it requires knowledge only of the conductivity and of the field in the corresponding slab of infinite thickness. Its use makes clear the role that the emergent surface of the slab plays in sharpening the peak in transmitted intensity at cyclotron resonance in a normal magnetic field.

I. INTRODUCTION

There is recent and continuing interest in a class of experiments in which electromagnetic radiation is transmitted through a conducting slab of pure single-crystal metal in a magnetic field at low temperatures.[1-10] If the strength and direction of the magnetic field and the frequency of the radiation are suitably chosen, one can arrange to have no collective mode propagate through the plasma formed by the electrons in the interior of the conductor. Under these conditions, the primary mechanism of energy transport is likely to be single-particle excitations wherein individual electrons acquire energy from the incident electromagnetic field, carry that energy across the slab, and give it up to the transmitted field. The interest in such experiments stems from the fact that the transport of carriers across the slab occurs along trajectories which are determined only by the mag-