OPTICAL PROPERTIES OF ALUMINUM AND SOME DILUTE Al-Mg
AND Al-Li ALLOYS FROM 0.2 TO 3.0 eV AT 4.2 K

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Optical properties of aluminum and some dilute Al-Mg
and Al-Li alloys from 0.2 to 3.0 eV at 4.2 K

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The optical properties of aluminum and dilute alloys of lithium or magnesium in aluminum have been determined at 4.2 K for photon energies from 0.2 to 3.0 eV. A parallel band theory based on pseudopotentials has been fitted, along with a free electron contribution, to the data. Two pseudopotential Fourier coefficients and a free electron- and two interband relaxation times were used as adjustable parameters to achieve the fit. The variation of the inverse relaxation time with impurity concentration has been found to be approximately linear, as expected. Variations in the values of the two pseudopotential parameters with impurity concentration have also been found and are partially explained on the basis of a simple "virtual crystal" approximation. The most important results of the experiment are that for pure aluminum (1) the interband relaxation times are different than the free electron relaxation time; (2) the two interband relaxation times are different; and (3) the $T = 0$ values for the pseudopotential parameters are $U_{111} = 0.218 \pm 0.02$ eV and $U_{200} = 0.802 \pm 0.02$ eV.

INTRODUCTION

The optical properties of aluminum are among the most studied and best known of all metals. The reason for this is quite practical: aluminum is the material most often used for coating front-surface mirrors. The reflectance at normal incidence of aluminum is high in the visible light range and is also nearly as high in the near ultraviolet and remains there well into the vacuum ultraviolet region of the electromagnetic spectrum, being approximately seventy-five percent at a photon energy of 14 eV. Virtually the complete spectrum of aluminum has been studied from the far infrared and microwave regions to the hard X-ray region, and values have been given for the optical constants n and k from about 0.01 to 2000 eV with extrapolations added on to extend the range (1,2).

The knowledge of aluminum extends beyond the optical constants. The Fermi surface of aluminum is reasonably well known (3) and several good band structure calculations are available. Among these we count the recent one by Smrčka (4), one by Brust (5), and early ones by Segall (6), Harrison (7), and Ashcroft (3). These were calculated by various means and differ in the quantitative details of the bands, but they are qualitatively quite similar. The more complicated augmented plane wave (APW) calculation by Smrčka and the Green's function (or KKR) calculation by Segall agree well enough with the simpler pseudopotential method used by the others. In his Fermi surface work, Ashcroft (3) used a local pseudopotential model and was able to fit de Haas-van Alphen data very well by being able to specify just two pseudopotential Fourier coefficients. In

later work, Harrison (8) pointed out that the simple pseudopotential method could be used to predict absorptance maxima for the polyvalent metals and predicted two such maxima in the case of aluminum. These maxima show up as peaks in the optical conductivity of aluminum at photon energies of twice the pseudopotential Fourier coefficient. Bos and Lynch (9) showed conclusively that such was the case. They measured the absorptance at 4.2K and found peaks in the conductivity at about 0.5 and 1.5 eV. The low energy peak could not be observed at higher temperatures because of the strength of the free-electron absorption. At about the same time, Brust (5), by using the pseudopotential parameters of Ashcroft which best fit the Fermi surface data, demonstrated that the pseudopotential, or nearly-free-electron (NFE) model could be used to compute adequately the optical conductivity. Brust also observed that because the Fermi level is intersected by the crossing point of two bands in aluminum, interband absorption could extend down to zero photon energy.

Golovashkin et al. (10) made a calculation of the optical conductivity of the polyvalent metals and showed that from the measured conductivity, they could determine the pseudopotential Fourier coefficients. Ashcroft and Sturm (11) made a similar calculation and obtained an expression in closed form for the complex optical conductivity of the polyvalent metals. Mathewson and Myers (12) fit the latter theory to data on thin films of aluminum at several temperatures and in the process predicted $T = 0$ values for the pseudopotential Fourier coefficients U_{111} and U_{200} . Their data did not include the region of the spectrum containing the absorption peak caused by U_{111} so values of U_{111}

are subject to larger uncertainties than for U_{200} . In the present work, values of U_{111} and U_{200} at $T = 0$ are reported.

Mathewson and Myers also determined that the interband relaxation time is only about half that associated with the free electron absorption. The interband relaxation time was determined to be strongly temperature dependent, suggesting that the scattering is primarily due to electron-phonon interactions. It was assumed that the interband relaxation time is not energy dependent.

The present work centers on the determination of the parameters of the theory of Ashcroft and Sturm at low temperatures. Specifically, the absorptance of aluminum was measured at 4.2K and free electron and interband relaxation times and two pseudopotential Fourier coefficients were determined. Similar measurements and determinations were made for six dilute alloys of aluminum containing either lithium or magnesium. It was hoped to demonstrate that if the theory could be fitted to the data for the alloys, and if the fit were better for the alloys, that one could say something about the need for energy dependence in the various relaxation times. The idea is that in the most concentrated alloys impurity scattering should dominate and that it should be mostly energy-independent. The measurements extend from 0.2 to 3.0 eV. This range includes both prominent absorption peaks in the interband part of the optical conductivity.

THEORETICAL CONSIDERATIONS

Optical Properties of Metals

When electromagnetic radiation is incident on the surface of a metal, a fraction, R , of it will be reflected. The rest will either be absorbed or transmitted. If we restrict the discussion to bulk materials and omit thin films, we need not worry about transmission. R is called the reflectance of the metal. The reflectance at normal incidence is related to the complex index of refraction relative to the vacuum $\hat{n} = n + ik$, by

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (1)$$

n is the index of refraction and k the extinction coefficient. To learn anything meaningful about the metal, we must be able to determine n and k .

If we have n and k , we can solve for the complex dielectric constant,

$\hat{\epsilon} = \epsilon_1 + i\epsilon_2$. $\hat{\epsilon}$ is defined for nonmagnetic materials by

$$\hat{\epsilon} = \hat{n}^2, \quad (2)$$

$$\text{or by} \quad \epsilon_1 = n^2 - k^2 \quad (3a)$$

$$\text{and} \quad \epsilon_2 = 2nk. \quad (3b)$$

$\hat{\epsilon}$, and in particular, ϵ_2 , is the quantity most easily compared directly with theory, so it is desirable to extract ϵ_2 from the reflectance data.

To do so, we need to consider the electric field vector $\vec{E}_1$ of the incident

electromagnetic wave. The electric field vector $\vec{E}_r$ of the reflected wave is related to $\vec{E}_i$ by

$$\vec{E}_r = \hat{r} \vec{E}_i. \quad (4)$$

$\hat{r}$ is the amplitude reflection coefficient. In general the reflected wave is phase shifted with respect to the incident wave, so we write

$$\hat{r} = r \exp(i\theta) = \frac{\hat{n}-1}{\hat{n}+1}. \quad (5)$$

θ is the phase shift of the reflected wave relative to the incident wave at the surface. The intensity of the radiation is proportional to the square of the amplitude of the electric field vector, so we find that

$$R = |\hat{r}|^2 = r^2. \quad (6)$$

R , r , and θ are all dependent on the frequency of the radiation. In the case where R and θ can be measured simultaneously, the problem of determining n and k is solved. If, as is more frequently the case, only R is measured, we see that we need an alternate means for determining θ .

Fortunately, there is a convenient method for determining the phase, and this consists of the Kramers-Kronig integral for the phase. The appendix of the book by Wooten (13) contains a rather long and complicated argument for the purpose of showing that such a relation exists. The result is

$$\theta(\omega) = -\frac{\omega}{\pi} \int_0^{\infty} \frac{\ln R(\omega') - \ln R(\omega)}{\omega^2 - \omega'^2} d\omega' \quad (7)$$

The second term in the integral contributes nothing to the value of the integral but has the effect of removing from the integral a singularity at $\omega' = \omega$.

One problem with the Kramers-Kronig integral is that we need to know $R(\omega)$ over an infinite range of frequencies, while measurements are made over a rather limited range. If data of another experimenter are available in a range outside our own, we may be able to patch them together to get an extended range, or ranges. The growth of synchrotron radiation as a light source has greatly extended the range over which optical data exist for many materials. However, even with the availability of a wealth of data, there are gaps in existing data, and there will be a maximum and a minimum frequency above and below which no data exist. Beyond these, it is necessary to extrapolate. Usually, reliable estimates of the phase of the reflected light can be made from Equation (7) and the results used to calculate n and k .

Free Electron Absorption

In regions of the optical spectrum where there is no absorption due to interband transitions (discussed later), we may adopt a semiclassical model for absorption by conduction electrons--the Drude model. The Drude model begins with the assumption that electrons are bound to atoms by a mechanism obeying Hooke's law. The Hooke's law mechanism is accompanied

by damping. For conduction electrons, the restoring force constant is allowed to go to zero, but the damping parameter Γ is retained. The result is that we have

$$\epsilon = 1 - \frac{4\pi N e^2}{m} \frac{1}{\omega(\omega + i\Gamma)} \quad (8)$$

The quantity $(4\pi N e^2/m)^{1/2}$ is called the plasma frequency ω_p . N is the volume density of electrons. For the real and imaginary parts of the dielectric constant we have

$$\epsilon_1 = 1 - \frac{\omega_p^2}{\omega^2 + \Gamma^2} \quad (9a)$$

$$\epsilon_2 = \frac{\omega_p^2 \Gamma}{\omega(\omega^2 + \Gamma^2)} \quad (9b)$$

The Drude theory finds application mainly in the infrared and far infrared regions of the spectrum, i.e., below the frequency at which interband absorption sets in. The Drude theory is fitted to the low frequency end of the data (if this is below the interband edge) by adjustment of two parameters, Γ and ω_p . The damping parameter Γ is usually identified as $1/\tau$, where τ is the relaxation time or inverse scattering rate. Variation in ω_p comes from replacing m by the optical effective mass m^0 .

Actually, there should be Drude absorption throughout the spectrum,

but it generally is masked by interband transitions wherever they occur. In determining interband contributions to the dielectric constant, we must subtract the Drude term from the result of a Kramers-Kronig analysis to get the true interband dielectric constant.

Interband Absorption

In dealing with metals, the optical conductivity $\sigma = \omega\epsilon_2/4\pi$ is usually given instead of ϵ_2 , because at $\omega = 0$, ϵ_2 is singular, while σ converges to the dc conductivity. When the Drude conductivity is subtracted from the result of Kramers-Kronig analysis, there is always something remaining. The part remaining is attributed to interband transitions, although occasionally the remainder can be reduced with frequency-dependent relaxation times (14,15).

To expand upon the theory, we need to take into account the quantum nature of electrons and use the band picture of the electronic structure. In the solid the electron energies are strong functions of the wave vector $\vec{k}$ of the electron. For any $\vec{k}$ there are several electron states and each state corresponds to a unique energy level (which may be degenerate). A direct consequence of the periodicity of the crystal lattice is that we need consider only the $\vec{k}$ -vectors which lie within the first Brillouin zone--the unit cell of the reciprocal lattice. The energy levels for a given electron state are continuous functions of $\vec{k}$. The energy levels are filled up to a maximum energy E_F called the Fermi energy. A given band may be either completely filled or empty, or it may be only partially filled.

If we consider that usually the photon wave vector $\vec{q}$ of the incident light is much smaller than the electron wave vector $\vec{k}$, then we may say approximately that $\vec{q} = 0$ and consider only direct transitions from one energy state to another, for which the initial and final electron wave vector are the same. Direct interband transitions may occur only from a filled state to an empty state, i.e., the Fermi level must lie between the two bands. In Figure 1, transitions may begin for photon energy $\hbar\omega_0$ and will cease for energies greater than $\hbar\omega_1$, unless there is a larger separation of the bands at an intervening $\vec{k}$. For direct transitions from one band to another (we shall not consider nondirect interband contributions at all), we have

$$\sigma(\omega) = \frac{e^2}{4\pi m^2 \omega} \int d\vec{k} |\vec{a}_0 \cdot \vec{p}_{fi}|^2 \delta(E_{fi} - \hbar\omega), \quad (10)$$

where $\vec{a}_0$ is a polarization vector, $E_{fi} = E_f - E_i$ is the difference between the energies of the final and initial Bloch states, and $\vec{p}_{fi} = -(i\hbar/V_c) \int_c u_f^* \nabla u_i dr$ is the dipole matrix element between the states. V_c is the unit cell volume in real space.

A function closely related to $\epsilon_2(\omega)$ and hence to $\sigma(\omega)$ is defined by

$$J(E_{fi}) = \frac{2}{(2\pi)^3} \int d\vec{k} \delta(E_{fi} - \hbar\omega). \quad (11)$$

This is quite similar to the integral in Equation (10) but with the matrix element removed. Actually, any conclusion we draw from Equation (11) will

Figure 1. Hypothetical energy bands along a direction in k -space showing region where direct optical transitions can occur

apply to Equation (10) equally well. We note that the energy E_{fi} must equal $\hbar\omega$ everywhere as a requirement of the delta function, effectively defining a constant energy surface in k-space. We can transform the integral to an integral over that surface, the result being

$$J(E_{fi}) = \frac{2}{(2\pi)^3} \int_{S=E_{fi}} dS / |\nabla_{\mathbf{k}} E_{fi}|. \quad (12)$$

$J(E_{fi})$ is called the joint density of states. J is singular whenever $\nabla_{\mathbf{k}} E_{fi} = 0$. This happens at points of high symmetry in the Brillouin zone where the gradients of both energy bands vanish. Such points are called symmetry critical points, and absorption is enhanced at the critical points. However, critical points usually do not show up in the optical spectra of metals, but rather, have to be detected through some kind of modulation spectroscopy measurement.

There is another possibility not related to symmetry points, and that is whenever

$$\nabla_{\mathbf{k}f} E = \nabla_{\mathbf{k}i} E \neq 0. \quad (13)$$

Equation (13) would appear to represent an unlikely occurrence. However, there is a class of metals, the polyvalent metals, where band theory predicts the existence of parallel or nearly parallel bands in relatively large regions of the Brillouin zone--say one or two percent. If the bands were exactly parallel, the integral in Equation (12) would be singular

over large regions of the zone and we would have enhanced absorption over that same region.

Parallel Bands

Aluminum is an example of a polyvalent metal. The electron energy bands are somewhat free-electron like and aluminum is called a nearly free electron (NFE) metal. It is face-centered cubic in structure and has the Brillouin zone shown in Figure 2. To see how parallel bands arise, consider first the empty lattice model. We build the empty lattice by stacking Brillouin zones so as to fill all space. There is symmetry present, but there is zero potential everywhere. We focus attention on a common face of two zones side by side. In the upper part of Figure 3 we show the free electron parabolas for the symmetry line joining the centers of the two zones, one band for each zone. The bands intersect at the zone face. The energy of one such band is simply $\hbar^2 k^2 / 2m$, where now $k = |\vec{k}|$. If we turn our attention to the zone face, we find that for whichever direction we move from the center we can write the energy of the (doubly degenerate) band as

$$E_{\vec{k}} = (\hbar^2 / 2m) (\frac{1}{4}K^2 + k_{\perp}^2). \quad (14)$$

K is the magnitude of the reciprocal lattice vector joining the centers of the zones, and $k_{\perp}$ is the magnitude of the component of $\vec{k} = \frac{1}{2}\vec{K} + \vec{k}_{\perp}$ perpendicular to $\vec{K}$. The band described by Equation (14) is doubly degenerate exactly in the face, but splits into two bands when k does not

Figure 2. Brillouin zone for fcc lattice

Figure 3. Free electron energy bands in periodic zone scheme
 (a) Along symmetry line joining the centers of the zone
 (b) Doubly degenerate band lying in the zone face

quite lie in the face. The doubly degenerate band is shown in the lower part of Figure 3.

To get a more realistic picture we now include the crystal potential. Instead of using the actual crystal potential, it is easier to consider aluminum from a pseudopotential point of view (16). Bands computed from pseudopotentials and pseudo wave functions agree at least qualitatively with bands calculated from the more rigorous points of view (4-6). Because of the smallness of the pseudopotential (discussed in Appendix A), we can use degenerate perturbation theory. The secular equation for points near the zone face is given by the determinant

$$\begin{vmatrix} E_{\vec{k}} - E & U_K \\ U_K & E_{\vec{k}-\vec{K}} - E \end{vmatrix} = 0. \quad (15)$$

Here, $E_{\vec{k}} = (\hbar^2/2m)|\vec{k}|^2$, $E_{\vec{k}-\vec{K}} = (\hbar^2/2m)|\vec{k}-\vec{K}|^2$, and the matrix elements W_K of the pseudopotential are replaced by the "folded Fourier component" (11) of the pseudopotential U_K :

$$U_K = W_K + \sum_{K' \neq K} \frac{W_K W_{K-K'}}{E_{\vec{k}} - E_{\vec{k}-\vec{K}}}. \quad (16)$$

Equation (16) is a perturbation correction (11,17) to W_K to partially compensate for the fact that Equation (15) is the result of truncation of an infinite-order secular determinant.

The solution to Equation (15) is

$$E = \frac{1}{2} \{ E_{\vec{k}} + E_{\vec{k}-\vec{K}} \pm \sqrt{(E_{\vec{k}} - E_{\vec{k}-\vec{K}})^2 + 4U_K^2} \} . \quad (17)$$

For $\vec{k}$ exactly in the zone face

$$E = (\hbar^2/2m) (\frac{1}{2}K^2 + k_{\perp}^2) \pm |U_K| . \quad (18)$$

In Figure 4a we show the NFE band beginning at the center of the zone and its continuation in an extended zone scheme. Now it is discontinuous at the zone face. In Figure 4b we show the same thing in the reduced zone scheme. Above each view of the bands, we show schematically the intersection of the Fermi surface with the zone face. In Figure 4c we show the bands in the zone face for a particular direction of $\vec{k}$. These are the bands given by Equation (18). Above is shown the region of the zone face where the Fermi level is expected to lie between the parallel bands given by Equation (18).

In their extensive early study of the optical properties of aluminum, Ehrenreich et al. (18) proposed that parallel band absorption made large contributions to the structure in the optical spectrum of aluminum at 1.5 eV. Harrison (8) later supported their conclusion and predicted the absorption edge to be at $2|U_K|$ as given by Equation (18), and because there are two U_K 's, predicted a second absorption edge at much lower energy. Golovashkin et al. (10) and also Ashcroft and Sturm (11) made detailed calculations of the optical conductivity of polyvalent metals based on the pseudopotential model. We shall examine in detail the results of Ashcroft

(1)

(2)

Figure 4a. Schematic representation of the zone face

- (1) Schematic intersection of the Fermi sphere with the zone face
- (2) NFE bands in extended zone scheme showing discontinuity at zone boundary

Figure 4b. Same as Figure 4a, but in reduced zone scheme

Figure 4c. Schematic representation of the zone face intersected by the Fermi surface

- (1) The shaded area represents the region of the zone face where the Fermi energy lies between the parallel bands
- (2) Parallel bands in zone face along a direction perpendicular to symmetry axis in Figure 4b

(1)

(2)

and Sturm and apply them specifically to aluminum and the aluminum alloys. The model is characterized by local pseudopotential parameters and interband relaxation times. We shall observe how these parameters are affected by the alloying process.

Parallel Band Absorption in Aluminum

Ashcroft and Sturm (11) have made a model calculation of parallel band absorption in polyvalent metals. Their model is based on the local pseudopotential approximation. They managed to calculate in closed form the parallel band absorption associated with a single pseudopotential Fourier coefficient U_K near a zone face. To get the total absorption associated with a particular U_K we must multiply by the number of equivalent zone faces. For the Brillouin zone shown in Figure 2 there are two distinct types of zone face, so we need to include the calculation for the first two Fourier components of the pseudopotential beyond U_{000} , which just causes an overall shift of the bands.

The calculation proceeded in two phases. The first did not include any scattering or lifetime effects. The result is

$$\sigma_{PB} = \sigma_a a_0 K (2U_K / \hbar\omega)^2 (1 - (2U_K / \hbar\omega)^2)^{-1/2}. \quad (19)$$

a_0 is the first Bohr radius and $\sigma_a = e^2 / 24\pi a_0 \hbar = 5.48(10)^{14} \text{ sec}^{-1}$ is a convenient constant to factor out. Equation (19) predicts an infinite absorption edge in the conductivity at $\hbar\omega_e = 2|U_K|$ followed by a rapid decrease in value for energies slightly in excess of $\hbar\omega_e$.

A more realistic approach includes lifetime effects for broadening of the peak produced by Equation (19). This is the second phase of the work by Ashcroft and Sturm. The formalism is quite complicated and the result is quite long. We get a complex conductivity $\hat{\sigma} = i\hat{\epsilon}/4\pi$ from the replacement of the delta function in Equation (10) with factors proportional to $((E_{fi} - \hbar(\omega + i/\tau))^{-1} + (E_{fi} + \hbar(\omega + i/\tau))^{-1})$. The result for the real part is

$$\text{Re } \sigma_{PB}(\omega) = \sigma_a a_o K \left| \frac{2 U_K}{\hbar\omega} \right|^2 \frac{1}{1 + 1/(\omega\tau)^2} \\ \times \left\{ \left[1 - \left(\frac{2U_K}{\hbar\omega} \right)^2 + \frac{1}{(\omega\tau)^2} \right]^2 + \frac{4}{(\omega\tau)^2} \right\}^{-1/4} J(\omega) . \quad (20)$$

$J(\omega)$ —not to be confused with the density of states function—is a long and complicated function which is given in Appendix B. The imaginary part of the conductivity was also evaluated and is also presented in Appendix B.

It is now possible to do two things in the subsequent analysis of the data:

- 1) The reflectance data may be Kramers-Kronig analyzed to obtain $\epsilon_2 = \text{Re } \sigma$ and the result compared to the theory; or
- 2) The theory, including both the parallel band and Drude terms, may be fitted directly to the absorptance data.

Scattering Rates

In both the Drude term and the interband term we introduced relaxation times. The relaxation times are derived from several sources. For the free electron (Drude) term we first note that at room temperature the dominant contribution to scattering in the dc conductivity is from electron-phonon scattering. The effect is strongly temperature dependent, as evidenced by the fact that for pure (zone-refined--at least 99.9975% pure) aluminum, resistivity ratios $\rho_{\text{RmT}}/\rho_{4.2\text{K}}$ may have values of nearly 7000 (19). Since

$$\rho = 1/\sigma = m/ne^2\tau, \quad (21)$$

and since neither m , n , nor e exhibit such strong temperature dependence, apparently

$$\tau_{4.2\text{K}}/\tau_{\text{RmT}} \approx 7000. \quad (22)$$

If that were the whole story, one would expect optical relaxation times to become very large at liquid helium temperature. Such behavior has not been observed. Holstein (20), and more recently, Gurzhi (21) have derived expressions for the temperature dependence of the relaxation time for electron-phonon scattering. Gurzhi's expression also included photon energy dependence. At room temperature, the relaxation time is nearly constant for all photon energies, being only slightly larger for photon energies less than kT than for those greater than kT . At liquid helium

temperatures, τ is still almost constant for photon energies greater than kT , but can become up to seven orders of magnitude larger for photon energies between zero and kT . This would tend to support the contention that optical relaxation times are not as large at low temperatures as resistivity ratios predict, at least for pure samples. Impurity concentrations as low as a few ppm will severely limit relaxation times at low temperatures, so that in alloys impurity scattering will dominate. Specifically, Gurzhi has

$$\tau(T) = \tau^{(Cl)}(T)/\varphi(T). \quad (23)$$

$\tau^{(Cl)}(T) \sim 1/T$ is the relaxation time from resistivity theory, and

$$\varphi(T) = \frac{2}{\alpha} \left(\frac{\theta}{T} \right)^{-4} \int_0^{\theta/K} dv v^4 \left(\frac{2\alpha}{e^v - 1} + \frac{v - \alpha}{e^{v - \alpha} - 1} - \frac{v + \alpha}{e^{v + \alpha} - 1} \right). \quad (24)$$

$\alpha = \hbar\omega/kT$ and θ is the Debye temperature. For $\hbar\omega \gg k\theta \gg kT$ we find

$$\varphi(T) \approx 2\theta/5T \text{ so that} \quad (25)$$

$$\tau(T) \approx (5/2)\tau^{(Cl)}(\theta), \quad (26)$$

in agreement with the earlier work by Holstein (20).

In pure samples at low temperatures it may become possible for the mean free path to become comparable to or greater than the sample

dimensions, in which case we need to consider surface or boundary scattering. Gurzhi (21) has gone to considerable lengths to show that one may add the scattering rates for surface and volume (electron-phonon) scattering. With $1/\tau^s = 3\omega_p v_o / 8c$ (v_o being the mean electron velocity at the Fermi surface) we will have

$$\frac{1}{\tau} = \frac{1}{\tau^s} + \frac{1}{\tau^{ep}} \quad (27)$$

Gurzhi (22) has also derived an expression for the scattering rate due to electron-electron correlations. By considering the Fermi liquid theory of Landau (23), he has derived the following expression for the scattering rate due to the electron-electron correlations:

$$\frac{1}{\tau^{ee}} = \omega_p \left[\left(\frac{kT}{\hbar\omega_p} \right)^2 + \left(\frac{\omega}{2\pi\omega_p} \right)^2 \right]. \quad (28)$$

The assumption was made that $\hbar\omega$, kT , and $k\theta \ll E_F$, the Fermi energy of the metal. For aluminum at liquid helium temperature, $kT = 0.00362$ eV. The Debye temperature is 395K so that $k\theta = 0.0336$ eV. The Fermi energy is about 11.7 eV so Equation 28 should be valid over the range of the experiment discussed below.

In the alloys we must include scattering of electrons by impurities. The d.c. relaxation times for a number of impurities in aluminum can be determined from resistivity data (19), and it is hoped that these relaxation times are valid for the optical conductivity. The experiment was

performed on alloys of lithium and magnesium in aluminum. The scattering rate for lithium impurities is higher than that for a comparable concentration of magnesium impurities.

Work by Kliewer and Fuchs (24) has revealed that there is an energy dependence of the apparent free electron relaxation time in the infrared region of the spectrum. If one assumes that their result extends into the visible spectrum, one finds their expression reduces approximately to (at normal incidence)

$$\frac{1}{\tau'} = \frac{1}{\tau_{s'}} + \frac{1}{\tau} \left(1 - \frac{1}{\omega_p \tau} + \frac{1}{2} \left(\frac{\omega}{\omega_p} \right)^2 \right) \quad (29)$$

We consider τ to be an effective relaxation time given by

$$\frac{1}{\tau} = \frac{1}{\tau_{ep}} + \frac{1}{\tau_{ee}} + \frac{1}{\tau_i} \quad (30)$$

The impurity scattering is included as $1/\tau^i$. The result of Equation (29) is to cause an $(\hbar\omega)^2$ -dependence in the scattering rate which is even stronger than that predicted by the electron-electron scattering of Gurzhi.

When we examine the data below we should keep in mind that probably any energy dependence associated with the relaxation time is of the form

$$\frac{1}{\tau} = A + BE^2, \quad (31)$$

with E being the photon energy.

The above discussion of scattering rates is applicable mainly to free electron scattering. We have no prior knowledge of the scattering rate for interband transitions except the empirical results of Mathewson and Myers (12) which suggest that in pure aluminum, the interband scattering rate is approximately twice that for free electrons, and that the strong temperature dependence of the interband scattering rate suggests it also is due mainly to electron-phonon scattering.

Rigid Band Theory of Alloys

There are other effects of alloying in addition to increased scattering rates. The introduction of impurities destroys the periodic nature of the lattice and this immediately raises questions about whether we can speak in terms of Brillouin zones and energy bands as such. $\vec{k}$ is no longer a good quantum number since there is no longer a clearly defined correspondence between $\vec{k}$ and discrete energy levels.

One model which occasionally works for dilute alloys of metals of not too dissimilar natures is the rigid band model. In the rigid band model it is assumed that the band structure is essentially preserved but that all bands are shifted with respect to the Fermi level--or if a different reference is chosen--that the Fermi level has shifted because a different number of electrons is available to fill the same set of bands. Less naively, it is frequently stated that the density of states has shifted with respect to the Fermi level upon alloying.

We need to consider the electronic structure upon alloying because the Drude parameters and a few others necessary for the parallel-band

theory may change slightly upon alloying. Basically the Fermi wave vector (for a spherical Fermi surface) has a magnitude given by

$$k_F = (3\pi^2 ZN)^{1/3} \quad (32)$$

where Z is the number of electrons per atom and N is the density of atoms per unit volume. If the lattice constant should change upon alloying, N would change accordingly. Z will change if the valencies of the constituents are different. The plasma frequency ω_p will also change because of the same changes in N and Z that affect the Fermi energy. For truly parallel bands, on the other hand, shifting the Fermi level should not cause a change in the amount of parallel band absorption at a particular photon energy, but if the bands were not strictly parallel, a shift in the Fermi level could cause a shift in the location of the main absorption peak.

EXPERIMENTAL PROCEDURES

Sample Preparation

The aluminum sample was a single crystal which had been spark cut from a larger piece. The alloys were all polycrystalline and were spark cut from larger pieces. In the case of the alloys, the original large pieces were prepared by arc-melting the constituents together under vacuum in a water-cooled hearth. To ensure good mixing of the constituents, the piece of alloy was inverted and remelted. The process was repeated five or six times.

The next step in preparation is the mechanical polish given to produce a flat, smooth surface. The sample is first lapped flat on number 600 emery paper covered with water. This continued until visible evidence of spark-cutter damage disappeared. Then polishing continued on polishing cloth covered first with a slurry of water containing 1.0 micron average diameter particles of alumina, and then with 0.3 micron alumina. The result is a very shiny but amorphous surface.

To rid the surface of the damage from mechanical polishing, the samples were all electropolished in a standard solution of 6% perchloric acid in methyl alcohol at dry ice temperature. As much electropolish was permitted as the sample would allow before the surface would deteriorate to the point that it was too rough to use in the experiment. It was found that pure aluminum and the least concentrated alloys electropolished very nicely, leaving a smooth, shiny surface. The more concentrated alloys tended not to electropolish as well, but rather the surface would

begin to roughen, and under a microscope would show tiny pits scattered across the surface. The pitting is probably due to islands of the solute which have precipitated out upon cooling of the mixture of constituents in the arc-melter. This is not desirable, but it is not surprising since these alloy systems are all eutectic systems. None of the more concentrated alloys are solid solutions at room temperature and none appear to retain the composition of a solid solution in complete form as they are cooled in the arc-melter. More will be said about this below. Some of the alloys, then, were not electropolished as much as desired for removal of surface damage, but more than preferred when surface roughness was considered. The main effect of surface roughness is to cause scattering of the light reflected from the sample. As discussed below, this causes the apparent value of the absorptance to be higher than it really is.

After the heavy electropolishing, the aluminum single-crystal and the aluminum-magnesium alloys were annealed up to 100 hours at 550°C. The annealing is primarily to relieve strain. The aluminum-lithium alloys were not annealed because it was feared that the lithium might diffuse out of the samples.

The final step after annealing was to re-electropolish the samples. The appearance of the surface deteriorated after annealing. This second electropolish was always quite light. The sample was then mounted on the sample holder and then the sample holder was evacuated as quickly as possible to prevent further oxidation, although an aluminum surface quickly oxidizes to a thickness of about 30 Å and then is quite stable.

The oxide has little effect in the visible and infrared regions of the spectrum.

It had been hoped that a larger number of dilute alloys could be studied. The phase diagrams indicate that several substances exhibit moderate solid solubility in aluminum. Frequently, this amounts to about 2 atomic percent at 500°C. Silicon and germanium are two such substances. Alloys prepared as above produced systems that definitely had a two phase microstructure. Annealing at 550°C did not remedy the situation. Diluting the composition from about 2 atomic percent to 1 atomic percent did not seem to help. Annealing followed by quenching to room temperature did not break down the existing microstructure.

The phase diagrams for aluminum-zinc and aluminum-gallium look even more promising. At 400°C zinc appears to be about 60 atomic percent soluble in aluminum although the solubility drops to about one percent at room temperature. Aluminum-zinc did look like a good candidate for a quench, or since cooling in the arc-melter is quite rapid, that it might come out directly in solution. Such was not the case. Zinc produced the usual two phase system. Annealing did nothing more than to cause the zinc to evaporate directly out of the sample. Spectra taken on supposedly 2- and 4 atomic percent samples after annealing produced nearly identical results which were not much different than pure aluminum.

Aluminum-gallium was the most promising system of all. The phase diagram indicates that the maximum solubility of gallium in aluminum is right at room temperature. However, gallium is a peculiar substance. It melts just above room temperature, and in alloys, it has a tendency to

collect at grain boundaries. The appearance of the 2 atomic percent sample was that of a two phase system. Annealing did not improve it.

Attempts were made to put small amounts of manganese into aluminum, but the phase diagram indicates that even at 630°C (melting point), the solubility is only 0.8 atomic percent. A sample was made which contained 0.5 atomic percent manganese, but the result was a two phase system.

There are other possibilities which were not tried. Thus data were obtained only on Al-Mg and Al-Li alloy systems.

Experimental Apparatus

The measuring apparatus is the calorimeter built by Bos (25). Briefly, the sample is mounted onto a copper block in which are mounted two resistors, the first of which is a carbon resistor, the resistance of which is a strong function of temperature. The second is a metal film resistor, with nearly constant resistance for a wide range of temperatures. The carbon resistor is used as a thermometer to detect small changes in temperature in the copper block in which it is mounted, while the metal film resistor is used to cause small temperature changes.

Also in the sample chamber is a gold-black absorber, the function of which is to absorb all the light reflected from the sample. It is mounted on a copper block with two resistors, just as is the sample.

The two copper blocks are mounted on a blank ultra-high-vacuum flange which seals the end of the calorimeter, as shown schematically in Figure 5. The two copper blocks are mounted on the flange by means of stainless steel rods which have low thermal conductivities. The end of the

Figure 5. Schematic drawing of sample holder

calorimeter is kept in a liquid helium bath, and thermal contact between the copper blocks and the helium bath is maintained by means of thin copper wires. The lengths of the wires are adjusted to give each block a characteristic time in which to reach an equilibrium temperature whenever a small amount of heat is supplied to them. The times involved are typically several seconds to a minute.

Each carbon resistor is (separately) in series with several other resistors and a battery, all of which are external to the calorimeter. A potentiometer measures the voltage across one of the external resistors. If the resistance of the carbon resistor changes, the voltage across the potentiometer will also change.

When monochromatic light is focussed onto the sample, a fraction of it is absorbed and converted into heat which causes the temperature of the block and sample to rise a small amount. The light that is reflected by the sample is absorbed by the gold-black absorber, and the temperature of the associated copper block also rises a small amount. Note that if the sample is rough, light will be scattered so that not all that is reflected is collected by the absorber. The absorptance calculated under such conditions will be higher than the true value. This effect is more important at the higher photon energies.

Measurement of the absorptance of the sample begins by shining monochromatic light onto the sample. When both the copper blocks (sample and absorber) have reached the equilibrium temperatures, the respective potentiometers are balanced. Then the light is turned off, and small currents are supplied to the metal film resistors and adjusted until the

potentiometers are balanced again. Then the voltages across the heater resistors are measured. If P_a and P_s are the powers delivered to the resistors corresponding to the absorber and sample respectively, then the absorptance of the sample is simply

$$A = P_s / (P_s + P_a). \quad (33)$$

The denominator is proportional to the incident intensity of light I_o , but I_o need never be determined absolutely.

The calorimeter and cryosystem are shown schematically in Figure 6. The lens is used to focus the light onto the sample. The image from the spherical mirror above is at the aperture about halfway down the calorimeter, and the light would be too spread out to be of any use in heating the sample and absorber. The CaF_2 lens is useful in the visible and ultraviolet region of the spectrum, while the NaCl lens is useful in the infrared region of the spectrum. There is considerable overlap in the useful range of both lenses. The monochromator is a Leiss double prism monochromator with prisms for use from infrared to ultraviolet.

Figure 6. Schematic drawing of sample holder in place in the cryosystem. The optical path is shown by the dashed line

ANALYSIS OF THE DATA

Since the features of the conductivity of aluminum are well explained, the purpose of the analysis is not to search for new features, but rather to add to the details of the accepted explanations. This is best accomplished by attempting to fit the theoretical calculation to the experimental data. It would appear that we ought to be able to fit the theory directly to the data. However, the direct method involves a nonlinear least squares approach or some other complicated approach.

We have a closed-form mathematical model for the absorptance so at every point for which we have data, we have an equation in n variables. The variables are the U_K 's and τ 's. For each sample we have m such equations, one for each datum point. For each sample $m \gg n$ and the parameters (variables) are greatly overspecified. This would appear to make a nonlinear least squares approach feasible. This was attempted with a computer library program three times with three sets of parameters. The first set consisted of two U_K 's, two interband τ 's, the plasma energy $\hbar\omega_p$, and two parameters A and B such that the free electron relaxation time is given by $\tau^{-1} = A + B(\hbar\omega)^2$. The result was that the computer routine refused to converge within reasonable convergence criteria. The second set of parameters was the same as the first set with the omission of the plasma energy as a variable. $\hbar\omega_p$ was used as calculated under the rigid band model. Unfortunately, the program did not converge for the reduced set of variables. The third set was the same as the second, but the value of A was fixed by Kramers-Kronig analysis (below). Even with

the reduction to five variables, the method did not converge. The non-linear least squares fit approach was abandoned.

There is another technique which was attempted. The Newton-Raphson iterative technique is designed to provide a solution to n equations in n unknowns, given a reasonably good initial guess. The method may be outlined briefly as follows (26): Given a system of equations, $f_j(\vec{x}) = 0$, where $\vec{x} = (x_1, x_2, \dots, x_n)$, make a Taylor's series expansion to first order in terms of the n unknowns for each equation:

$$f_j(\vec{x}) = f_j(\vec{x}_0) + \sum_{i=1}^n \frac{\partial f_j(\vec{x})}{\partial x_i} \bigg|_{\vec{x}=\vec{x}_0} (\vec{x} - \vec{x}_0)_i, \quad (34)$$

for each j ($1 \leq j \leq n$). $\vec{x}_0$ is the initial guess. We then have a matrix equation for the $\Delta x_i = (\vec{x} - \vec{x}_0)_i$:

$$\frac{\partial f_i(\vec{x})}{\partial x_j} \bigg|_{\vec{x}=\vec{x}_0} \Delta x_j = f_i(\vec{x}) - f_i(\vec{x}_0). \quad (35)$$

Upon solution for the $\Delta \vec{x}$, we set $\vec{x}_0' = \vec{x}_0 + \Delta \vec{x}$ and repeat the procedure. Convergence of the method requires that in the neighborhood of a point $\vec{x}'$ where $f(\vec{x}') = 0$, that all the $\partial f_j / \partial x_i$ must be continuous near $\vec{x}'$, and the Jacobian of the system must not be zero at $\vec{x} = \vec{x}'$.

An attempt was made to fit the theory to the absorptance data. No six points were found where the method converged. The six variables were chosen to be two U_K 's, two τ 's for interband terms, and the free electron

τ and $\hbar\omega_p$. (Energy dependence in the free electron relaxation time was dropped for the sake of simplicity.)

Since the direct approach was unsuccessful another approach was tried. The data for all seven samples were Kramers-Kronig analyzed. The high energy extrapolation consisted of data assembled by Hagemann et al. (2). Their data were adjusted between 3.0 and 15.0 eV to provide a smooth match to the present data at 3.0 eV. The same extrapolation was used in the case of the alloys with only the above adjustment. It was felt that while the changes in plasma frequency and Fermi energy would alter the shape of the reflectance at higher energies, the corrections to the Kramers-Kronig integral, even from the region near the plasma energy, should be minor. The changes in relaxation time could have greater effect, but at higher energies, the electron-electron correlations should dominate, leaving the relaxation time essentially unchanged. The low energy extrapolation was constructed by estimating the parallel band parameters and then, by fitting the total calculated absorptance to the lowest energy datum point, the (constant) free electron relaxation time was determined. (This is the number which was used for the parameter A above.) Then the low energy reflectance was calculated to zero energy. The integration was performed numerically and the dielectric constants were determined. Then the free electron contribution (assuming the same constant relaxation time) was subtracted from the resulting optical conductivity. The parallel band theory was fitted to the interband conductivity by means of a least squares technique. The end product was a rather poor fit to the conductivity, and was not

satisfactory.

The Newton-Raphson iteration was used to fit the parallel band theory to the interband conductivity at four points. The four variables were the two U_K 's and two interband τ 's. It was observed that convergence of the iteration was extremely sensitive to which four points were selected. The interband conductivity of aluminum is shown in Figure 7. The four points had to be selected such that two points were in the vicinity of each of the two peaks, and no point was allowed in the region roughly midway between the two peaks. If a point were selected in the middle region, the iteration would invariably diverge. Because of this, the results of the fit to the conductivity were highly biased in favor of the regions near the peaks. The four points were selected, one each from four nonoverlapping regions of the spectra, and the iteration performed. If convergence occurred, it would usually come after three or four steps. Fifty sets of points were chosen at random so that fifty sets of parameter values were obtained for each sample. For each parameter, the mean value and standard deviation were calculated. In general, the standard deviations for the two U_K 's were just a few percent of the mean value. The standard deviations for the relaxation times were quite large, often of the order of 50 percent of the mean value.

The result of this iterative process is a fair fit to the conductivity in the peak regions and a poor fit in the remaining regions. The recalculation of the absorptance was in general quite poor.

The best fit to the data was obtained in the least satisfying manner. One parameter was varied and the value which minimized the

function

$$F = \left(\sum_{i=1}^n (\Delta A_i / A_i)^2 \right)^{1/2} \quad (36)$$

was assigned to that parameter. Here $A_i = A(E_i)$ and $\Delta A_i = A(E_i) - A_{th}(E_i)$, where $A_{th}(E_i)$ is the absorptance calculated at energy E_i . Then a different parameter was made variable and again F was minimized. This process was repeated as many times as necessary for each parameter in turn until no further improvement could be obtained.

The conductivities for just the interband terms resulting from Kramers-Kronig analysis are shown as the plotted points in Figures 7 through 13. The solid curves are the conductivities calculated from the parameters obtained from the direct fit to the absorptance and the dashed curves represent the fit obtained from the Newton-Raphson method. In Figures 14 through 20 the absorptance data are the plotted points. The curves are absorptances calculated from the same sets of parameters as in the previous seven figures.

Figure 7. Interband conductivity of single crystal aluminum. In this and in Figures 8-13, the data points represent the result of Kramers-Kronig analysis; the solid line is a calculation based on the parameters obtained from a direct fit of the theory to the absorptance; and the dashed curve was calculated from the parameters obtained from the Newton-Raphson iterative fit to the conductivity

Figure 8. Interband conductivity of Al + 2.2% Li

Figure 9. Interband conductivity of Al + 4.0% Li

Figure 10. Interband conductivity of Al + 5.5% Li

Figure 11. Interband conductivity of Al + 1.0% Mg

Figure 12. Interband conductivity of Al + 2.5% Mg

Figure 13. Interband conductivity of Al + 5.5% Mg

Figure 14. Absorbance of single crystal aluminum. In this and in Figures 15-20, the data points are the measured absorbance; the two curves are the absorbances calculated from the same sets of parameters used in Figures 7-13.

Figure 15. Absorptance of Al + 2.2% Li

Figure 16. Absorbance of Al + 4.0% Li

Figure 17. Absorbance of Al + 5.5% Li

Figure 18. Absorptance of Al + 1.0% Mg

Figure 19. Absorptance of Al + 2.5% Mg

Figure 20. Absorbance of Al + 5.5% Mg

RESULTS OF ANALYSIS

There are a number of observations to be made, some of which are expected and some of which are unexpected. First it is to be noted that two interband relaxation times are required. Neither is the same as the free electron relaxation time, and they may be ordered as follows: $\tau_{\text{free}} > \tau_{111} > \tau_{200}$. It was argued not very convincingly by Ashcroft and Sturm (11) that the interband and free electron relaxation times should be the same. It was observed by Mathewson and Myers (12) that such is definitely not the case. They reported that the interband relaxation time was approximately half the free electron relaxation time. What they reported was actually τ_{200} . There is no way they could determine if a separate relaxation time is required to accompany U_{111} since their data begin at 0.7 eV, well above the absorption edge. It turns out that the theory of Ashcroft and Sturm for no scattering is an excellent approximation to the theory with scattering just above the edge. This means it is possible to make a determination U_{111} from data above the edge, but not τ_{111} , since it is effective only near the edge.

It is expected that the addition of any impurity should cause an increase in the scattering rate and that the increase should be linear with increasing impurity content. We expect to predict what the increase should be by looking at the change in dc conductivity, or preferably resistivity. The change in resistivity is linear with increasing impurity content. The resistivity is given by

$$\rho = 1/\sigma = m/ne^2\tau \quad (37)$$

and for the alloys we can write

$$\rho = \rho_{\text{pure}} + x \cdot \Delta\rho_i \quad (38)$$

where x is the impurity concentration in atomic percent. $\Delta\rho_i$ is the change in resistivity for one atomic percent of impurity concentration.

If we rewrite Equation (38) as

$$\rho = \rho_{\text{pure}} (1 + x \cdot \Delta\rho_i / \rho_{\text{pure}}) \quad (39)$$

then we could say, because of Equation (37) that

$$1/\tau = (1/\tau_{\text{pure}}) (1 + x \cdot \Delta\rho_i / \rho_{\text{pure}}). \quad (40)$$

We have the expectation of stating that

$$1/\tau = 1/\tau_{\text{pure}} + x \cdot (1/\tau_i). \quad (41)$$

The results for the alloys of lithium and particularly magnesium in aluminum suggest that for all three relaxation times, Equation (40) is to be preferred to Equation (41) if the appropriate zero-concentration (inter-band or free electron) scattering rate is substituted for $(1/\tau_{\text{pure}})$. In Figures 21-23 the reduced scattering rates $1/\tau$ are shown as functions of impurity concentration for the three relaxation times. Note that there is considerable departure from a straight line in some cases and that the two sets of relaxation times determined by two different methods show considerable differences. Remarkably, in the face of all the differences, straight lines fitted in a least squares sense are nearly parallel. In

no case do the lines have the same intercept, making difficult the decision of which value of $1/\tau$ to use for pure aluminum. Also shown are lines drawn according to Equation (40) with the scattering rate obtained from the direct fit used as $1/\tau_{\text{pure}}$. The fit, particularly for the magnesium impurities, is very good. Lines drawn according to Equation (41) would have slopes which are too shallow.

Because no energy-dependent scattering rate for free electrons was determined, it is difficult to say whether the agreement shown in Figures 21-23 is a fortuitous coincidence, or if it is quite real. There seems to be no theoretical work in this area. The values for the scattering rates are given in Table 1. The equations of the lines drawn in Figures 21-23 are given in Table 2.

Table 1. The free electron (constant) and two interband scattering rates for all seven samples

Sample	$\hbar/\tau_0$ (eV)	$\hbar/\tau_{111}$ (eV)	$\hbar/\tau_{200}$ (eV)
Single Crystal Al	0.060	0.079	0.108
Al + 2.2% Li	0.112	0.137	0.167
Al + 4.0% Li	0.143	0.115	0.200
Al + 5.5% Li	0.161	0.208	0.256
Al + 1.0% Mg	0.084	0.092	0.120
Al + 2.5% Mg	0.109	0.121	0.166
Al + 5.5% Mg	0.133	0.164	0.213

Figure 21. The Drude scattering rates. The solid line and circles are the results of the direct fits; the dashed line and triangles are the results of the iterative fit; and the dash-dotted line was calculated from Equation (40)

Figure 22. The interband scattering rates corresponding to U_{111} . The points and lines have the same significance as in Figure 21

Figure 23. The interband scattering rates corresponding to U_{200} . The points and lines have the same significance as in Figure 21.

Table 2. The equations for the scattering rates for Al-Li and Al-Mg alloy systems. DF refers to values obtained from a direct fit, KK refers to the iteration following the Kramers-Kronig inversion, and Res refers to values obtained from Equation (40). x is the impurity concentration in atomic percent. $\hbar/\tau$ is in eV

Free electron term	Al-Li	DF: $\hbar/\tau = 0.0185x + 0.065$
		KK: $\hbar/\tau = 0.0186x + 0.047$
		Res: $\hbar/\tau = 0.0197x + 0.060$
	Al-Mg	DF: $\hbar/\tau = 0.0128x + 0.068$
		KK: $\hbar/\tau = 0.0137x + 0.051$
		Res: $\hbar/\tau = 0.0110x + 0.060$
U_{111} term	Al-Li	DF: $\hbar/\tau = 0.0196x + 0.077$
		KK: $\hbar/\tau = 0.0245x + 0.077$
		Res: $\hbar/\tau = 0.0259x + 0.$
	Al-Mg	DF: $\hbar/\tau = 0.0157x + 0.079$
		KK: $\hbar/\tau = 0.0183x + 0.091$
		Res: $\hbar/\tau = 0.0144x + 0.079$
U_{200} term	Al-Li	DF: $\hbar/\tau = 0.0261x + 0.107$
		KK: $\hbar/\tau = 0.0239x + 0.128$
		Res: $\hbar/\tau = 0.0356x + 0.107$
		DF: $\hbar/\tau = 0.0197x + 0.107$
		KK: $\hbar/\tau = 0.0172x + 0.128$
		Res: $\hbar/\tau = 0.0198x + 0.107$

There are observations to be made concerning the values of the U_K . In the first place, they are larger for pure aluminum than predicted by Mathewson and Myers (12). They predicted that at zero temperature $U_{111} = 0.195 \pm 0.02$ and $U_{200} = 0.78 \pm 0.01$ eV. The best numbers available from the present work are presumably from the best fit to the data, in which case the values are $U_{111} = 0.218$ and $U_{200} = 0.802$ eV. The

Figure 24. The experimental values of U_{111} and U_{200} . The points and lines have the same significance as in Figure 21

experimental uncertainty in the data is expected to amount to about 2 percent at energies near 1.5 eV but may reach as much as 10 percent at the lower energies (25). We are further confounded by the fact that if we had an energy dependent free electron relaxation time, we would be confronted with slightly different values for all of the parameters. A recent study by Wooten et al. (27) shows that in the absence of extreme accuracy in the infrared portion of the spectrum, the data cannot produce accurate values of the optical constants. Based on the above percent uncertainties, the best we could hope for in our determination for either U_{111} or U_{200} is an absolute ± 0.02 eV. In this case we can claim good agreement with the values of Mathewson and Myers.

A more startling observation is the fact that addition of lithium causes the value of U_{111} to increase, while leaving U_{200} relatively unaffected. Addition of magnesium leaves U_{111} mostly unaffected but causes U_{200} to decrease with a slope of magnitude approximately equal to the increase in U_{111} caused by the addition of lithium. This shows consistent behavior for the two systems: i.e., the difference in slope for the two U_K 's is approximately the same for both alloy systems. The values of both U_K 's for all seven samples are given in Table 3 and are plotted along with lines fit to the points in a least squares sense in Figure 24. In the figure, points from the iterative method are included, mainly for comparison.

To explain the behavior of the U_K 's, we need to return to the basic pseudopotential formulation in Appendix A and make use of Equations (A7) and (A8) with $S(K) = 1$:

$$W_K = \langle \vec{k} + \vec{K} | w | \vec{k} \rangle : \quad (42)$$

Table 3. Values of U_{111} and U_{200} for all seven samples

Sample	U_{111} (eV)	U_{200} (eV)
Single-crystal Al	0.218	0.802
Al + 2.2% Li	0.230	0.799
Al + 4.0% Li	0.241	0.799
Al + 5.5% Li	0.253	0.799
Al + 1.0% Mg	0.219	0.796
Al + 2.5% Mg	0.220	0.785
Al + 5.5% Mg	0.219	0.768

This can be evaluated from the tables of Animalu presented in Reference 16. The OPW form factors in the tables are presented as a function of $q/2k_F$, the latter ranging from 0 to 1. Alloying causes the Fermi level to shift. Figure 25 shows that if the quantity $K/2k_F$ changes, so does $\langle \vec{k} + \vec{K} | w | \vec{k} \rangle$. Further along this line is the fact that a change in the lattice constant will change K and hence $K/2k_F$. The coefficient of linear expansion for lithium in aluminum is about $-0.00013 \text{ \AA/At\%}$, negligible for our purposes. The same quantity for magnesium in aluminum is $+0.0047 \text{ \AA/At\%}$ (19). This expansion of the crystal lattice causes a contraction in the reciprocal lattice for the Al-Mg alloys. Figure 25 shows that the slopes and curvature of the OPW form factor are different at the points $K/2k_F$ corresponding to the two Fourier coefficients. Thus it seems likely that

Figure 25. OPW form factors for aluminum (solid line), lithium (dashed line), and magnesium (dash-dotted line) as computed by Animalu (16)

alloying should change the two U_K 's differently.

There is another consideration. In Figure 25 the OPW form factors for lithium and magnesium are also presented for comparison. It seems unlikely that the effective OPW form factor should be just that of aluminum, even though in our rigid band model that is basically what we have assumed. The best approach to the combination of potentials seems to involve scattering theory (see, for example Reference 28). Such an elegant approach is beyond the scope of this discussion. We can learn what we want from a much cruder approximation, the virtual-crystal approximation. In this approximation, the effective OPW form factor is taken to be simply

$$\langle \vec{k} + \vec{K} | w_{\text{eff}} | \vec{k} \rangle = x \langle \vec{k} + \vec{K} | w_{\text{Al}} | \vec{k} \rangle + (1-x) \langle \vec{k} + \vec{K} | w_{\text{imp}} | \vec{k} \rangle. \quad (43)$$

Here x is the fraction of impurity present on an atomic basis. From the tabulation of Animalu (16) we combine the OPW form factors of Al and Li or Mg according to the above prescription. A four-point Lagrangian interpolation was used to obtain $\langle \vec{k} + \vec{K} | w_{\text{eff}} | \vec{k} \rangle$ at the corrected value of $K/2k_F$. The results are shown in Figure 26 along with values of $\langle \vec{k} + \vec{K} | w_{\text{Al}} | \vec{k} \rangle$ computed at the same values of $K/2k_F$. The numbers obtained are not the U_K 's. We have made no attempt to calculate the U_K 's from the w_K 's. All that was sought was the effect of alloying upon the pseudopotentials. In Table 4 we give the results of the calculation in the virtual crystal approximation. Note that for the Al-Li alloys U_{200} and U_{111} are both increasing while U_{111} is increasing more rapidly. The data show similar behavior, except with U_{200} unchanged. For the Al-Mg alloys, the calculation shows both U_{111} and U_{200} decreasing, but with U_{200} decreasing more rapidly. The data show that

Figure 26. Variation of W_{111} and W_{200} with addition of impurities in virtual crystal approximation. Isolated points are for uncorrected aluminum OPW form factor, calculated at the corrected value of $K/2k_F$.

U_{111} is essentially unchanged upon alloying with magnesium. What we have shown is that it is entirely reasonable that the two pseudopotential Fourier coefficients should behave differently when impurities are introduced into the aluminum lattice.

Table 4. Fermi wave vector, reciprocal lattice vectors, and values of corrected pseudopotential Fourier coefficients for seven samples

Sample	k_F (10^8 cm^{-1})	$K(1,1,1)$ (10^8 cm^{-1})	W_{111} (eV)	$K(2,0,0)$ (10^8 cm^{-1})	W_{200} (eV)
Aluminum	1.749	2.700	.256	3.117	.822
Al + 2.2% Li	1.742	2.700	.269	3.117	.831
Al + 4.0% Li	1.736	2.700	.284	3.117	.835
Al + 5.5% Li	1.731	2.700	.293	3.117	.837
Al + 1.0% Mg	1.745	2.696	.257	3.114	.821
Al + 2.5% Mg	1.739	2.690	.256	3.107	.818
Al + 5.5% Mg	1.730	2.679	.252	3.094	.808

An observation about the parallel band theory is now in order. The presence of scattering modifies the theory which includes no scattering more than just broadening the peak in the absorptance spectrum. If we merely increase the scattering rate, we cause the peak in the conductivity to shift to a higher energy. This is similar to the effect of increasing the value of U_K , except that by increasing the value of U_K , we do not get the

broadening of the peak which accompanies an increased scattering rate. Unfortunately, the theory seems incapable of fitting the data away from the main absorption peaks. Nilsson (29) has speculated upon the effects of including two U_K 's when constructing the energy bands near the zone face. If including the second U_K would cause the bands to be not quite parallel, this in turn should cause broadening in the absorption peaks. The results of his calculation show that the bands remain remarkably parallel; parallel even when a second U_K is included (29). Sturm and Ashcroft (30) have published what may be a fundamental improvement in the parallel band theory. They included nonlocal effects in the pseudopotentials and obtained bands which are not quite parallel. The result is that there is additional broadening of the absorption peak. The result is quite complex and is not available in closed form. Because of this complexity, the new theory was not included in the calculations of this study. It would be pure speculation to claim that the newer theory would create a better fit to the data, say in the region around 1.2 eV. It would be equally speculative to claim that an energy dependent relaxation time could accomplish the same thing.

CONCLUSION

We have made measurements on the absorptance of aluminum and several dilute alloys of aluminum at 4.2 K, hoping to determine the low-temperature values of the pseudopotential Fourier coefficients and relaxation times in the theory of Ashcroft and Sturm. It had been hoped to determine explicitly if energy dependence is necessary in the free electron term or even in the parallel band terms. In the case of the alloys, in general, the fit of the theory to the data improves with increasing impurity concentration. This was all done with constant relaxation times which suggests that if energy dependence is necessary for pure aluminum, the dependence is either suppressed or made relatively less important as impurity scattering increases. According to Kliever and Fuchs (24), the impurity scattering rate should be modulated by the factor $1 + \frac{1}{2}(\omega/\omega_p)^2$. This would make the energy dependence of the scattering rate of the alloys even stronger than for the pure metal. Apparently this would contradict the results which suggest that energy dependence is less important in the more concentrated alloys, although it is questionable if we could see the energy dependence predicted by this modulation effect, since it is expected to be small. In all probability a small energy dependence in τ would not be sufficient to create a better fit to the data in the region between the absorption peaks--say at 1.2 eV. It seems more likely that some fundamental change--such as nonlocal effects (30)--is required in the basic theory (11). Such a change might even reduce the number of independent relaxation times.

The changes in the U_K 's upon alloying are nicely explained by the

virtual crystal approximation, suggesting that there are still a few simple applications for such an unrefined theory.

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APPENDIX A

In the nearly free electron model, it is often found that a pseudopotential approach is sufficient to describe the bands. The pseudopotential $W(\vec{r})$ is related to the actual crystal potential $V(\vec{r})$ by

$$W(\vec{r}) = V(\vec{r}) + (E_{\vec{k}} - H)P. \quad (A1)$$

In (A1), $P = \sum_{\alpha} |\alpha\rangle\langle\alpha|$ is a projection operator which projects an arbitrary function onto the core states and H is the Hamiltonian operator

$$H = -(\hbar^2/2m)\nabla^2 + V(\vec{r}). \quad (A2)$$

Quite often, the complicated operator term in (A1) is replaced by a scalar which is then only a function of position. In this case we are left with a local pseudopotential. The operator in (A1) makes a repulsive contribution while the potential is attractive. There are strong cancellation effects and the pseudopotential is actually a weak form of the potential. It is this weakness which makes the pseudopotential approach especially useful. It frequently is used as a perturbation correction to the free electron part of the Hamiltonian. In passing it should be noted that the pseudopotential defined in (A1) is not unique, and care must be taken to choose it properly.

The pseudopotential may be used in a Schrödinger wave equation

$$\{-(\hbar^2/2m)\nabla^2 + W(\vec{r})\} \varphi_{\vec{k}} = E_{\vec{k}} \varphi_{\vec{k}}. \quad (A3)$$

$\varphi_{\vec{k}}$ is the pseudo wave function and is related to the actual wave function by

$$\psi_{\vec{k}} = (1 - P)\varphi_{\vec{k}}. \quad (A4)$$

It is frequently convenient to expand $W(\mathbf{r})$ in a Fourier lattice series:

$$W(\mathbf{r}) = \sum_{\mathbf{K}'} W_{\mathbf{K}'} \exp(i\mathbf{K}' \cdot \mathbf{r}) \quad (\text{A5})$$

The matrix elements of the pseudopotential between two plane wave states are simply

$$\langle \mathbf{k} + \mathbf{q} | W(\mathbf{r}) | \mathbf{k} \rangle = \sum_{\mathbf{K}'} W_{\mathbf{K}'} \delta_{\mathbf{K}', \mathbf{q}} = W_{\mathbf{q}}. \quad (\text{A6})$$

But in this case $\mathbf{q}$ must be a reciprocal lattice vector, say, $\mathbf{K}$. So

$$W_{\mathbf{K}} = \langle \mathbf{k} + \mathbf{K} | W(\mathbf{r}) | \mathbf{k} \rangle. \quad (\text{A7})$$

But $\langle \mathbf{k} + \mathbf{q} | W(\mathbf{r}) | \mathbf{k} \rangle$ may be written as

$$\langle \mathbf{k} + \mathbf{q} | W(\mathbf{r}) | \mathbf{k} \rangle = S(\mathbf{q}) \langle \mathbf{k} + \mathbf{q} | w(\mathbf{r}) | \mathbf{k} \rangle, \quad (\text{A8})$$

where $w(\mathbf{r})$ is the pseudopotential due to a single ion. This comes about because we can write

$$W(\mathbf{r}) = \sum_j w(\mathbf{r} - \mathbf{r}_j). \quad (\text{A9})$$

j denotes the individual lattice sites. $S(\mathbf{q})$ is called the structure factor and is just a geometrical constant. In the case of a perfect metal lattice, $S(\mathbf{q}) = 1$ if $\mathbf{q}$ is equal to a reciprocal lattice vector or $S(\mathbf{q}) = 0$ otherwise. The quantity $\langle \mathbf{k} + \mathbf{q} | w(\mathbf{r}) | \mathbf{k} \rangle$ is called the OPW form factor. Suitable tables of the OPW form factors of the polyvalent metals are tabulated by Harrison (16). Note that the form factors are defined for $0 \leq q/2k_F \leq 1$ even though the structure factor exists only for $\mathbf{q} = \mathbf{K}$, $\mathbf{K}$ being a reciprocal lattice vector.

APPENDIX B

The formulae for the real and imaginary parts of the conductivity came from integrating

$$\sigma_{PB}(\omega) = \frac{\sigma_a a_o K \epsilon_K^2}{4 \hbar \omega \pi |U_K|} \int \frac{dk_{||}}{K} \left[\frac{k_{||}(k_{||})}{K} \right]^2 \left[\frac{\hbar \omega}{2U_K(1+\gamma^2)^{\frac{1}{2}}} \right]^2$$

$$\times \frac{1}{1+\gamma^2} \left(\frac{1}{(1+\gamma^2)^{\frac{1}{2}} - z - ib} + \frac{1}{(1+\gamma^2)^{\frac{1}{2}} + z + ib} \right) \quad (B1)$$

where $z = \hbar \omega / 2 |U_K|$, and $b = (\hbar / \tau) / 2 |U_K|$. The result of integration with

$$\left[\frac{k_{||}(k_{||})}{K} \right]^2 = \frac{2U_K}{E_K} (1 + \gamma^2)^{\frac{1}{2}} \quad (B2)$$

and with the substitution $y = 1 + \gamma^2$ is Equation (20). The function $J(\omega)$ is given by

$$J(\omega) = (1/\pi(b^2 + z^2)) \{ 4zb \tan^{-1} t_o$$

$$+ \frac{1}{2} [(z^2 - b^2) \cos \phi_2 + 2zbs \sin \phi_2] \ln \frac{t_o^2 + 2t_o \rho \sin \phi_2 + \rho^2}{t_o^2 - 2t_o \rho \sin \phi_2 + \rho^2}$$

$$+ [(z^2 - b^2) \sin \phi_2 - 2zbc \cos \phi_2] \left(\tan^{-1} \frac{t_o - \rho \sin \phi_2}{\rho \cos \phi_2} \right.$$

$$\left. + \tan^{-1} \frac{t_o - \rho \sin \phi_2}{\rho \cos \phi_2} \right) \} \quad (B3)$$

where

$$\phi_2 = \frac{1}{2}(\frac{1}{2}\pi - \tan^{-1}(\frac{1 + b^2 - z^2}{2bz})) ,$$

$$\rho^2 = [(1 + b^2 - z^2)^2 + (2zb)^2]^{\frac{1}{2}}$$

$$z_o = \hbar\omega_o / 2|U_K|$$

$$t_o = (z_o^2 - 1)^{\frac{1}{2}} .$$

$\hbar\omega_o$ is the energy at which parallel band absorption ceases and is given by $2(E_K E_F + U_K^2)^{\frac{1}{2}} - E_K$. The result for $\text{Im}\sigma_{PB}(\omega)$ is

$$\begin{aligned} \text{Im}\sigma_{PB}(\omega) = & \frac{\sigma_a a_o K}{2\pi b \rho} \left\{ \frac{1}{2} \sin\phi_1 \ln \left(\frac{t_o^2 + 2t_o \rho \cos\phi_1 + \rho^2}{t_o^2 - 2t_o \rho \cos\phi_1 + \rho^2} \right) \right. \\ & + \cos\phi_1 \left[\tan^{-1} \left(\frac{t_o + \cos\phi_1}{\sin\phi_1} \right) + \tan^{-1} \left(\frac{t_o - \cos\phi_1}{\sin\phi_1} \right) \right] \\ & \left. + \frac{b^2 - z^2}{b^2 + z^2} (\pi J(\omega)) \right\} \end{aligned} \quad (B4)$$

where

$$\phi_1 = \frac{1}{2}\pi - \phi_2 .$$