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Optical Properties and Electronic Structures of d- and
f-electron Metals and Alloys, Ag-In, Ni-Cu, AuGa₂, PtGa₂,
 β' -NiAl, β' -CoAl, CeSn₃, and LaSn₃

by

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Optical properties and electronic structures of d - and f -electron metals and alloys,
Ag-In, *Ni-Cu*, *AuGa₂*, *PtGa₂*, β' -*NiAl*, β' -*CoAl*, *CeSn₃*, and *LaSn₃*

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Optical properties and electronic structures of disordered $Ag_{1-x}In_x$ ($x = 0.0, 0.04, 0.08, 0.12$) and $Ni_{1-x}Cu_x$ ($x = 0.0, 0.1, 0.3, 0.4$) alloys and ordered *AuGa₂*, *PtGa₂*, β' -*NiAl*, β' -*CoAl*, *CeSn₃*, and *LaSn₃* have been studied. The complex dielectric functions have been determined for $Ag_{1-x}In_x$, $Ni_{1-x}Cu_x$, *AuGa₂*, and *PtGa₂* in the 1.2 - 5.5 eV region and for *CeSn₃* and *LaSn₃* in the 1.5 - 4.5 eV region using spectroscopic ellipsometry. Self-consistent relativistic band calculations using the linearized-augmented-plane-wave method have been performed for *AuGa₂*, *PtGa₂*, β' -*NiAl*, β' -*CoAl*, *CeSn₃*, and *LaSn₃* to interpret the experimental optical spectra. In $Ag_{1-x}In_x$, the intraband scattering rate increases with increasing *In* concentration in the low-energy region (< 3.5 eV). As the *In* concentration increases, the onset energy of the $L_3 \rightarrow L'_2(E_F)$ transitions, 4.03 eV for pure *Ag*, shifts to higher energies, while that of the $L'_2(E_F) \rightarrow L_1$ transitions, 3.87 eV for pure *Ag*, shifts to lower energies. This is only partly attributable to the rise of the Fermi level E_F caused by an increase in the average number of electrons per atom due to the *In* solute and to the narrowing of the *Ag* 4*d*-bands. The L_1 -band may also lower as *In* is added. In $Ni_{1-x}Cu_x$, the 4.7-eV edge (from transitions between the *s-d*-hybridized bands well below E_F and the *s-p*-like bands above E_F , e.g., $X_1 \rightarrow X'_4$)

shifts to higher energies, while the 1.5-eV edge (from transitions between a p -like band below E_F and a d -band above E_F , e.g., $L_2' \rightarrow L_3$) remains at the same energy as the Cu concentration increases. A structure grows in the (2 - 3)-eV region as Cu is added, and it is interpreted as being due to transitions between the localized Cu subbands. For $AuGa_2$ and $PtGa_2$, both compounds show interband absorption at low photon energies (<1.3 eV). The interband absorption for $AuGa_2$ is strong at about 2 eV while that for $PtGa_2$ shows a broad structure in the range 2.5 - 4.5 eV, with a shoulder at 3.3 eV. The observed interband features in the imaginary parts of the complex dielectric functions ϵ_2 can be interpreted in terms of band calculational results. For β' - $NiAl$ and $CoAl$ all of the structures found in the optical spectra of both compounds involve states with some Ni/Co d -character in both the initial and the final states of the transitions. A self-energy correction for the excitation spectrum has been used for β' - $CoAl$ to improve the agreement. The optical conductivities of $CeSn_3$ and $LaSn_3$ show structures due to interband absorption at about 2 and 3 eV, which are mostly due to transitions between band-like Ce/La d - and f -states. The larger strengths of the structures in $CeSn_3$ than in $LaSn_3$ may be due to the existence of more f -character near E_F in $CeSn_3$ than in $LaSn_3$.

Optical properties and electronic structures of *d*- and *f*-electron metals
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LaSn₃

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CHAPTER 1. INTRODUCTION

Preliminary Remarks

In order to aid the understanding of the physical properties of solids various optical measurements have been performed by a large number of workers, with continuing attempts to increase the experimental accuracy. Historically, the usual way to determine the optical properties of solids is to shine monochromatic light onto a sample and then to measure the amplitude of reflectance or transmittance as a function of photon energy. Ellipsometry can measure the complex reflectance ratio (product of the phase difference and the ratio of the amplitudes) between the *p*-polarized (parallel) and the *s*-polarized (perpendicular) radiations. To interpret optical data in terms of the microscopic structures of the solid (e.g., electrons and phonons) requires an understanding of the interaction of electromagnetic radiation with matter which is described by Maxwell's equations and an understanding of the nature of the response functions (e.g., complex dielectric function) from a microscopic viewpoint. During the past two decades photoemission and characteristic electron-energy-loss measurements in ultra-high-vacuum have been developed and proved useful in investigating the electronic structures of solids. These techniques are closely related to optical measurements in terms of the kind of information they provide. Theoretically, electronic band-structure calculations have been shown to be a good tool in helping

interpret some optical data at low photon energies.

This thesis will focus on optical measurements (mostly by ellipsometry) of *d*- and *f*-electron metals and alloys ($Ag_{1-x}In_x$;4*d*, $Ni_{1-x}Cu_x$;3*d*, $AuGa_2$, $PtGa_2$;5*d*, β' - $NiAl$, β' - $CoAl$;3*d*, $CeSn_3$, $LaSn_3$;4*f*) and the results will be interpreted in terms of the electronic structures based on the one-electron band theory. Band-structure calculations on the ordered compounds of the above materials were performed and quantitative comparisons between the experimental data and the theoretical calculations of the dielectric functions were made.

Optical Responses of Solids

Optical Constants

The information about the electronic structure of a solid obtainable from optical measurements comes from the spectral dependence of the optical response which can be described by Maxwell's equations:

$$\nabla \cdot \mathbf{D} = 4\pi\rho \quad (1.1)$$

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} \quad (1.2)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (1.3)$$

$$\nabla \times \mathbf{H} = \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} + \frac{4\pi}{c} \mathbf{J}. \quad (1.4)$$

The linear response of homogeneous material to an applied electromagnetic field is characterized by additional constitutive relations,

$$\mathbf{D} = \epsilon \mathbf{E}, \quad \mathbf{B} = \mu \mathbf{H}, \quad \text{and} \quad \mathbf{J} = \sigma \mathbf{E}, \quad (1.5)$$

where ϵ , μ , and σ do not depend on the field if it is not strong. At optical frequencies there is no magnetic response, so μ may be taken as unity. By using these relations and assuming no external charge density ($\rho=0$, $\nabla \cdot \mathbf{E} = 0$), a differential equation for $\mathbf{E}$ is found to be

$$\nabla^2 \mathbf{E} = \frac{\epsilon}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} + \frac{4\pi\sigma}{c^2} \frac{\partial \mathbf{E}}{\partial t}. \quad (1.6)$$

This equation has a plane wave solution as

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}. \quad (1.7)$$

and this leads to a complex wave vector,

$$k^2 = \frac{\omega^2}{c^2} \left(\epsilon + i \frac{4\pi\sigma}{\omega} \right). \quad (1.8)$$

The quantity in parentheses defines a complex dielectric function needed to describe the response of matter to applied electromagnetic fields at optical frequencies.

$$\tilde{\epsilon} = \epsilon + i \frac{4\pi\sigma}{\omega} = \epsilon_1 + i\epsilon_2. \quad (1.9)$$

One also can define the complex conductivity,

$$\tilde{\sigma} = \sigma + i\frac{\omega\epsilon}{4\pi} = \sigma_1 + i\sigma_2, \quad (1.10)$$

which is related to $\tilde{\epsilon}$ as

$$\tilde{\sigma} = -i\frac{\omega}{4\pi}(\tilde{\epsilon} - 1). \quad (1.11)$$

For absorbing media, the real and imaginary parts are comparable in magnitude, indicating that displacement current is comparable to conduction current:

$$\frac{\epsilon_2}{\epsilon_1} = \frac{J}{|\partial\mathbf{D}/\partial t|}. \quad (1.12)$$

These physical quantities involve the characteristic energies of prominent excitations, the joint density of states, and the oscillator strengths of the excitations. Cubic crystals, and polycrystalline samples of non-cubic materials are optically isotropic. Their optical properties can be described by a complex scalar function with the real and imaginary parts related by the Kramers-Krönig (K-K) relations

$$\epsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega' \epsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega', \quad (1.13)$$

$$\epsilon_2(\omega) = \frac{2\omega}{\pi} \int_0^\infty \frac{\epsilon_1(\omega')}{\omega'^2 - \omega^2} d\omega'. \quad (1.14)$$

If the material is a crystal of symmetry lower than cubic, the optical properties are anisotropic and the dielectric function becomes a tensor, each component of which has a real and imaginary part. Other quantities often used are the complex refractive index,

$$\tilde{N} = n + ik = \tilde{\epsilon}^{1/2}, \quad (1.15)$$

from which

$$\epsilon_1 = n^2 - k^2, \quad \epsilon_2 = 2nk. \quad (1.16)$$

At normal incidence from vacuum, the reflectance of an opaque sample is

$$R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}. \quad (1.17)$$

There are a number of cases in which the optical properties are inadequately described by just a frequency-dependent dielectric function, $\tilde{\epsilon}(\omega)$. These are cases in which the optical properties are non-local. This means that the response of the material $\mathbf{D}$ at a point $\mathbf{r}$ depends on the electric field $\mathbf{E}$ in a region around that point, making the dielectric function depend on $\mathbf{r}$ and $\mathbf{r}'$, the latter in a region around $\mathbf{r}$. Thus,

$$\mathbf{D}(\mathbf{r}) = \int \epsilon(\mathbf{r}, \mathbf{r}') \mathbf{E}(\mathbf{r}') d^3 r'. \quad (1.18)$$

For periodic systems, the spatial dependence simplifies to that of $\mathbf{r} - \mathbf{r}'$, and it can be Fourier-transformed, leading to a dielectric function which depends on both frequency and wavevector.

Intraband and Interband Transitions

The electronic transitions that contribute to the complex dielectric function can be decomposed into the sum of an intraband term and an interband term:

$$\tilde{\epsilon} = \tilde{\epsilon}^f + \tilde{\epsilon}^b. \quad (1.19)$$

Intraband transitions are the dominant physical process determining the optical properties of metals at low photon energies. This process is due to electron scattering through a variety of mechanisms. The intraband term of a cubic metal can be treated quantitatively within the framework of the Drude model [1] as

$$\tilde{\epsilon}^f = \epsilon_1^f + i\epsilon_2^f = 1 - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2} + i \frac{\omega_p^2 \tau}{\omega(1 + \omega^2 \tau^2)}, \quad (1.20)$$

where ω_p is the plasma frequency ($\omega_p^2 = 4\pi N e^2 / m^*$ with N , the electron density and m^* , the effective optical mass of the electrons) and τ is the relaxation time. In the limit $\omega\tau \gg 1$, the real and imaginary part become

$$\epsilon_1^f = 1 - \frac{\omega_p^2}{\omega^2}, \quad (1.21)$$

$$\epsilon_2^f = \frac{\omega_p^2}{\omega^3 \tau}. \quad (1.22)$$

In estimating the real part of the dielectric function, $\epsilon_1 (= \epsilon_1^f + \epsilon_1^b)$ at low energies below the onset energy ($\hbar\omega_0$) of the interband transition, the evaluation of ϵ_1^b is necessary and it can be done by using the K-K relation,

$$\epsilon_1^b = \frac{2}{\pi} \int_{\omega_0}^{\infty} \frac{\omega' \epsilon_2^b(\omega')}{\omega'^2 - \omega^2} d\omega' \simeq \frac{2}{\pi} \int_{\omega_0}^{\infty} \frac{\epsilon_2^b(\omega')}{\omega'} d\omega', \quad (1.23)$$

if $\omega \ll \omega'$. So, the contribution of the interband transitions at high energies to the intraband term at low energies can be approximated as a constant. Therefore, at low energies where interband transitions are negligible the real and the imaginary part of the dielectric function are approximated as

$$\epsilon_1 = \epsilon_{\infty} - \frac{\omega_p^2}{\omega^2}, \quad (1.24)$$

$$\epsilon_2 = \frac{\omega_p^2}{\omega^3 \tau} = \frac{\epsilon_{\infty} - \epsilon_1}{\omega \tau}, \quad (1.25)$$

where $\epsilon_{\infty} = 1 + \epsilon_1^b$.

The interband term can also be estimated quantitatively by a one-electron model. This calculation of the one-electron optical properties of solids often are analogous to the calculation of the optical absorption spectrum of an atom. The electric field of the incident electromagnetic wave causing the optical transitions is treated as

a time-dependent perturbation to the crystal Hamiltonian. In the presence of the electromagnetic field the Hamiltonian for an electron in the crystal is modified by replacing the momentum operator, $\mathbf{p}$, by $(\mathbf{p} + \frac{e}{c}\mathbf{A})$, where $\mathbf{A}$ is the vector potential of the electromagnetic field,

$$\mathbf{A} = \mathbf{A}_0 e^{i(\mathbf{q}\cdot\mathbf{r} - \omega t)}. \quad (1.26)$$

This introduces several new terms into the Hamiltonian:

$$H' = \frac{1}{2m} \left[\frac{e}{c} (\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) + \frac{e^2}{c^2} A^2 \right]. \quad (1.27)$$

The last term is negligible when considering only linear optical absorption. By expanding the exponential and keeping only the first term, we obtain the electric-dipole approximation, which is adequate for all observable interband transitions except at energies high enough that q^{-1} approaches the interatomic distance. Then, $\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p} = 2\mathbf{A} \cdot \mathbf{p}$, and $H' = \frac{e}{mc} \mathbf{A} \cdot \mathbf{p}$. By applying H' between the initial (filled), $|i\rangle$, and final (empty), $|f\rangle$, states which are eigenstates of the unperturbed crystal Hamiltonian we can obtain

$$|\langle f | H' | i \rangle|^2 = (e/mc)^2 |\mathbf{A}_0 \cdot \mathbf{P}_{fi}|^2 \quad (1.28)$$

with $\mathbf{P}_{fi} = \frac{1}{\Omega} \langle f | \mathbf{p} | i \rangle$, the electric-dipole matrix element where Ω is the unit-cell volume. These are related to the interband contribution to the imaginary

part of the complex dielectric function, ϵ_2^b , by

$$\epsilon_2^b = \frac{4\pi^2 e^2}{3m^2 \omega^2} \sum_{fi} \int_{BZ} d^3k \frac{2}{(2\pi)^3} |\mathbf{P}_{fi}|^2 \delta(E_f - E_i - \hbar\omega) \quad (1.29)$$

which is to be compared with the experimental results.

Optical Measurements

To measure the complex dielectric function we need to measure the complex reflectance ($\tilde{r}$). This necessarily introduces the interface between the material under study and an ambient medium. For a planar, infinitely sharp interface between two media, a and b , the boundary conditions derived from Maxwell's equations lead to the Fresnel relations for the ratio of the reflected and transmitted electric fields to the incident field from medium a .

$$\tilde{r} = r e^{i\theta} = \frac{\tilde{g}_b - \tilde{g}_a}{\tilde{g}_b + \tilde{g}_a}, \quad \tilde{t} = 1 - \tilde{r}, \quad (1.30)$$

with

$$\tilde{g}_i = \tilde{N}_i \cos \tilde{\varphi}_i \quad \text{for } s - \text{polarization} \quad (1.31)$$

$$\tilde{g}_i = \cos \tilde{\varphi}_i / \tilde{N}_i \quad \text{for } p - \text{polarization} \quad (1.32)$$

and

$$\tilde{N}_a \sin \tilde{\varphi}_a = \tilde{N}_b \sin \tilde{\varphi}_b. \quad (1.33)$$

When the ambient medium, a , is air or vacuum, $\tilde{N}_a = 1$ and $\tilde{\varphi}_a$ is real.

Reflectance

The complex reflectance is not directly measurable at optical frequencies because we can not measure fields at such high frequencies. Instead, we can measure average power which is proportional to $|\mathbf{E}|^2$. The reflectance R is related to the complex reflectance as $R = |\tilde{r}|^2$. This is a function of frequency, angle of incidence, and polarization. The simplest reflectance measurement is at near normal incidence, for which knowledge of the degree of polarization is not necessary because $\tilde{r}_p = -\tilde{r}_s$. However, only one measurement is insufficient to obtain the real and imaginary parts of the dielectric function. A common method for obtaining optical constants is to measure the reflectance at two angles of incidence, then use the Fresnel relations to obtain the dielectric function. At higher photon energies, usually above 30 eV, reflectances at near-normal incidence become very small. Thus at high photon energies, most of the optical data are taken by transmission measurements on thin films. At low photon energies (infrared) reflectances of metals are large ($> 90\%$) so that a measurement of reflectance to an accuracy of 1% (relative) is vastly inferior to a measurement of absorptance ($A = 1 - R$) to the same accuracy (1% of A is equivalent to 0.1% of R). Hence, absorptance measurements are more advantageous in giving greater sensitivity for infrared structure than is expected for reflectance measurements.

K-K relations usually have been used for obtaining the dielectric function $\tilde{\epsilon}$ from

the measured reflectance. The phase change θ due to reflection can be obtained from the K-K integral given below:

$$\theta(\omega) = -\frac{\omega}{\pi} \int_0^{\infty} \frac{\ln R(\omega')}{\omega'^2 - \omega^2} d\omega'. \quad (1.34)$$

Once θ is obtained, the real and the imaginary part of the complex refractive index are obtained from

$$n = \frac{1 - R}{1 + R - 2\sqrt{R}\cos\theta} \quad (1.35)$$

$$k = \frac{2R\sin\theta}{1 + R - 2\sqrt{R}\cos\theta} \quad (1.36)$$

for the case of normal incidence. As can be seen from the above K-K integral, measurement of the reflectance over a wide energy range and extrapolation of the reflectance to zero energy and to very high energies are necessary. However, the extrapolation procedures may cause errors in addition to the errors in the reflectance measurement itself, making the accuracy poorer than that of previously described methods. Nevertheless, the fact that only one quantity needs to be measured apparently has been viewed as a great advantage for the technique. Most of its practitioners have been interested in the shapes of the dielectric function spectra, not in the magnitudes, and the K-K method usually provides spectra with the correct shapes, even when the magnitudes may be in error.

Ellipsometry

Linearly polarized radiation at non-normal incidence is reflected from a material interface as elliptically polarized radiation, unless the incident radiation is pure p - or s -polarized.

$$E_{rs} = \tilde{r}_s E_s, \quad E_{rp} = \tilde{r}_p E_p. \quad (1.37)$$

Ellipsometry uses this property of light to measure the complex reflectance ratio [2], the ratio of the reflected electric fields (p - and s -polarized), given by

$$\tilde{\rho} = \frac{\tilde{r}_p}{\tilde{r}_s} = \rho_0 e^{i\Delta}, \quad (1.38)$$

where $\rho_0 = |\tilde{r}_p/\tilde{r}_s|$ and $\Delta = \theta_p - \theta_s$. The measured quantities in ellipsometry are ρ_0 and Δ . For an ideal two-phase situation, the reflecting system consists of an optically thick bare substrate and a transparent ambient with isotropic complex dielectric functions $\tilde{\epsilon}_s$ and ϵ_a , respectively. If the plane wave with an incidence angle ϕ reflects from the interface between these two phases, the complex dielectric function $\tilde{\epsilon}_s$ is then related to $\tilde{\rho}$ through the equation

$$\frac{\tilde{\epsilon}_s}{\epsilon_a} = \sin^2 \phi + \sin^2 \phi \tan^2 \phi \frac{(1 - \tilde{\rho})^2}{(1 + \tilde{\rho})^2}. \quad (1.39)$$

Ellipsometry is less sensitive than other methods to surface roughness of the sample because it is the polarization of the reflected radiation that is measured, not its

absolute intensity. Details of the ellipsometry system that has been used in this study will be discussed in a later section.

Theoretical Approaches

It is well known that studies of the optical properties of metals and calculations of the one-electron band structures of metals complement each other. The optical constants cannot be interpreted in any detail without some knowledge of the band structure, while band-structure calculations can be checked, and parameters adjusted, by comparison with observed optical spectra. Since the early '60s, the band structures of many elemental metals and compounds have been calculated to help interpret optical spectra as well as other electrical and magnetic properties. Also, theoretical approaches to the understanding of disordered alloys have long been taken, ever since the rigid-band model [3], and they were successful in explaining many experimental results. In this section, theoretical models based on the one-electron band picture are reviewed, which have been frequently used in interpreting optical spectra of metals and alloys.

Ordered System

In the one-electron band picture, the Born-Oppenheimer approximation is made first to allow the separation of the treatment of the electrons and ions, i.e., ignoring the electron-phonon interaction. Secondly, the electrons are assumed to move independently in a periodic effective crystal potential which determines their wavefunctions. Exchange and correlation effects can be included by reducing the nonlocal problem to a local one via some formulation of the Local Density Approximation

(LDA) or Local Spin Density Approximation (LSDA), depending on whether the calculation is spin-polarized or not [4] [5]. The augmented-plane-wave (APW) method has been the most successful and widely applied method for calculating the band structures of metallic systems. It is a way of solving the Schrödinger (or Dirac) equation variationally, which was suggested by Slater in 1937 [6]. APW calculations were not particularly feasible until the early '60s because of the large amount of computation involved. The essence of the APW method involves the partitioning of the unit cell into two separately treated regions, a spherical region around each ion, and the remaining interstitial region. A further simplification generally used is the muffin-tin (MT) approximation, first suggested by Slater in 1935 [7], in which the potential is assumed to be spherically symmetric inside the MT spheres around each ion, and equal to a constant, which can be set equal to zero by shifting the energy, in the interstitial region. One then proceeds to solve the Schrödinger equation by use of the variational principle. The final solution is reached by means of minimizing the energy in a variational expression, using the variational wave function

$$\Psi = \sum_i C_i \phi_i, \quad (1.40)$$

where the ϕ_i are the APW basis functions. The solution of Schrödinger's equation inside the sphere for a given MT potential is given by a product of spherical harmonics and radial functions which satisfy the radial part of Schrödinger's equation. In the interstitial region, the solutions are the solutions to Schrödinger's equation with zero potential, which are plane waves. Thus, a dual representation for the variational function is used. Inside the MT sphere, atomic-like solutions are taken:

$$\phi = \sum_{l,m} A_{lm} u_l(\varepsilon_l) Y_m^l(\hat{r}). \quad (1.41)$$

In the interstitial region:

$$\phi = e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (1.42)$$

The values of the two sets of variational functions are matched at the MT boundary by means of a Rayleigh expansion of the plane waves in terms of spherical harmonics which determines the coefficients A_{lm} . However, the derivatives of the functions are allowed to be discontinuous at the MT boundary. A secular equation is formed from a variational expression for the energy in terms of Ψ for minimizing the energy with respect to the expansion coefficients C_i :

$$\det | H(\varepsilon_l)_{ij} + S(\varepsilon_l)_{ij} - \varepsilon_l D(\varepsilon_l)_{ij} | = 0, \quad (1.43)$$

where H is the MT Hamiltonian, S is a surface term which represents the contribution to the kinetic energy from the remaining discontinuity in the slope of the variational function at the MT boundary, and D is an overlap matrix. This is a less convenient form of secular equation to solve than the standard eigenvalue-eigenvector type problem. The solution is more difficult since it requires searching the determinant as a function of energy to find its zeros, due to the implicit dependence of the APW functions themselves inside the MT spheres upon the energy. Furthermore, the secular equation for the determinant contains singularities. These problems can

be eliminated by including not only the radial solution but its energy derivative as well. In the linearized-augmented-plane-wave (LAPW) method [8], one proceeds in essentially the same manner as in the APW method, except for the inclusion of an energy derivative in the radial equation, i.e., one expands u_l in a Taylor series about some energy parameter E_0 . The basis functions inside the MT become:

$$\phi = \sum_{l,m} A_{lm} u_l + B_{lm} \frac{\partial u_l}{\partial \epsilon_l} Y_l^m. \quad (1.44)$$

Then one can use the additional variational freedom included by the derivative term to match both the functions and their derivatives at the MT boundary, which eliminates the surface terms in the variational expression for the energy. Furthermore, the energy can now remain fixed within a fairly wide region, rather than requiring the search of the determinant for zeroes over a range of energies. Some care is still required in choosing the energy parameter E_0 , particularly for states of higher angular momentum, which tend to be more localized.

The Exchange-Correlation Potential

Hohenberg, Kohn, and Sham [4] have shown that the electronic charge density ρ implies all properties of the ground state. Furthermore, they showed that ρ could be obtained by standard one-electron techniques from a Schrödinger equation containing, in addition to the usual electrostatic interaction of an electron with the nuclei and the electronic charge density, an exchange-correlation potential V_{xc} which is also uniquely determined by the charge density. The earliest attempts to take exchange and correlation effects into account in band calculations, i.e., to include some many-

body effects in the single-body equations, were based upon Thomas-Fermi type local density approximations where the exchange-correlation potential is assumed to be a function of the local charge density. The best known approximation of this type is Slater's statistical exchange $\rho^{1/3}$ potential [9] which was originally of the form:

$$V_{xc}(\mathbf{r}) = -\frac{3}{2\pi} [3\pi^2 \rho(\mathbf{r})]^{1/3}. \quad (1.45)$$

However, Gaspar [10] and later Kohn and Sham [4], rederived Slater's exchange potential with a coefficient two thirds as large:

$$V_{gks}(\mathbf{r}) = \frac{2}{3} V_{xc}(\mathbf{r}). \quad (1.46)$$

Then Slater and Johnson [11], and soon many others, began to use the so called Slater $X\alpha$ approach,

$$V_{X\alpha}(\mathbf{r}) = \alpha V_{xc}(\mathbf{r}), \quad (1.47)$$

where α is usually between 2/3 and 1, and is often chosen such that the resultant atomic ground-state energy is precisely the energy obtained from the Hartree-Fock method. However, it should be noted that the atomic system differs considerably from the solid, mainly in that the atom has a large low-density region. The $X\alpha$ method is mainly a high-density approximation, which is corrected for the low-density atomic regions by the adjustment of α . Hence, the best choice of α for the atom is probably not the best choice for the solid, which does not have a large low-density region. A

better and more physical approximation with no adjustable parameters is that of Hedin and Lundqvist [12],

$$V_{xc}(\mathbf{r}) = \beta(\mathbf{r})V_{gks}(\mathbf{r}). \quad (1.48)$$

This formulation is based upon the theorems of Hohenberg and Kohn [4], which exploit the aforementioned concept of a system of nearly independent quasiparticles. These two theorems, which form the basis of all density-functional theories, show that for an inhomogeneous, interacting electron gas the ground-state properties, such as bulk modulus, are unique functionals of the electron density, and that the total energy of the system is a minimum for the correct density. Here, the β function is essentially an extrapolation between high- and low-density results for an interacting electron gas, where the results can be more easily and accurately calculated. In fact, the Hedin-Lundqvist results are exact in the limit of high and low densities.

Disordered System

In the earlier studies of the optical properties of metal alloys the rigid-band model was used to predict the shift of absorption edges by assuming that the alloy possesses the same band structure and density of states as the host and that the perturbation in the crystal potential caused by the solute simply shifts the energy eigenvalues of the band structure by constant amounts. Physically, this means that the electrons in the valence bands are equally distributed between host and solute sites and only a small constant change in the periodic potential is introduced. Thus, the band structure shifts rigidly in energy and the Fermi level (E_F) shifts with respect to the

bottom of the valence band by an amount determined by the density of states of the host when the solute valence differs from that of host. However, many subsequent measurements cast doubt on the applicability of the rigid-band model because this model frequently overestimates the shift of E_F . Another model for estimating the shift of E_F was proposed by Friedel [13] which describes the screening of the excess charges on the solute atoms by the conduction electrons. It leads to very small changes in E_F with respect to the vacuum level in dilute alloys. This screening model usually underestimates the shift of E_F upon alloying.

The same basic idea as the rigid band model is used in the virtual-crystal-approximation [14] description in which the random array of potentials, V_A and V_B , of a binary alloy is replaced with an ordered array of potentials, $V_{alloy} = (1 - x)V_A + xV_B$, where x is the concentration of species B . In common with the rigid-band model, the virtual-crystal approximation predicts one common delocalized band structure which shifts smoothly upon alloying, but it allows for deformation of the band shapes when the atomic composition is changed. This model can be a good approximation in describing the shape of the s - p -bands of the alloy.

A different theoretical approach, called the minimum-polarity model [15] was proposed which assumes that the electronic configuration of each component in its pure state carries over into the alloy. This implies local charge neutrality at each site and can be understood in the band picture as the limit in which the localization of the crystal potential is strong while the rigid-band model represents the opposite limit. Hence, the band structures of the constituents coexist without mixing with each other due to heavy scattering at the potential barrier between the constituents. However, this model may also represent an oversimplification. For dilute alloys where

the interaction between solute is not significant, the virtual-bound-state model [16] was proposed to explain the change of the electronic structures and the related optical properties of the alloys. It assumes that highly localized (in space and in energy) impurity states around the solute atom are broadened in energy through a resonant scattering interaction with the nearly-free-electron-like bands of the host which are extended enough to overlap with the localized states. This model has been successful in describing the *Ni*-impurity *d*-states in *Cu*-rich *Ni-Cu* alloys, because they occur well separated in energy from the high-density *Cu d*-bands.

It is more realistic to include the mixing of the adjacent states of the host and the solute because they are expected to interact with each other. The theoretical approaches to this problem have involved multiple scattering theory using the single-site approximation, which amounts to replacing the disordered, substitutional alloy by an equivalent perfect crystal of effective atoms where the electrons travel without being scattered. Two representative methods are the coherent-potential approximation (CPA) [17] [18] and the average t-matrix approximation (ATA) [19], the latter having the advantage of being simpler to implement than the former. For a disordered, substitutional alloy the crystal momentum $\mathbf{k}$ is not a good quantum number and no well-defined E - $\mathbf{k}$ relation exists. Hence, the Bloch spectral function $a(\mathbf{k}, E)$, which can be interpreted as the density of states per $\mathbf{k}$ -point, is as close as we can get to describing the electronic structure of the alloy. For an ordered system $a(\mathbf{k}, E) = \sum_{\nu} \delta(E - E_{\nu, \mathbf{k}})$, where $E_{\nu, \mathbf{k}}$ is the energy of a Bloch state with band index ν and wave vector $\mathbf{k}$. Thus, for a given $\mathbf{k}$, $a(\mathbf{k}, E)$ consists of a set of δ -function peaks and the positions of these peaks as a function of $\mathbf{k}$ is the E - $\mathbf{k}$ curve in an ordered system. In the case of a random alloy, $a(\mathbf{k}, E)$ broadens but usually remains

well defined, the peak position and the width representing the quasiparticle energy and inverse lifetime of the complex energy band respectively. The integral of $a(\mathbf{k}, E)$ over the first Brillouin zone (BZ) is the configurationally averaged density of states $N(E) = (1 - x)N^A(E) + xN^B(E)$, where N^A and $N^B(E)$ are the contributions to the $N(E)$ from A and B sites, respectively. Despite the mathematical complexity of these calculations, the resultant electronic structure and density of states do not suffer the restrictions of the previous simple models.

CHAPTER 2. EXPERIMENTAL

$Ag_{1-x}In_x$ ($x = 0.0, 0.04, 0.08, 0.12$) samples were polycrystals and $Ni_{1-x}Cu_x$ ($x = 0.0, 0.1, 0.3, 0.4$) samples were single crystals. The $AuGa_2$ sample is a polycrystal made by arc-melting in an argon atmosphere. The weight loss during melting did not exceed 0.1%. The $PtGa_2$ sample is a single crystal which is stable at room temperature. It was grown by the Bridgeman method which is described in detail elsewhere [20], oriented using Laue X-ray diffractometry, then cut to reveal a (111) surface. The $AuGa_2$ sample has a slight bluish hue and the $PtGa_2$ sample is a yellow color like that of gold. The lattice parameters obtained by X-ray diffraction measurements are $6.036 \text{ \AA}$ for $AuGa_2$ and $5.911 \text{ \AA}$ for $PtGa_2$ which are in good agreement with the values in the literature [21] [22]. Both $CeSn_3$ and $LaSn_3$ samples were single crystals oriented to (111) and (100) respectively. All of the samples were made in the Ames Laboratory. Before the measurements, the samples were mechanically polished with abrasives, the final grade being a paste of $0.05\text{-}\mu\text{m}$ -diameter alumina, and afterwards cleaned by acetone and methanol. $CeSn_3$ and $LaSn_3$ samples oxidize very fast, so, just after polishing they were put into a vacuum chamber with a base pressure of 1×10^{-10} Torr and measured.

The scanning photometric rotating-analyzer-polarizer (RAP) ellipsometer [23] was used to determine the dielectric functions of the samples at room temperature.

Figure 2.1 shows the optical system in which the polarizer and the analyzer rotate synchronously at 25.5 Hz and 51 Hz respectively. For the measurements of $CeSn_3$ and $LaSn_3$ the vacuum chamber was set up between the polarizer and the analyzer so that the light beam went through two pyrex windows, one located between the polarizer and the sample and the other located between the sample and the analyzer.

The reflected field in the present system is described as

$$I = g_0 + g_1 \cos A + g_2 \cos 2A + g_3 \cos 3A, \quad (2.1)$$

where A is the analyzer angle, related to the polarizer angle, P , as $A = 2P$ all the time and they affect the final field as

$$\begin{aligned} E_f &= \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} \cos A & \sin A \\ -\sin A & \cos A \end{pmatrix} \begin{pmatrix} \tilde{r}_s & 0 \\ 0 & \tilde{r}_p \end{pmatrix} \begin{pmatrix} \cos P & -\sin P \\ \sin P & \cos P \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} E \quad (2.2) \\ &= (\tilde{r}_s \cos A \cos P + \tilde{r}_p \sin A \sin P) E, \end{aligned}$$

with $I \propto |E_f|^2$. The amplitudes of the dc, 51 Hz, 102 Hz, and 153 Hz components of Eq. (2.1) are

$$g_0 = 2\eta(1 + \rho_0^2), \quad (2.3)$$

$$g_1 = \eta(3 - \rho_0^2 + 2\rho_0 \cos \Delta), \quad (2.4)$$

$$g_2 = 2\eta(1 - \rho_0^2), \quad (2.5)$$

$$g_3 = \eta(1 + \rho_0^2 - 2\rho_0 \cos \Delta), \quad (2.6)$$

where η is an arbitrary number related to the light intensity. Solving for ρ_0 and $\cos \Delta$,

$$\cos \Delta = \frac{g_1 - g_2 - g_3}{[(g_1 + g_3)(g_1 + g_3 - 2g_2)]^{1/2}}, \quad (2.7)$$

$$\rho_0 = \frac{(g_1 + g_3 - 2g_2)^{1/2}}{(g_1 + g_3)^{1/2}}. \quad (2.8)$$

The present system is advantageous in that the optical parameters determining the complex dielectric function are encoded only in the amplitudes of the three ac components of the reflected light. The dc signal error and phase-shift correction can be eliminated. The three ac amplitudes can be measured by three filters with a certain bandwidth.

Measurements were made in the 1.2 - 5.5 eV range at energy intervals of 0.01 eV in the 1.2 - 2.5 eV range and 0.02 eV in the 2.5 - 5.5 eV range. The light sources were a 100-W quartz-halogen-filament lamp for the low-energy range and a 150-W Xe-arc lamp for the high-energy range. A GM 252 high-intensity 0.25-m grating monochromator, with a spectral dispersion of 3.3 nm/mm for a 1180-line/mm grating blazed at 240 nm, was used to produce quasi-monochromatic light. A fused SiO_2 quarter-wave retarder was used to reduce the polarization effect of the monochromator. As detectors photomultipliers with an S1 cathode with an operational energy range of 1 - 3 eV and an S20 cathode with 1.5 - 5.5 eV range were used. Measurement errors did not exceed 1% in ϵ_2 . Systematic errors caused by oxide overlayer formation appear to be small. Such errors can cause a small shift in the absolute values of the spectra but

do not alter the positions of the spectral features. The effect of the pyrex windows attached to the vacuum chamber in measuring the optical parameters for $CeSn_3$ and $LaSn_3$ was found to be negligible in the energy range 1.5 - 4.5 eV by measuring a Au film with and without the windows which produce identical results.

Figure 2.1: Schematic diagram of the optical system of the RAP ellipsometer. 1. photomultiplier; 2. aperture; 3. focal lens; 4. cogged pulley; 5. analyzer; 6. timing belt; 7. sample; 8. polarizer; 9. quartz-wave retarder; 10. spherical mirror; 11. front mirror; 12. monochromator; 13. lamp; 14. bearing pulley; 15. motor; 16. shaft

CHAPTER 3. BAND-CALCULATIONAL DETAILS

Electronic band structure calculations for $AuGa_2$ and $PtGa_2$ with the cubic fluorite (CaF_2) structure, β' - $NiAl$ and β' - $CoAl$ with the cesium chloride ($CsCl$) structure, and $CeSn_3$ and $LaSn_3$ with the Cu_3Au structure were performed using the LAPW program developed by Harmon. The standard muffin-tin (MT) approximation was used for the crystal potential for the first four materials and the warped-muffin-tin (WMT) approximation [24] was used for $CeSn_3$ and $LaSn_3$, which allows the interstitial potential to vary, rather than remain constant. This has been used for rare-earth systems and can account for a 5-10 mRy difference in the energy eigenvalues. Both are known to provide a good approximation for a cubic-close-packed structure. The calculations were scalar-relativistic [25] in which the Dirac equation is reduced to omit initially the spin-orbit interaction (thus keeping spin as a good quantum number but retaining all other relativistic kinematic effects). The spin-orbit interaction is added perturbatively after the semi-relativistic bands and wavefunctions have been obtained.

The starting MT crystal potentials were constructed from the superposition of neutral atomic charge densities obtained from self-consistent atomic calculations by the Dirac-Slater method using a variation of the Liberman, Waber, and Cromer program [26], which includes relativistic effects. The exchange-correlation contribution

to the potential was calculated by using the LDA of Hedin and Lundqvist [12] to the density-functional formalism. This local density potential has the advantage of being self consistent and containing no adjustable parameters and has proved successful in accounting for the ground-state properties of a variety of metals [27] [28] [29] [30]. The crystal charge density was calculated from the wavefunctions of the filled states obtained by solving the Hamiltonian containing the effective crystal potential. By mixing the new charge density with the old charge density we can construct the new potential from this mixture and the self-consistency procedure was continued until the change in the charge in each MT sphere converged to within 10^{-4} electron and the energy eigenvalues to within 10^{-4} Ry in successive iterations.

In $AuGa_2$ and $PtGa_2$ the MT sphere radii were chosen so that the sphere surrounding the *Au* and *Pt* sites extended 57% and 56% respectively of the way up to the *Ga* site. With this arrangement only 47% of the unit cell volume is occupied by the three MT spheres for both compounds. In other words, the crystal potential is taken as constant over 53% of the unit-cell volume. This is a questionable approximation to the real crystal potential. This problem of approximating the potential as a constant in a large region can be alleviated by including more of the unit-cell volume inside an additional sphere. This is accomplished by considering one additional sphere at the unoccupied octahedral site (one-half of the way up the body diagonal and between the *Ga* atoms). The size of this sphere is taken to be as large as possible without changing the sizes of the other spheres. By including this sphere the amount of the unit-cell volume enclosed within the MT sphere becomes 70% for $AuGa_2$ and 71% for $PtGa_2$. Although no nucleus is at the center of the added sphere, upon self-consistency it contains 0.70 electron for $AuGa_2$ and 0.66 electron for $PtGa_2$. In

β' -*NiAl* and β' -*CoAl* the MT sphere radii of *Ni* and *Co* were chosen so that the spheres surrounding their sites extended 51% of the way up to the *Al* sites. With this arrangement 66% and 67% of the unit cell volumes are occupied by the MT spheres for *NiAl* and *CoAl* respectively. In *CeSn₃* and *LaSn₃* the MT sphere radii of *Ce* and *La* in the WMT potential obtained from Koelling [31] were chosen to make the spheres surrounding their sites extend 50% of the way up to the *Sn* sites. With this arrangement 74% of the unit cell volumes is occupied by the MT spheres for both *CeSn₃* and *LaSn₃*.

The size of the LAPW basis function set for each calculation was set to satisfy $K_{max}R_{mt} = 7.5$ for the smallest MT radius, R_{mt} for *AuGa₂* and *PtGa₂*, 7.0 for β' -*NiAl* and β' -*CoAl*, and 8.0 for *CeSn₃* and *LaSn₃*. These yielded about 170-200 LAPW's for *AuGa₂*, *PtGa₂*, *CeSn₃*, and *LaSn₃*, and about 60-80 LAPW's for β' -*NiAl* and β' -*CoAl*. Inside R_{mt} , the wavefunctions were expanded in terms of spherical harmonics of angular momentum up to $l = 12$. There were 46 k-points in the 1/48th of the BZ included for the self-consistent iterations for *AuGa₂* and *PtGa₂* and 56 k-points for β' -*NiAl* and β' -*CoAl*. The physical parameters used for this work are listed in Table 3.1.

Calculation of the density of states was done using the linear-energy-tetrahedron method [32] which was also used to calculate the interband contribution to the imaginary part of the dielectric function, ϵ_2^b or the real part of the conductivity, σ_1^b . In calculating these quantities as in Eq. (1.29), we needed to compute the electric-dipole matrix elements as in Eq. (1.28). The electric-dipole matrix element $\mathbf{P}_{fi}$ between the occupied ($E_i(\mathbf{k})$) and unoccupied ($E_f(\mathbf{k})$) one-electron states was calculated by using the corresponding ground-state one-electron wavefunctions within the volume

of the unit cell Ω . The energy eigenvalues were evaluated at the four corners of elementary tetrahedra in the irreducible 1/48th of the BZ and the electric-dipole matrix elements were calculated using the wavefunctions at the centers of the tetrahedra. We assumed the electric-dipole matrix elements to be constant within any one tetrahedron, and equal to the matrix element calculated at the center of the tetrahedron. The calculated optical spectra have been compared with experimental data and the transitions responsible for the structures in the spectra are identified.

Table 3.1: Parameters used in the band calculations

	<i>AuGa₂</i>	<i>PtGa₂</i>
Lattice constant (Å)	6.06	5.91
Muffin-tin radius (Å)	<i>Au</i> 1.50 <i>Ga</i> 1.13	<i>Pt</i> 1.43 <i>Ga</i> 1.13
	<i>β'</i> - <i>NiAl</i>	<i>β'</i> - <i>CoAl</i>
Lattice constant (Å)	2.880	2.861
Muffin-tin radius (Å)	<i>Ni</i> 1.270 <i>Al</i> 1.193	<i>Co</i> 1.270 <i>Al</i> 1.193
	<i>CeSn₃</i>	<i>LaSn₃</i>
Lattice constant (Å)	4.719	4.761
Muffin-tin radius (Å)	<i>Ce</i> 1.668 <i>Sn</i> 1.668	<i>La</i> 1.682 <i>Sn</i> 1.682

CHAPTER 4. RESULTS AND DISCUSSION

Disordered Alloys

$Ag_{1-x}In_x$

The optical properties of *Ag* and *Ag*-based alloys have been extensively studied to obtain information on the electronic structure of *Ag* and how it is altered by alloying [33] [34] [35] [36] [37] [38] [39]. The $Ag_{1-x}In_x$ alloy system has an advantage that the center of the 4*d*-bands of pure *Ag* is very widely separated (by approximately 10 eV) from that of *In* so that the hybridization between the 4*d*-bands of *In* and the *s-p*-bands of *Ag* is negligible and the effect caused by changing the composition can be more easily resolved. In Fig. 4.1 the ϵ_2 spectra of various $Ag_{1-x}In_x$ alloys are presented. As *In* is added we can clearly see the splitting of the two transition edges, the strong $L_3 \rightarrow L'_2(E_F)$ at about 4.1 eV and the weak $L'_2(E_F) \rightarrow L_1$ at about 3.8 eV, which were not resolved in pure *Ag* [39]. We can also see the increase in the magnitude of ϵ_2 at low photon energies as the *In* concentration increases. This can be interpreted in terms of the increased intraband scattering rate of the conduction electrons below the interband absorption edge due to the added impurities.

Figure 4.1: Imaginary part of the complex dielectric functions of $\text{Ag}_{1-x}\text{In}_x$

The low-energy region of the spectra of noble metals arises solely from intraband absorption. By linear-regression fitting of the real part of the dielectric functions below the onset of the first interband transition using Eq. (1.24) we can obtain ϵ_∞ and ω_p . Also, it is known that in order to fit ϵ_2 for a variety of metals τ needs to be frequency-dependent [40] and is given by

$$\tau^{-1} = \tau_0^{-1} + \beta\omega^2 \quad (4.1)$$

which is best viewed as an empirical relation. We used this relation to fit the imaginary parts of the dielectric functions to get τ_0 and β . Causality requires that ω_p also be frequency dependent [41], and this dependence has once been observed from a heavy-fermion compound UPt_3 [42]. For noble metals, the origins of the β term are electron-electron scattering [43] [44] [45] [46], electron-phonon scattering [40] [45], and electron-impurity scattering [40], where applicable. Quantitative agreement between calculated values of β and experiment has not yet been achieved [40]. The parameters obtained from the above procedure are listed in Table 4.1. For pure *Ag*, the value of τ_0^{-1} from the optical data is about 20% of the value obtained from the dc resistivity. τ_0^{-1} increases linearly with increasing *In* concentration as can be seen in Fig. 4.2 but the rate of increase is only about one-third of that of the dc resistivity [47]. β similarly increases approximately linearly with *In* concentration. This is surprising in view of the one calculation of the effect of impurities on β [40]. That calculation assumed a spherical Fermi surface and isotropic scattering from an impurity represented by a screened Coulomb potential.

Table 4.1: Least-squares fitted values of free-electron Drude parameters at low photon energies ($E < 2.5$ eV) for $Ag_{1-x}In_x$

x	ϵ_∞	$\hbar\omega_p$ (eV)	τ_0 (10^{-14} sec)	β ($10^{14} \text{ sec}^{-1} \text{ eV}^{-2}$)
0.0	2.98	9.21	0.54	0.09
0.04	2.33	7.95	1.26	0.58
0.08	1.40	7.55	1.92	0.78
0.08 (film)	1.69	7.02	1.94	0.64
0.12	0.81	6.95	3.15	1.89

It predicted a β that was linearly proportional to the impurity concentration, but with a negative sign for all reasonable values of the screening length. With this model, a positive β results only if the screening length becomes less than a few tenths of an angstrom. The positive value of β we have obtained indicates that this model needs to be extended. It is known that the screened Coulomb potential predicts a value for the rate of change of the dc resistivity with impurity concentration that is too high [48], one that is improved by using the Friedel model [49]. Moreover, impurity (*Sn*, *Au*) scattering on the Fermi surface of *Ag* is known to be anisotropic [50], so a nonspherical Fermi surface may also have to be considered. Anisotropic scattering by a vacancy in *Cu* and *Au* has been calculated recently [51].

In Fig. 4.3 the volume energy-loss function, $\text{Im}(-1/\bar{\epsilon})$, which is proportional to the probability that an energetic electron will lose energy E by producing longitudinal excitations in the volume of the system, is presented.

Figure 4.2: The dependence of the Drude parameters on *In* concentration

Figure 4.3: Volume energy-loss functions of $Ag_{1-x}In_x$

In the case of pure *Ag*, the energy of the first interband transition around 3.9 eV and its strength are within the range of values needed to shift the zero of ϵ_1 from around 9.2 eV to around 3.8 eV. The collective motion of the electrons is now the result of their mutual Coulomb repulsion screened by the polarization of the *d*-electrons responsible for the interband transition, and an implicit equation for the frequency of the screened plasma oscillations ω'_p is

$$\omega'_p = \frac{\omega_p}{[1 + \epsilon_1^b(\omega'_p)]^{1/2}}, \quad (4.2)$$

where $\omega'_p \tau \gg 1$, $\epsilon_2^b(\omega'_p) \simeq 0$, and ϵ_1^b and ϵ_2^b are the interband terms of $\tilde{\epsilon}$. Equation (4.2) is valid for pure *Ag*, but not for the alloys. For them, ϵ_2^b is not negligible as can be seen in Fig. 4.1, so that Eq. (4.2) must be generalized. For pure *Ag*, $\text{Im}-1/\tilde{\epsilon}$ shows a sharp peak at 3.77 eV in our experimental data, as can be seen in Fig. 4.3, and as *In* is added the broadening and splitting of the structure into two small peaks are seen, which is indirect evidence of the splitting of the two transition edges. Figure 4.4 shows $\Delta\epsilon_2 (= \epsilon_{2(\text{alloy})} - \epsilon_{2(\text{pure})})$ spectra. We see two peaks, positive and negative, due to the shifts of the two transition edges, $L'_2(E_F) \rightarrow L_1$ and $L_3 \rightarrow L'_2(E_F)$, respectively, and the position of the positive peak shifts to lower energies while that of the negative peak shifts to higher energies. The positions of the two peaks are listed in Table 4.2 and they nearly coincide with the maximum of the numerically calculated first derivative of ϵ_2 within 0.02 eV, the interval of scanned photon energies. For pure *Ag*, we take the photon energy leading to the minimum reflectance as the $L'_2(E_F) \rightarrow L_1$ transition edge and take the photon energy leading to the maximum of the numerically calculated $d\epsilon_2/d\omega$ as the $L_3 \rightarrow L'_2(E_F)$ transition

edge. Their energies are found to be 4.03 eV and 3.87 eV which agree well with other results [35]. We can estimate the shifts of the two transition edges due to alloying by just subtracting the transition energies for pure *Ag* from the peak energies in Fig. 4.4. The simplest model for alloys is the rigid-band model as explained in Chapter 1. According to this, E_F will rise as the addition of *In* increases the electron-to-atom ratio. Using the electronic specific heat [39] [52] as a measure of the density of states at E_F , this rise is 0.29 eV for 4% *In* as listed in Table 4.3. The $L_3 \rightarrow L'_2(E_F)$ transition energy should then increase by this amount, and the $L'_2(E_F) \rightarrow L_1$ transition energy decrease by nearly 0.29 eV, the band along Q near L_1 being quite flat. This gives the right sign for the shifts, but grossly overestimates their magnitudes. The Friedel model emphasizes the small change in E_F as the polyvalent solute is added, but this is with respect to its original value. The extra electrons are accommodated below E_F by the downward motion of the bands, especially the *s*-bands, whose electrons best sample the unscreened center of the impurity potential. In the band picture this can be mimicked to zero order by leaving E_F fixed and lowering the conduction bands, the *d*-bands remaining unshifted because of the better localization of the *d*-electrons. The end result is that the $L'_2 \rightarrow L_1$ transition energy should decrease by more than 0.29 eV, the additional shift being due to the downward shift of L_1 (*s*-like) with respect to L'_2 (*p*-like), and the $L_3 \rightarrow L'_2$ transition energy should increase by the amount the Friedel screening model predicts E_F to rise, for this rise may be measured against the fixed *d*-bands. For 4% *In*, this is about 0.01 eV as listed in Table 4.3. That such an increase of E_F with respect to the bands actually occurs is borne out by the measured increase of the neck of the Fermi surface of *Ag* as *Mg* or *Cd* are added [53], and of *Cu* as diverse polyvalent solutes are added [54] [55].

Figure 4.4: The change in the imaginary part of the complex dielectric functions of $Ag_{1-x}In_x$

An additional effect expected is that as the solute is added, any solute, the d -bands narrow because of the missing d - d overlap as nearest-neighbor solvent atoms are replaced by solute atoms. This lowers L_3 and further increases the energy of the $L_3 \rightarrow L'_2(E_F)$ transition, already from the Fermi-level motion in the rigid-band model, but in a direction to improve agreement with the Friedel model. The shift of the top of the $4d$ -bands as In is added can be seen in photoemission measurements [56] [57]. There the $4d$ -bands narrow by 0.132 eV at 4% In [57]. If the band narrows symmetrically, the L_3 -point then drops 0.066 eV below E_F . In fact, the top of the $4d$ -bands should drop more than the bottom of the $4d$ -bands rise.

The above-mentioned picture can be applied to the corresponding transitions in Cu as polyvalent solutes are added. Cu is a solvent whose band structure is better understood than that of Ag , and a wider variety of solutes have been studied. The rise of E_F for 4% Ga , the $3d$ analog of In , is 0.27 eV from the electronic specific heat [58]. The observed shifts of the $L_3 \rightarrow L'_2(E_F)$ and $L'_2(E_F) \rightarrow L_1$ transition energies are 0.054 and 0.52 eV, respectively, from Staines's piezoreflectance study of Cu alloys [59]. Note that the shift of the $L'_2 \rightarrow L_1$ transition is about a factor of 8-9 larger in $Cu-Ga$ than in $Ag-In$. The $L_3 \rightarrow L'_2(E_F)$ shift can be reconciled with the Friedel model if the $3d$ -bands narrow, but the $L'_2(E_F) \rightarrow L_1$ shift is too large. Staines [59] and others [60] [61] analyzed these results further, but there is not still good agreement between experiment and theory. An example is that the d -bands should narrow for increasing solute addition, no matter what the solute. Pells and Montgomery [62] showed that for Cu alloys the narrowing was more nearly constant for equal electron-to-atom ratios rather than equal impurity concentrations.

Table 4.2: Photon energies of the two transition edges obtained by taking the two (negative and positive) peak positions in the $\Delta\epsilon_2$ spectra for $Ag_{1-x}In_x$

x	$L_3 \rightarrow L'_2$	$L'_2 \rightarrow L_1$
0.0	4.03 ^a	3.87 ^b
0.04	4.11	3.81
0.08	4.17	3.79
0.12	4.23	3.77

^aPhoton energy of maximum $d\epsilon_2/d\omega$ for pure *Ag*.

^bPhoton energy of minimum reflectance for pure *Ag*.

Table 4.3: Comparison of the experimentally determined Fermi-level shift ΔE_F with calculations based on the Friedel model and the rigid-band model for $Ag_{1-x}In_x$

x	This work (eV)	Friedel (eV)	Rigid band (eV)
0.04	0.06	0.01	0.29
0.08	0.08	0.02	0.58
0.12	0.10	0.04	0.88

Modern alloy theory allows a better understanding. CPA calculations incorporate all of the above-mentioned effects. Adding polyvalent solutes to Cu raises E_F some, lowers the conduction bands, especially the s -like parts, and narrows the d -bands. Calculations have been carried out for several such solutes in Cu [63] [64], but not all the solutes for which data exist, and qualitative agreement for most of the shifts exist. For these alloys, the $L'_2 \rightarrow L_1$ gap was adjusted [64] to fit optical data. All other calculated gaps were then in agreement with experiment. For Ag alloys, two calculations exist, an empirical calculation [65], fitting parameters to experimental data, and one using the ATA [66]. Both were for Ag-Cd, and both began with parameters for the bands of Ag that do not give results in as good agreement with a variety of experimental data as do the corresponding parameters for Cu. They found that, with respect to a fixed E_F , the d -bands dropped some, and the s - p -bands dropped even more, as Cd was added. In addition, the empirical calculation required the L'_2 - L_1 gap to decrease significantly in order to produce agreement with experiment.

The L'_2 - L_1 gap is sensitive to a number of parameters. It is volume sensitive. However, the fractional volume increases upon adding In to Ag and Ga to Cu are nearly identical [67]. The calculated deformation potentials for this gap, although they differ by about a factor of 2 in the two calculations done to date [68] [69], are nearly the same for Cu and Ag [69]. [The smaller of the two values for Cu [68] leads to a shift of the $L'_2(E_F) \rightarrow L_1$ transition that is about half of that observed [70].] This gap is also sensitive to shifts in the L_3 level, for the L_1 level interacts strongly with the L_3 level, via orthogonalization and second-order hybridization [71]. Finally, the L_1 level is sensitive to the impurity potential more than the L_3 and L'_2 levels, for the s -electrons sample the impurity core. All these features are taken into account

in some approximation in CPA or ATA, with the former (not carried out yet on *Ag* alloys) treating the possible charge transfer that the latter does not treat. The shift of the $L_2'-L_1$ gap upon alloying is important in understanding the optical properties of *Cu*-, *Ag*-, and presumably, *Au*-based alloys with elements of larger valence. This shift is significantly greater for *Cu-Ga* than for *Ag-In*, for reasons that are not completely clear at present.

$Ni_{1-x}Cu_x$

The real parts of the measured complex optical conductivities σ_1 of pure *Ni* and the three *Ni-Cu* alloys are displayed in Fig. 4.5. The spectrum for pure *Ni* shows two representative structures, a peak near 1.5 eV and a broad structure around 4.7 eV. As *Cu* is added, the intensities of both structures decrease, while a broad structure grows in the (2-3)-eV region. The peak position of the 4.7-eV structure shifts to higher energies as the *Cu* concentration increases, while that of the 1.5-eV structure remains unchanged, as listed in Table 4.4. In Fig. 4.6, $\Delta\sigma_1(=\sigma_1(alloy) - \sigma_1(pure))$ spectra are shown to demonstrate the evolution of the above-mentioned structures more clearly. The intensities of the two structures reduce gradually from those of pure *Ni* as the *Cu* concentration increases. We also can see that a broad structure in the (2-3)-eV region develops and its peak position shifts to lower energies as the *Cu* concentration increases. This shift is nearly linear with *Cu* concentration from 3.0 eV for 10 at.% *Cu* to 2.7 eV for 40 at.% *Cu*. The intensity of this structure increases nearly linearly in the *Cu* concentration as shown in Fig. 4.7.

Figure 4.5: Real part of the complex optical conductivities of $\text{Ni}_{1-c}\text{Cu}_c$

Figure 4.6: The change in the real part of the complex optical conductivities of $Ni_{1-c}Cu_c$

Figure 4.7: The change in the real part of the complex optical conductivity divided by the Cu concentration of $Ni_{1-c}Cu_c$

Figure 4.8: Combined-interpolation-scheme band structure for ferromagnetic *Ni*

The structure at about 1.5 eV has been assigned to direct interband transitions between a p -like band below E_F and a d -like band above E_F along the L - W direction [72] [73], e.g., $L'_2 \rightarrow L_3$, as indicated in the ferromagnetic band structure for Ni (Fig. 4.8), which has been obtained empirically by fitting angle-resolved photoemission results [74] [75]. The structure at about 4.7 eV has been assigned to direct interband transitions between the spatially extended s - d -hybridized states well below E_F and the s - p -like conduction states above E_F [72] [76], e.g., $X_1 \rightarrow X'_4$, as indicated in Fig. 4.8. The oscillator strength of these transitions is expected to be very sensitive to changes in the crystal potential because it is a sum of two interfering terms. It decreases significantly from Ni to Cu [76].

As the Cu concentration increases a structureless, broad "peak" appears in the (2-3)-eV region in the σ_1 spectra. It grows at the expense of the Ni -derived structures around 1.5 and 4.7 eV. Its peak position in the $\Delta\sigma_1$ spectra shifts to lower energies with increasing Cu concentration. Cu is known to have a main absorption edge at about 2.1 eV due to $L_3 \rightarrow L'_2(E_F)$ transitions [77] [78] [79], indicating that the position of the L_3 -band is about 2.1 eV below E_F in pure Cu . Hence, the shoulder in the (2-3)-eV region is attributable to transitions involving the d -states of Cu , which occur at lower energies than those of Ni [19]. The shift of the peak position in the $\Delta\sigma_1$ spectra is an indication of the upward shift of the L_3 -band of Cu , which is attributable to the increase of the d -band width of Cu due to the increase of d - d overlap interactions among Cu atoms as the Cu concentration increases.

Therefore, it is expected that the d -states of Cu and Ni are formed separately, even at low Cu concentrations. According to the CPA calculation by Muñoz et al. [80], the partial densities of d -like states, $N^{Ni}(E)$ and $N^{Cu}(E)$, are quite different

Table 4.4: Experimentally determined maximum positions in the optical conductivity σ_1 and minimum positions in the reflectance R for $Ni_{1-x}Cu_x$

x	First maximum σ_1 (eV)	Second maximum σ_1 (eV)	Minimum R (eV)
0.0	1.47	4.65	4.07
0.1	1.47	4.67	4.27
0.3	1.47	4.89	4.69
0.4	1.49	4.97 ^a	4.71

^aPhoton energy of minimum $d\sigma_1/d\omega$.

below E_F , which indicates that the wave functions tend to localize either on the Ni sites or on the Cu sites. Thus, below E_F the electronic structure of the $Ni-Cu$ system is in the split-band behavior in which there are nearly separate Ni and Cu states. This behavior persists even above E_F in their result, but reduces rapidly to $N^{Ni}(E) \simeq N^{Cu}(E)$ at higher energies, to make the amplitude of the wavefunction comparable on both sites. Thus, a common band structure accommodates the electrons from both Ni and Cu well above E_F . In the band structure of pure Ni [72], the L'_2 -band is completely filled and is located below the L_3 -band while the L'_2 -band is not completely filled and is located above the L_3 -band in pure Cu . This is due to a big difference in the crystal potential between Ni and Cu that helps maintain the split-band behavior in the $Ni-Cu$ alloy. Thus, the p -like L'_2 -band of Cu is expected not to be shared by the electrons from Ni so that the intensity of the $L_3 \rightarrow L'_2$ transitions is directly proportional to the concentration of Cu . The existence of a large density of

Cu *d*-states around 2-3 eV below E_F in *Ni-Cu* alloys has been confirmed in several photoemission measurements [81] [82] [83] [84].

According to the CPA calculations for paramagnetic *Ni-Cu* alloys by Stocks et al. [17] and Faulkner et al. [85], the density of *Cu* *d*-states is broad, with its center at about 3.5 eV below E_F and a half-width of about 2 eV for 11 at.% *Cu*, as shown in Fig. 4.9. As the *Cu*-derived structure grows, the strength of the 4.7-eV structure in the σ_1 spectra, which is due to the transitions between the lower *s-d*-hybridized states and *s-p*-like states above E_F , is reduced and its maximum position shifts to higher energies. The gradual decrease in the intensity of the structure is attributable to the decrease of the density of states of the *Ni* subbands as *Ni* atoms are replaced by *Cu* atoms. However, the *s-d* hybridization is not expected to decrease because both of the *d*-bands are expected to hybridize with the conduction band, and the separation between the *d*-states at about L_1 and the bottom of the conduction band, Γ_1 , in *Cu*, to which the hybridization is inversely proportional [71], is close to that in *Ni*, from 4.5 eV in *Ni* to 3 eV in *Cu* [19].

It is reasonable to assume that the alloy has a common *s*-band because the conduction electrons are expected to be highly delocalized. In this case it seems reasonable to treat the position of the bottom of the *s*-band, Γ_1 , in the virtual crystal approximation in which

$$\Gamma_1 = (1 - x)\Gamma_1^{Ni} + x\Gamma_1^{Cu}. \quad (4.3)$$

Similarly, we suppose that the position of the *s-d*-hybridized bands in the alloy takes an average of the positions of those in pure *Ni* and pure *Cu*,

Figure 4.9: Density of states for 11-at.-%-Cu and 39-at.-%-Cu alloys calculated using the CPA (energies in eV)

$$E_{sd} = (1 - x)E_{sd}^{Ni} + xE_{sd}^{Cu}. \quad (4.4)$$

According to the calculated band structure [19], the positions of X_1 and L_1 of pure *Cu* are lower by about 1 eV than those of pure *Ni*. Hence, as the *Cu* concentration increases, the nearly delocalized *s-d*-states around X_1 and L_1 are expected to shift down, making the edge of the 4.7-eV transitions shift to higher energies. By applying Eq. (4.4) we have the magnitudes of the shifts of the *s-d*-hybridized states which agree with the shifts of the experimental spectra as listed in Table 4.5.

The evolution of the 1.5-eV structure in the σ_1 spectra is expected to be related to the change of the ferromagnetism in *Ni-Cu* alloys because the transitions causing the structure involve the minority-spin *d*-states of *Ni* along the *L-W* direction.

As was seen earlier, upon alloying, the *d*-bands of *Cu* in *Ni-Cu* alloys are at lower energies than those of pure *Cu*, so that the alloy's *Cu s-p*-bands occur at lower energies than in pure *Cu*. Hence, E_F of the *Ni-Cu* may not shift upward with respect to the bottom of the conduction band, even though *Cu* has one more valence electron than *Ni*, and this does not agree with the rigid-band model. According to the CPA calculation of Gordon et al. for a paramagnetic *Ni-Cu* alloy [18], E_F shifts down in the *Ni*-rich region as the *Cu* concentration increases, shifting by 0.3 eV at 39 at.% *Cu*. However, they interpreted this result as a failure in their description of the crystal potential. The Fermi energies of pure *Ni* and *Cu* are very close to each other, E_F of *Ni* being higher by only 0.08 eV than that of *Cu*, calculated from the bottom of each conduction band, and Γ_1^{Ni} is located higher by only 0.18 eV than Γ_1^{Cu} relative to the MT zero [19].

Table 4.5: Comparison of the shift of the minimum position of the reflectance spectra with the calculated shift of the L_1 point based on Eq. (4.4) for $Ni_{1-x}Cu_x$ (the positions of L_1 for pure Ni and Cu are from Ref. 19)

x	Shift of minimum R (eV)	Shift of L_1 (eV)
0.1	0.20	0.17
0.3	0.62	0.50
0.4	0.64	0.67

The density of states of pure Ni obtained from the calculated band structure [86] shows a sharp change of the density of minority-spin d -states at E_F . Hence, if E_F shifts relative to the location of the minority-spin d -bands of Ni upon alloying, then the intensity of the 1.5-eV structure as the Cu concentration changes. Our experimental result does not show a rapid decrease in the intensity of the 1.5-eV structure as the Cu concentration increases. Instead, it shows a rather gradual linear decrease in intensity, and this is more attributable to the decrease of Ni d -states as Ni atoms are replaced by Cu atoms than to the relative shift of E_F from the d -bands of Ni .

The CPA calculation of Inoue and Shimizu [87] for a ferromagnetic $Ni-Cu$ alloy on the assumption of the Hubbard model results in a gradual decrease in the ferromagnetism due to a relative shift of the majority-spin band of Ni relative to the minority-spin band to make the net magnetic moment of Ni approach zero. In other words, the magnetic exchange splitting between the majority- and minority-

spin *Ni*-derived bands decreases as the *Cu* concentration increases. This behavior was predicted for *Ni-Cu* [88] and the temperature dependence of the energy gap for pure *Ni* was observed by polarization-dependent photoemission [74]. In this process, some of the *d*-electrons from the majority-spin band of *Ni* transfer to the *s*-band, leaving majority *d*-holes which reduce the net magnetic moment of the alloy. The density of states of the alloy obtained from this calculation are found to be strongly smoothed out by lifetime effects caused by a rather large difference in the crystal potential between *Ni* and *Cu* sites. In this case it is expected that there is negligible charge transfer from *Cu* sites to *Ni* sites due to strong scattering at the potential barrier between the two sites.

Therefore, the above result strongly suggests that the *d*-holes at *Ni* sites are not filled by *d*-electrons transferred from *Cu* sites, even at large *Cu* concentration, and this is close to the result from the minimum-polarity model proposed by Lang and Ehrenreich [15] and Kirkpatrick et al. [89]. According to this model, which assumes a random scattering potential strong enough to produce nearly independent *Ni* and *Cu* subbands, the *d*-electrons of *Cu* are confined to the *Cu* site, so that the *Cu d*-bands are completely filled and reside below E_F . Then the *d*-electrons near E_F come from only *Ni*-sites. This charge neutrality of the *Ni-Cu* system was also indicated by the soft-x-ray-emission [90] and -absorption measurements [80] [91]. Therefore, as the *Ni* concentration decreases, the density of states of the minority *d*-bands decreases in proportion to that of the majority *d*-bands and it leads to reducing the difference between the number of *d*-electrons with majority spin and that with minority spin so the ferromagnetism becomes reduced.

Ordered Compounds

AuGa₂ and *PtGa₂*

The binary intermetallic compounds *AuGa₂* and *PtGa₂* have the *CaF₂* structure in which *Au* or *Pt* atoms form a *fcc* sublattice and the *Ga* atoms occupy the tetrahedral sites located one-quarter of the way up the body diagonals. Earlier studies of the electrical properties of *AuGa₂*, *AuAl₂*, and *AuIn₂* [92] showed that they are good metallic conductors with room-temperature conductivities about one-fifth that of Cu. Also, Fermi-surface studies on these compounds [93] [94] indicated that they behave nearly-free-electron-like to some extent. Optical reflectances were measured on these compounds [95] [96] and dielectric functions were calculated by using K-K analyses. Chen and Lynch [97] measured the complex dielectric functions of *AuAl₂* and *PtAl₂* by spectroscopic ellipsometry. Using published band structures of the compounds [98] they were able to assign some interband transitions to the structures observed in the dielectric functions.

As is well known, the electronic band structure of Au [99] [100] [101] is characterized by narrow *5d*-bands which hybridize significantly with the *s-p*-bands around the BZ boundary. Also, the spin-orbit interaction splits the *5d*-states into states with $j = 3/2$ and $j = 5/2$. This ordering combines with crystal-field effects so that at the Γ -point, the spin-orbit and crystal-field interactions cause the four-fold $j = 3/2$ states (upper Γ_8^+) to shift to higher energy and the $j = 5/2$ states to split into four-fold (lower Γ_8^+) and two-fold (Γ_7^+) levels. The spin-orbit interaction enhances the *d*-band width, and the energy gap between the $j = 5/2$ levels at the Γ -point is about 1 eV for *Au*, a gap large enough to be detected in photoemission measurements [102] [103].

In $AuGa_2$, according to the earlier band calculations on this compound [21] [98], the width of the Au -derived $5d$ -bands is narrower than that of elemental Au because by forming a compound with Ga the distances between Au atoms become approximately 1.5 times larger than in elemental Au which results in weaker d - d overlap interactions between Au atoms. Also, the lowest-lying s -band reaches the zone boundary (e.g., X_1) without crossing the d -bands. This results in less s - d hybridization and the d -bands reside within a bandgap between s - and p -bands. Therefore, in $AuGa_2$, the electronic states near E_F are expected to have mostly s - p -character of both constituents and the interband transitions between them are expected to contribute to the low-energy (< 5 eV) optical properties of the compound. This is in contrast to the case for pure Au which has interband contributions below 5 eV involving the d -bands [104] [105] which extend higher in energy compared to those of $AuGa_2$. The electronic properties of $PtGa_2$, on the other hand, are not so well studied as those of $AuGa_2$. However, we can at least estimate the qualitative differences in the electronic structure between $PtGa_2$ and Pt based on those between $AuGa_2$ and Au .

The real and imaginary parts of the measured complex dielectric functions of $AuGa_2$ and $PtGa_2$ in the 1.2 - 5.5 eV range are shown in Fig. 4.10. For $AuGa_2$, the imaginary part of the dielectric function, ϵ_2 , shows a broad structure at around 2 eV, due to interband absorption. For $PtGa_2$, a structure in ϵ_2 due to interband absorption starts at about the same energy as in $AuGa_2$ but it is weaker in intensity. We also can see a broad structure peaked at about 3.3 eV in $PtGa_2$. Figure 4.11 shows the normal-incidence reflectivities of $AuGa_2$ and $PtGa_2$ calculated from their dielectric functions. For both compounds the reflectances at low energies (< 2 eV)

are rather small compared to those of the noble metals in the same energy range. The reflectance of $AuGa_2$ decreases to a minimum at 1.90 eV where its value of less than 60% agrees well with other results [95] [96]. This is due to an onset of interband transitions around that energy. The reflectance increases towards a maximum of about 70% at about 3.1 eV after which it decreases slowly. By comparing the reflectances of $AuGa_2$ and $AuAl_2$ [95] [96] [97] we can see that the reflectance of $AuGa_2$ is smaller than that of $AuAl_2$ at lower energies (< 2 eV) but larger at higher energies (2 - 5 eV) and the reflectance minimum of $AuAl_2$ is located at higher energy ($\simeq 2.2$ eV). The reflectance of $PtGa_2$ decreases to a minimum of less than 40% at 2.92 eV, then it slowly increases to a maximum at about 4.0 eV, after which it decreases slowly. We also can see a similarity between the reflectances of $PtGa_2$ and $PtAl_2$, in which both have minima at about 3 eV and shoulders at about 4 eV, as a result of which they exhibit a yellow color [106].

To estimate the interband contributions to the imaginary part of the dielectric function, ϵ_2^b , quantitatively from our optical data, we need to subtract the intraband contributions, ϵ_2^f , from the measured ϵ_2 . By assuming that the optical properties of these compounds are governed by intraband transitions of the quasifree conduction electrons at low energies (here less than 0.5 eV) we can fit the low energy behavior of the dielectric function to the Drude model if we have the dielectric functions at low energies for both compounds. This assumption has been a good approximation for noble metals. Then we can obtain the free-electron (Drude) parameters for both compounds which can be used to estimate the intraband contributions at higher energies.

Figure 4.10: Real and imaginary parts of the complex dielectric functions of AuGa_2 and PtGa_2

Figure 4.11: Normal incidence reflectance spectra of AuGa_2 and PtGa_2 . Note that the zero of the reflectance is suppressed

We obtained the dielectric functions at low energies (< 1 eV) by K-K analyses of the reflectance data in the 0.02 - 6.2 eV range measured by Wieliczka et al. [107] at room temperature for both compounds. For energies larger than 6.2 eV and up to 100 eV reflectances were assumed to drop off as ω^{-p} , and for still higher energies as ω^{-4} , where $p(< 4)$ is an adjustable parameter to make the calculated dielectric functions agree in magnitude with the ellipsometry data in the 1.2 - 5.5 eV region. The structure of the spectra is not sensitive to values of p .

In estimating the Drude parameters we assume that $\bar{\epsilon} \simeq \bar{\epsilon}^f$ for the dielectric functions at low energies (< 0.5 eV) obtained from K-K analyses of the reflectance data for both compounds, which means we neglect the contributions from interband absorption at low energies. We also assume that $\omega\tau \gg 1$ at the same energy range which has been a good approximation for noble metals. For $AuGa_2$ [92], the dc relaxation time, τ_{dc} , was estimated to be 8.0×10^{-14} sec from the d.c. resistivity, so that the above condition is satisfied at 0.5 eV. By linear-regression fitting of the real part of the dielectric functions below 0.5 eV using Eq. (1.24) we can obtain ϵ_∞ and ω_p . Also, by assuming Eq. (4.1) for the energy dependence of the relaxation time in fitting the imaginary parts of the dielectric functions below 0.5 eV to Eq. (1.25) τ_0 and β can be obtained. The parameters obtained from the above procedure are listed in Table 4.6. We used the above four-parameter sets for both compounds to estimate the intraband parts of the dielectric functions at higher energies (> 1.2 eV). The intraband parts were subtracted from the ellipsometry data to get the interband parts. The ϵ_2^b for $PtGa_2$ obtained from the above procedure shows the structure at about 1.3 eV more developed than in Fig. 4.10. However, the ϵ_2^b 's for both compounds still show increasing low-energy ends which might mean that there are

Table 4.6: Least-squares fitted values of free-electron Drude parameters for $AuGa_2$ and $PtGa_2$ used to estimate the intraband part of the complex dielectric function

Compound	ϵ_∞	$\hbar\omega_p$ (eV)	τ_0 (10^{-14} sec)	β ($10^{14} \text{ sec}^{-1} \text{ eV}^{-2}$)
$AuGa_2$	2.70	4.72	0.602	10.2
$PtGa_2$	4.94	6.29	1.27	5.38

strong interband transitions below 1.2 eV, the low energy limit of our measurements. For this reason, the Drude parameters may not be meaningful for both compounds. They are used only to try to separate $\tilde{\epsilon}$ into two parts.

Relativistic band structures of $AuGa_2$ and $PtGa_2$ including the spin-orbit interaction are shown in Figs. 4.12 and 4.13 along certain high-symmetry directions. In both structures, the bands near E_F are of Ga s - p -character mixed with Au or Pt s - p -character and these s - p -bands along the Γ - K and L - W directions have quite similar shapes in the two materials except for the difference in E_F . Also, these bands do not shift much in energy by including the spin-orbit interaction as a perturbation while the lower-lying d -bands shift and split significantly due to the combined spin-orbit and crystal-field effect.

The lowest band for both compounds consists of a mixture of Au 6s- or Pt 6s- Ga 4s bonding states. Its hybridization with 5d-states of Au or Pt is much weaker than those in elemental Au or Pt . The narrow set of bands above this s -band are 5d-bands of Au or Pt . The positions of these 5d-bands in $AuGa_2$ agree within 0.5 eV with the results of angle-resolved-photoemission measurements on the (100) surface

of $AuGa_2$ [108]. Also, the measured energy gap between Γ_7^+ and the lower Γ_8^+ from the above measurement is 1.6 eV while our calculation gives 1.1 eV. In $PtGa_2$ these 5d-bands are located at higher energies than in $AuGa_2$: the upper Γ_8^+ is located 2.3 eV higher in $PtGa_2$ than in $AuGa_2$ relative to E_F . In Table 4.7 a comparison is made between the 5d-states at Γ with and without the spin-orbit interaction for both compounds. It is seen that the widths of the 5d-bands are increased due to the rise of the doubly-degenerate $\Gamma_{12}(eg)$ level to Γ_8^+ and also due to the splitting of the triply-degenerate $\Gamma'_{25}(t_{2g})$ level into the twofold Γ_7^+ and fourfold Γ_8^+ . The width of the 5d-bands of $AuGa_2$ agrees well with the result of the valence-band XPS measurement [109] [110].

The main difference between the band structures of $AuGa_2$ and $PtGa_2$ near E_F is that for $AuGa_2$ the band originating from the Γ_7^- is located below E_F along the Γ -X, Γ -K, and Γ -L directions while for $PtGa_2$ it is above E_F along the Γ -X direction and partially unfilled along the Γ -K and Γ -L directions. This band is derived mostly from Ga 4s antibonding states among neighboring Ga atoms. In $AuGa_2$, this band is quite flat along the Γ -X direction and located 0.26 eV below E_F at the Γ -point. However, this band does not cause a high density of states at about 0.26 eV because it disperses significantly in the other directions of the BZ. In other calculations [21] [98], this band lies at lower energies and at the Γ -point it is located about 1.4 eV below E_F , differing from our result by more than 1 eV.

We calculated the interband contributions to the imaginary part of the dielectric function, ϵ_2^b , for both $AuGa_2$ and $PtGa_2$ according to Eq. (1.29) including the effect of the electric-dipole matrix elements.

Figure 4.12: Relativistic energy band structure and density of states of $AuGa_2$ including spin-orbit coupling

Figure 4.13: Relativistic energy band structure and density of states of $PtGa_2$ including spin-orbit coupling

Table 4.7: States at Γ for $AuGa_2$ and $PtGa_2$ with and without spin-orbit splitting. Zero-energy refers to the muffin-tin zero

$AuGa_2$		$E_F = 0.6980$	
non s-o		s-o	
$\Gamma_{12}(e_g)$	0.2556	Γ_8^+ ($j=3/2$)	0.2801
$\Gamma'_{25}(t_{2g})$	0.2049	Γ_7^+ Γ_8^+ ($j=5/2$)	0.2388 0.1613
$PtGa_2$		$E_F = 0.7160$	
non s-o		s-o	
$\Gamma_{12}(e_g)$	0.4246	Γ_8^+ ($j=3/2$)	0.4366
$\Gamma'_{25}(t_{2g})$	0.3363	Γ_7^+ Γ_8^+ ($j=5/2$)	0.3601 0.3101

In Figs. 4.14 and 4.15 we compare our calculation results with the spectra obtained after subtracting the Drude model calculations from the optical data. We can see that overall agreement is good between the two quantities for both the peak positions and the strengths of the structures for both compounds in our ellipsometry data range (1.2 - 5.5 eV). An interesting result is that both compounds show strong calculated interband absorptions below our ellipsometry data range: for $AuGa_2$ there is a peak at 0.65 eV and for $PtGa_2$, at 0.97 eV. At 1.2 eV, the strength of this interband absorption compared to the total absorption strength, ϵ_2^b/ϵ_2 , is 86% for $AuGa_2$ and 66% for $PtGa_2$. The reflectance data of Wieliczka et al. [107] for both

compounds do not show any structure at energies below 1 eV so that the dielectric functions obtained from them do not show any structure related to the interband absorptions in this range. This is possible if the strengths of the intraband absorptions at room temperature are much greater than those of the interband absorptions so that the reflectance measurements could not resolve the weaker interband contributions from the stronger intraband contributions. Another possibility is that our calculations might overestimate the strengths of the low-energy interband absorptions, or place them slightly too high in energy, where they would appear to be more observable. By calculating the interband contribution to ϵ_1 from our calculated interband ϵ_2 , adding these to the Drude $\tilde{\epsilon}$, and calculating the reflectance, we find no detectable reflectance structure is expected in $PtGa_2$ due to the low strength of these interband transitions. Such structure should be detectable in $AuGa_2$ if the calculations are accurate.

As a good example, the reflectance measurement on Al [111] at room temperature could not resolve a structure due to the interband absorption at low energies (<1 eV) from the background of intraband absorption. Also, K-K analysis [112] using various room-temperature optical data, including the above, could not produce the low-energy structure. However, an absorptance measurement on Al at 4.2 K [113] showed an interband absorption peaked at about 0.5 eV. Therefore, for some metals, phonon-assisted intraband absorption might increase dramatically as the temperature rises so that at room temperatures we might not resolve the interband absorptions at low energies.

Figure 4.14: Comparison of the interband contribution to the imaginary part of the complex dielectric function from the band calculation (broadened by convolution with a Lorentzian of full width at half maximum of 0.05 eV) and the experiment for $AuGa_2$

Figure 4.15: Comparison of the interband contribution to the imaginary part of the complex dielectric function from the band calculation (broadened by convolution with a Lorentzian of full width at half maximum of 0.05 eV) and the experiment for $PtGa_2$

To find the regions in $\mathbf{k}$ -space which contribute significantly to the structures in ϵ_2^b we calculated the integral part of Eq. (1.29) for each of the 110 tetrahedra for selected energy windows centered at the peaks of each structure for both compounds. The intensities of all the interband transitions having energy differences between the initial and final states falling in the energy window were summed for each tetrahedron to represent the contribution from the tetrahedron to the structure. In Figs. 4.16 and 4.17 each tetrahedron is represented by a rectangle if it makes a contribution to the structure, with the size of the rectangle denoting the strength of the contribution. Figure 4.16 shows the distribution of the transitions for the 0.65-eV peak of $AuGa_2$ in the $1/48$ th of the BZ. The largest contribution comes from around the middle of the Γ - X line. These transitions occur between bands having mostly s - p -character. As shown in Fig. 4.12 there are three nearly-parallel bands along the Γ - X direction. The lowest band of the three at the X -point (band 8) has Au s - p -character and the other two upper bands (bands 9 and 10 respectively) have mixtures of Au p - and Ga p -character at around the middle of the Γ - X line. The 0.65-eV peak is caused primarily by transitions between bands 8 and 9. At about 1 eV the strength of the transitions between bands 8 and 10 is comparable to that of the transitions between bands 8 and 9 so that a small shoulder occurs on the falling slope of ϵ_2^b in Fig. 4.14. Figure 4.17 shows the distribution for the 0.97-eV peak of $PtGa_2$. The largest contribution comes from the region between the middle of the Γ - X line and the middle of the Γ - K line in the ΓXWK -plane. As can be seen in Fig. 4.13 the band structure of $PtGa_2$ along the Γ - X direction also has three nearly-parallel bands. Giving the same indices to these bands as those in $AuGa_2$, band 8 has Pt s - p -character and band 9 and 10 have mixtures of Pt p - d - and Ga p -character.

Figure 4.16: Regions in the irreducible wedge of the Brillouin zone of AuGa_2 contributing to interband transitions in the (0.61-0.75)-eV and (1.9-2.1)-eV spectral region. Larger rectangles show the locations of the small tetrahedra with the larger contributions (from the product of dipole-matrix elements and joint density of states). Smaller rectangles show weaker transitions

Figure 4.17: Regions in the irreducible wedge of the Brillouin zone of $PtGa_2$ contributing to interband transitions in the (0.88-1.02)-eV and (2.9-3.1)-eV spectral region

In $PtGa_2$ the d -bands of Pt are located higher than those of Au in $AuGa_2$ so that the bands near E_F have significant d -character through the hybridization. The strength of the 0.97-eV peak is mainly due to transitions between bands 8 and 9. The strength of the transitions between bands 8 and 10 grows as the energy increases to make a shoulder at about 1.3 eV in ϵ_2^b of $PtGa_2$. The contributions to the 2-eV structure of $AuGa_2$ are from throughout nearly all of the irreducible wedge and the contribution from the high-symmetry regions is very small compared to the total strength, as can be seen in Fig. 4.16. These contributions come mainly from transitions between filled bands having mixtures of Au p - and Ga p -character (like bands 9 and 10 along the Γ - X direction) and unfilled bands having Ga s - p -character. Figure 4.17 also shows the contributions to the 3.3-eV structure of $PtGa_2$. The contributions occur throughout all of the irreducible wedge. These transitions are mostly between the filled bands with Pt s - p -character and the unfilled bands with Pt p - d -character mixed with Ga p -character.

β' - $NiAl$ and β' - $CoAl$

The 3d-transition metals, Ni and Co , form stable alloys with Al over a wide range of composition. These alloys form in the β' -phase near stoichiometry in which they are ordered in the $CsCl$ crystal structure. In the Al -poor region of the β' -phase Ni/Co atoms substitute on Al sites while in the Al -rich region vacancies are formed at Ni/Co sites. The electronic structures of β' - $NiAl$ and $CoAl$ have been studied extensively both theoretically and experimentally because of the simplicity of their crystal structure and the variation of physical properties that are made possible by the width of the β' -phase range.

Optical-spectroscopic measurements have provided some information about the electronic structures of these alloys. In earlier years, reflectances of these alloys were measured and changes in the spectral features were found as the *Al* concentration changed [114] [115]. The dielectric functions of ordered β' -phase samples of both alloys were measured at room temperature by polarimetric techniques [116] [117]. Also, the optical absorptance of β' -*NiAl* [118] and *CoAl* [119] were measured at 4.2 K using a calorimetric technique and dielectric functions were obtained by K-K analysis. In these measurements, β' -*NiAl* showed five structures in the dielectric function between 0.7 and 6 eV. They occurred at about 1.5, 2.0, 2.5, 4.2, and 5.3 eV and were interpreted in terms of direct interband transitions. β' -*CoAl* also showed structures due to interband transitions in the same energy range, most of them occurring at low energies (< 3 eV).

The electronic band structures of both compounds have been calculated a number of times [120] [121] [122] [123] and the results were tested by comparison with the measured optical properties [120] [123], soft X-ray spectra [122] [124], and photoemission spectra [125] [126] [127].

Figures 4.18 and 4.19 show the band structures of β' -*NiAl* and *CoAl* respectively, calculated relativistically including the spin-orbit interaction along some high-symmetry directions. For both compounds, inclusion of the relativistic effect does not shift or split the energy spectra significantly so that our results are not so different from other author's results [120] [121] [122] [123] which did not consider relativistic effects. It is seen that both band structures look very similar except for the energy positions of the relatively flat bands near E_F .

Figure 4.18: Relativistic energy band structure of β' -NiAl including spin-orbit coupling

Figure 4.19: Relativistic energy band structure of β' -CoAl including spin-orbit coupling

As shown in Fig. 4.20 the densities of states of both compounds also look similar to each other except for the relative positions with respect to E_F of the high-density peaks which are due to the flat bands. These peaks are caused by localized d -bands of Ni/Co . It is also seen that the d -bands of Ni are located at lower energies than those of Co by about 0.5 eV, due to the greater attractive Coulomb potential from the Ni core with one additional nuclear charge. The smaller peaks near E_F (below E_F for $NiAl$ and above E_F for $CoAl$) are also contributed mostly by d -states. The d -bands are mostly filled in $NiAl$ while there is still some density of d -states above E_F in $CoAl$.

In Fig. 4.21 the calculated σ_1^b of β' - $NiAl$ is shown and compared with the optical data obtained from K-K analysis of the absorptance, $A = 1 - R$, with R the reflectance, measured at 4.2 K in the energy range of 0.2 - 4.4 eV using a calorimetric technique [118] which is advantageous for resolving small structures due to interband transitions by reducing the background in the dielectric function caused by phonon-assisted intraband transitions that grow as temperature rises. The intraband (Drude) contribution to the optical data which provides a smooth and structureless background is not subtracted. However, plotting σ_1 instead of the dielectric function (ϵ_2) emphasizes the interband term with respect to the Drude term. In the K-K analysis, a Drude term below 0.2 eV, room-temperature reflectance data [115] between 4.4 and 5.6 eV, a shifted average of Ni [128] and Al [129] reflectance data between 5.6 and 27 eV, and a power-law function above 27 eV are used. Calculational results show that interband transitions start as low as 0.2 eV between states with mostly Ni p - d -character around the R-point, where two bands are located close to each other across E_F , as can be seen along the R-X direction in Fig. 4.18.

Figure 4.20: Densities of states of β' -NiAl and CoAl

Figure 4.21: Comparison of the calculated optical conductivity to the experimental data for β' -NiAl

At higher energies there are two prominent peaks at about 2.5 eV and 4.3 eV with a shoulder at about 2.0 eV. It is seen that the positions and intensities of these structures agree well with the optical data, which show structures at about 2.0, 2.5, and 4.2 eV. At low energies (< 1.5 eV) the optical data increase rapidly so that the interband transitions, although they may make structures, may not be resolved from the background of intraband transitions, as can also be seen in other optical data [116] [118] measured at room temperatures. The contributions to the 2.0-eV structure come from transitions involving states with *Ni p-d*-character near E_F as initial or final states. The major contribution to the 2.5-eV structure comes from transitions between initial states with *Ni p-d*- and *Al p*-character near E_F and final states above E_F with *Ni s-p-d*- and *Al s*-character (e.g., bands 7 and 8 in the Γ -M direction respectively). The 4-eV structure is mostly due to transitions between states with *Ni p-d*-character mixed with *Al p*-character well below E_F and near E_F (e.g., bands 2 and 7 in the Γ -X direction respectively).

The regions in the BZ which have major contributions to the structures in σ_1 were found by calculating the integral part of Eq. (1.29) for each of the 220 tetrahedra for selected energy windows centered at around the peaks of each structure. The intensities of all the interband transitions having energy differences between the initial and final states falling in the energy window were summed for each tetrahedron to represent the contribution from the tetrahedron to the structure. Figure 4.22 show the distributions of the transition intensities for the 2.5-eV and 4-eV structures of *NiAl* in the 1/48th of the BZ. Each tetrahedron is represented by a parallelogram if it makes a contribution to the structure, with the size of the parallelogram denoting the strength of the contribution.

Figure 4.22: Regions in the irreducible wedge of the *sc* Brillouin zone of β' -NiAl contributing to interband transitions in the (2.38 - 2.52)-eV and (4.15 - 4.28)-eV spectral region. Larger parallelograms show the locations of the small tetrahedra with the larger contributions (from the product of electric-dipole matrix elements and joint density of states). Smaller parallelograms show weaker transitions

For the 2.5-eV structure, major contributions come from around the Γ -M-R plane of the BZ while for the 4-eV structure major contributions come from the central region of the BZ. The contributions to the structures from near symmetry directions are also denoted as arrows between initial and final states in the band structure in Fig. 4.18.

According to the room-temperature optical data for β' -NiAl [116] for Al concentrations between 38.4 and 54.8 at.%, the peak of the 2.5-eV structure shifts to lower energies as the Al concentration increases. This downward shift of the 2.5-eV structure can be explained by assuming a rigid-band behavior in which E_F moves upward as the Al concentration increases, resulting in a decrease in the energy of the 2.5-eV transitions which occur between initial states near the Fermi surface and final states above E_F . The structure at about 5.8 eV in the calculated spectrum is mainly due to transitions between initial states with Ni *p-d*- and Al *p*-character well below E_F and final states above E_F with Ni *s-p-d*- and Al *s-p*-character (e.g., bands 3 and 8 in the Γ -M direction). The corresponding structure in the experimental spectrum occurs at about 5.3 eV, which disagrees by about 0.5 eV with the calculational result.

In Fig. 4.23 the calculated optical conductivity of β' -CoAl is compared with the optical data obtained from K-K analysis of the absorptance measured at 4.2 K in the 0.1 - 2.5 eV range [119]. The extrapolation to high energy was achieved by using reflectance data [115] between 2.5 and 6 eV, data used for β' -NiAl to 30 eV, and a power-law extrapolation beyond. The calculated spectrum has several structures below 3 eV caused by interband transitions, located close in energy to each other (0.7 eV, 1.4 eV, 1.6 eV, 2.3 eV and 2.7 eV).

Figure 4.23: Comparison of the calculated optical conductivity to the experimental data for β' -CoAl

The experimental spectrum also shows several structures at nearly the same energies (0.7 eV, 1.2 eV, 1.7 eV and 2.3 eV) although there is clearly some quantitative disagreement with the positions and the intensities of the structures. These structures were not resolved in other experimental data taken at room temperatures due to a large Drude background [117]. At higher energies a broad structure occurs at about 4.3 eV in the experimental spectrum while the calculation produced the corresponding structure at about 5 eV. The optical property calculations by Knab and Koenig [130] also show some disagreement with experimental spectra for *FeAl*, *CoAl*, and *CoGa* while they show better agreement for *NiAl*, as do our results.

The discrepancies between the experimental spectra and the calculational results for both the energy positions and the intensities of the structures, which are slighter in *NiAl* than in *CoAl*, might be due to final-state effects for the transitions involving 3d-states which are known to have strong Coulomb correlations [131]. The *d-d* correlation for the states with large *d*-character is significant for 3d-systems due to the highly-localized nature of the 3d-orbitals, which maintain strong intra-atomic correlations in the solid. This can lead to significant discrepancies between the experimental results and the theoretical calculations assuming the ground-state configuration for the excited states even for low-energy excitations.

According to Sham and Kohn [132] application of the ground-state configuration to the excitation spectrum requires a self-energy correction which is obtained from the eigenvalues of the ground state by including the energy dependence of the self-energy. When the electronic charge density ρ is slowly varying the self-energy corrections are expected to have the effect of changing the excited-state energies $\hat{E}_n(\mathbf{k})$ relative to the ground-state energies $E_n(\mathbf{k})$ by an amount proportional to $E_n(\mathbf{k}) - E_F$, i.e.,

$$\hat{E}_n(\mathbf{k}) = E_n(\mathbf{k}) + \lambda_{n\mathbf{k}}[E_n(\mathbf{k}) - E_F] \quad (4.5)$$

for low-lying excited states near E_F , where

$$\lambda_{n\mathbf{k}} = \frac{\int d^3r |\psi_{n\mathbf{k}}|^2 [1 - m^*(\rho(\mathbf{r}))]}{\int d^3r |\psi_{n\mathbf{k}}|^2 m^*(\rho(\mathbf{r}))}. \quad (4.6)$$

Here, m^* is the effective mass (in units of the free-electron mass) for the interacting electron gas, evaluated for each $\mathbf{r}$ for an electron density equal to the ground-state charge density $\rho(\mathbf{r})$, and $\psi_{n\mathbf{k}}(\mathbf{r})$ is a ground-state wavefunction. By assuming λ in Eq. (4.6) to be a real constant independent of n and $\mathbf{k}$, and assuming this relation holds over the entire range of energies covered by optical conductivity, we can parametrize λ to fit theoretical results to experimental spectra [133] [134] [135].

If $V_{xc}(\mathbf{r}, E)$ is the excited-state exchange-correlation potential, Eq. (4.5) with constant λ can be obtained by writing

$$V_{xc}(\mathbf{r}, E) = V_{xc}(\mathbf{r}) + \frac{\lambda}{1 + \lambda}(E - E_F). \quad (4.7)$$

This potential differs from the ground-state exchange-correlation potential by a term which is energy-dependent but independent of position. Thus, there is no change in the one-electron wavefunctions, and, in particular, there is no change in the electric-dipole matrix elements evaluated using the ground-state wavefunctions. Furthermore, $\hat{\sigma}_1(\omega)$, the optical conductivity evaluated using the excited-state eigenvalues, is related to $\sigma_1(\omega)$, the optical conductivity evaluated using the ground-state eigenvalues

according to

$$\hat{\sigma}_1(\omega) = \frac{1}{1+\lambda} \sigma_1\left(\frac{\omega}{1+\lambda}\right). \quad (4.8)$$

Thus, in addition to supplying a single parameter to fit the experimental spectra, the assumption that λ is constant greatly simplifies the calculation by allowing the use of the ground-state electric-dipole matrix elements. With the parameter $\lambda (= -0.15)$ chosen to make the 5-eV theoretical structure coincide with the 4-eV structure in the experimental data of β' -*CoAl* the agreement in the low-energy region becomes much better as can be seen in Fig. 4.23. Janak et al. [133] found that the choice $\lambda = 0.08$ gave a good match between calculated and observed conductivities of *Cu*. For the transition metals *Fe* and *Ni* Laurent et al. [134] found that negative values of λ ($\lambda = -0.1$ for *Fe* and $\lambda = -0.12$ for *Ni*) are needed to produce agreement, which have the effect of reducing energy differences.

In the present case, *CoAl* needs a value of λ larger in magnitude than those of the two transition metals to fit the experimental spectrum which disagrees with the calculational result in the whole energy range. For *NiAl* there is a good agreement between the calculation and the experiment for the structures at about 2.0 eV and 2.5 eV. These structures are due to transitions involving states near and above E_F which have small amounts of *d*-character, as can be seen in Fig. 4.20. Hence, the final state effect for these transitions is weaker compared to that for the 4-eV and 5-eV transitions, which makes the peak positions of them shift by about 0.1 eV and 0.5 eV respectively.

The interband transitions responsible for the 0.7-eV structure are mainly between

states with *Co p-d*-character. The 1.2-eV structure is mainly due to transitions between initial states with *Co p-d*-character and final states with *Co d*-character near E_F (e.g. bands 6 and 7 along the R-X direction and the Γ -M direction). The 2-eV structure is also mainly due to transitions between initial states with *Co p-d*- and *Al p*-character and final states near E_F with *Co d*-character around the M-point (bands 4 and 7). The contributions to the structures coming from near symmetry directions in **k**-space are also denoted as arrows between initial and final states in the band structure in Fig. 4.19. The above transitions can not occur in *NiAl* because the bands responsible for them are located below E_F in *NiAl*. The 4-eV structure is mostly due to transitions between states with *Co p-d*- and *Al p*-character well below E_F and states above E_F having *Co s-d*- and *Al p*-character (e.g. bands 2 and 7 in the Γ -X direction). The small structure at about 5 eV is mainly due to transitions between initial states with *Co p-d*- and *Al p*-character well below E_F and final states above E_F with *Co s-p-d*- and *Al s-p*-character (e.g. bands 3 and 8 in the Γ -M direction). The initial and final states of the transitions for the 4-eV and 5-eV structures are of nearly the same nature as those for the 4-eV and 5-eV structures in *NiAl*.

Figure 4.24 shows the regions in the BZ which have major contributions to the 1.2-eV and the 4-eV structures respectively. For the 1.2-eV structure the major contribution comes from the X-M-R plane, while for the 4-eV structure the major contribution comes from a large volume in the central region of the BZ and the distribution of the strengths is very similar to that of the 4-eV structure of *NiAl*, indicating that the two structures are caused by almost the same sets of initial and final states in the band structures of both compounds. The reason for the larger

energy shift due to the final-state effect of the 4-eV structure of *CoAl* (0.7 eV) than the shift of the 4-eV structure of *NiAl* (0.5 eV) is that the unfilled states of *CoAl* near E_F have stronger *d*-character than those of *NiAl* as can be seen in Fig. 4.20, leading to the stronger final-state effect.

CeSn₃ and *LaSn₃*

The electronic structure of *Ce*-based systems has been studied extensively in recent years because of the unusual chemical and physical properties associated with the interactions of the 4*f*-states with the environment. The 4*f*-states of *Ce* in some *Ce*-based materials are located close to E_F and have somewhat more extended wave-functions than those of heavier rare-earth elements in which the 4*f*-states are spatially located deep within the ionic cores, preserving well their atomic character which is dominated by strong intra-atomic Coulomb correlations. A possible interaction of the 4*f*-states with the environment is provided by hybridization of these states with valence-band states, which gives a partial band-like character to the 4*f*-electrons.

In the study of the electronic structures of *Ce* and its compounds, the fundamental question to be addressed is whether the 4*f*-states are core-like or band-like. If the 4*f*-states can be treated as being very weakly perturbed by the valence electrons then the valence bands do not contain 4*f*-character and the *Ce* ions can be thought to have a definite integral valence. Many of the *Ce*-based materials do not fit into this localized system and show valence fluctuation (or mixed valency) to some extent.

Figure 4.24: Regions in the irreducible wedge of the *sc* Brillouin zone of β' -*CoAl* contributing to interband transitions in the (1.22 - 1.36)-eV and (4.83 - 4.96)-eV spectral region

In most of the *Ce*-based valence-fluctuating systems the ground state has been described as an intermediate-valence (or homogeneous mixed-valence) state where each *Ce* ion has the same, noninteger, valence due to the near degeneracy in energy of the two configurations, $4f^1(Ce^{3+})$, with one core-like *f*-electron, and $4f^0(Ce^{4+})$, with no core-like *f*-electron [136]. The coexistence of these two configurations gives rise to an intermediate-valence state, $\Psi = a |4f^1\rangle + b |4f^0\rangle$ with $|a|^2 + |b|^2 = 1$. Hence, the theoretical problem is one of simultaneously describing atomic-like configurations, extended band-like states, and sometimes transitions between them. The problem with the traditional band-theory approach in describing the ground state of the systems exhibiting valence fluctuations is that it can not treat the atomic-like correlation of the localized $4f$ -states properly. However, band theory may be a good starting point for describing the valence-fluctuating systems.

CeSn₃ is known to be one of the intermediate-valence system in which the band theory might break down [137]. Its lattice constant at room temperature is intermediate between that expected for Ce^{3+} and Ce^{4+} with an effective valence of about 3.3 [138]. Hence, each *Ce* ion has about 0.7 $4f$ -electrons. The electronic specific heat and thermal expansion are usually large [139]. The magnetic susceptibility follows a Curie-Weiss law at high temperatures and it is approximately constant in the 40-300 K region and increases rapidly with decreasing temperature below 40 K [140]. It shows no magnetic ordering down to 1.6 K according to a Mössbauer measurement [141]. *LaSn₃* is, on the other hand, not a mixed-valence system. Its magnetic susceptibility follows a Curie-Weiss law above 100 K and it is approximately constant below 100 K [142]. It has a relatively high superconducting transition temperature ($T_c = 6.42$ K). A detailed understanding of physical properties of *LaSn₃* can be

helpful in assessing the origin of the anomalous properties of its isostructural mixed-valence compound $CeSn_3$ which is believed to be due to its one f -electron.

Optical measurements on some Ce - and La -based materials have been performed to obtain the dielectric functions either from K-K analyses of the reflectance [136] [143] [144] [145] or from ellipsometry [146]. Recently, photoemission spectroscopy measurements in UHV have been performed to investigate the nature of the f -states of Ce -based systems [147] [148] [149] [150].

Figure 4.25 shows the optical conductivities of $CeSn_3$ and $LaSn_3$. For $LaSn_3$ a broad structure exists at about 2 eV and a weak structure at about 3 eV. The shape and strength of the curve look very similar to the spectrum taken from a La film [143]. For $CeSn_3$ the structure at about 2 eV becomes developed from the background and makes small peaks at 1.8 eV and 2.3 eV. The structure at about 3 eV also becomes stronger.

A band calculation for $CeSn_3$ has been carried out for the $Ce^{4+}(4f^0)$ state, in which the $4f$ -states on Ce are treated as valence states, and this is essentially the same as for $LaSn_3$ used as a reference material without a $4f$ -electron. Koelling [31] showed a good agreement between a band theory description and the experimental result for the Fermi surface topology of $CeSn_3$ as well as $LaSn_3$. However, it is generally accepted that except for a very few special cases in which $4f$ -states hybridize strongly with the valence-band states band theory is hardly applicable to most of the Ce -based systems.

Figure 4.26 shows the DOS of $CeSn_3$ and $LaSn_3$ obtained from the present band calculation. For both compounds peaks in DOS are caused by large densities of $4f$ -states and in $CeSn_3$ $4f$ -states are concentrated just above E_F . The DOS of

$CeSn_3$ at E_F is 70 states/Ry cell and this is smaller by about a factor of 2 than the observed value 153 states/Ry cell from a electronic specific heat measurement [151]. For $LaSn_3$ the DOS at E_F is 45 states/Ry cell while it is observed to be 68 states/Ry cell [152]. This might suggest that a certain many-body correlation effect is present for both compounds with larger correlation for $CeSn_3$, which is not adequately treated by the LDA for the exchange-correlation potential.

To verify the theoretical predictions that the 4*f*-states of some *Ce*-based systems exist very close to E_F photoemission measurements have been done on these *Ce*-based materials. The resulting 4*f*-spectra for a number of *Ce*-based materials [147] [148] [149] [153] including $CeSn_3$ [154] [155] show two peaks, one at about E_F and another at about 2 eV below E_F . There have been several theoretical models to explain the origin of the double-peak spectrum [156] [157] [158] [159]. They all treat 4*f*-states as localized with some hybridization.

Band-calculational results for both compounds also show that the 5*d*-character of *La/Ce* is quite spread in both energy and space. The bottom of the *d*-bands are located 3.3 eV below E_F for $LaSn_3$ and 5.4 eV for $CeSn_3$. For $LaSn_3$ states near E_F have *La d-f*-character mixed with strong *Sn p*-character. Transitions from lower-lying states with *La d*-character to these states near E_F cause 2-eV and 3-eV structures. For $CeSn_3$ there exists more *f*-character in the states near E_F than those in $LaSn_3$. Therefore, the strengths of the two structures which are due to transitions between *Ce d*- and *Ce d-f*-character may increase. As shown in Fig. 4.27 calculated optical conductivities for both compounds have broad structures at about 3 eV and 4 eV, which can be assigned to the 2-eV and 3-eV structures in the experimental spectra. The intensities of the structures in the calculated results are larger than

the experimental spectra for both compounds (by a factor of 2 for $CeSn_3$). These discrepancies in the transition strengths might be due to the overestimation by the band calculation using the LDA of the extendedness of the $4f$ -wavefunctions. It can lead to an enhanced density of $4f$ -character near E_F due to enhanced hybridization with valence states (Ce/La $5d$ and Sn $5p$) near E_F and it can also lead to an enhancement of the electric-dipole matrix elements due to enhanced overlap between $4f$ - and $5d$ -states. In real situations the $4f$ -states are expected to be highly localized near the atomic nucleus so that the hybridization with the valence states is expected to be weak. The discrepancies in the positions of the structures between the experimental spectra and the calculated results for both compounds, which are about 1 eV for both 2-eV and 3-eV structures, might be due to the final-state effect from the excitations involving highly correlated $4f$ - $5d$ -states as was seen in the $3d$ -systems. The problem of not being able to treat the highly atomic-like localized states using LDA in the standard band-theoretical technique is believed to be the main reason for the discrepancy between the experimental spectra and present band-calculational results for $CeSn_3$ and $LaSn_3$ compounds.

Figure 4.25: Real parts of the complex optical conductivities of CeSn_3 and LaSn_3

Figure 4.26: Densities of states of CeSn_3 and LaSn_3

Figure 4.27: Calculated real parts of the complex optical conductivities of CeSn_3 and LaSn_3

CHAPTER 5. CONCLUSIONS

The addition of small amounts of *In* to *Ag* causes a change in the optical properties compared to those of pure *Ag*. At low photon energies, below the onset of interband transitions, the Drude parameters change significantly and the frequency dependence of the relaxation time changes with a sign not in accord with a calculation based on the assumption of a spherical Fermi surface and isotropic scattering from an impurity represented by a screened Coulomb potential. At higher photon energies the shift in the interband absorption cannot be explained only by an increase in E_F and a narrowing of the *Ag* 4*d*-bands.

In the case of $Ni_{1-x}Cu_x$, although the 3*d*-states of both constituents are located close to E_F and to each other they do not mix to produce a single set of *d*-bands. Optical transitions involving *Ni* and *Cu* *d*-subbands are detected separately even at low solute concentrations. As the *Cu* concentration increases, the *Cu* *d*-subbands move up to make the $L_3-L'_2$ gap decrease. However, the dispersive *s-p*-bands of both constituents can mix to produce a single set of bands and the positions of these bands change in proportion to solute concentrations between those of pure *Ni* and pure *Cu*.

The optical spectra of *AuGa*₂ and *PtGa*₂ agree well with the band-calculational results. For both compounds the rising trend at low photon energies in the imaginary part of the dielectric functions are due in part to interband transitions and calcula-

tional results also predict interband transitions centered at 0.65 eV for $AuGa_2$ and 0.97 eV for $PtGa_2$. For $AuGa_2$ the 2-eV structure is contributed by transitions involving s - p -bands while for $PtGa_2$ the broad 3.3-eV structure has contributions from transitions involving Pt d -character due to the higher-lying nature of Pt 5 d -bands relative to E_F than those of Au in $AuGa_2$.

The calculated optical conductivity of β' - $NiAl$ agrees well with the experimental spectrum at low photon energies (<3 eV). At higher energies there is slight disagreement in peak position and half-width of the structures at about 4 eV and 5 eV. For β' - $CoAl$ the agreement is poorer than β' - $NiAl$ even at low photon energies. All of the structures found in both compounds involve states with Ni/Co d -character for both initial and final states of the transitions. For β' - $NiAl$ the peak at about 2.5 eV is found to be due to transitions between initial states near the Fermi surface and final states well above it while for β' - $CoAl$ there is no structure involving the same type of transitions. The discrepancies between the experimental spectra and the band-calculational results for the energy positions as well as the strengths of the structures might be due to a strong final-state effect for the transitions involving the well-localized 3 d -states which have strong Coulomb correlation so that the ground-state approximation for the final-state configuration of the system used to calculate the transitions may not work for some 3 d -systems, even for low-energy excitations.

The structures at about 2 eV and 3 eV for both $CeSn_3$ and $LaSn_3$ can be assigned to interband transitions between Ce/La d - and f -states. The larger strengths for both structures in $CeSn_3$ than in $LaSn_3$ may be due to the existence of more f -character near E_F in $CeSn_3$ than in $LaSn_3$. Band-calculational results produce optical conductivities larger than the experimental spectra as well as discrepancies in

the positions of the structures for both compounds. The discrepancies in the transition strengths might be due to the overestimation of the extendedness of the $4f$ -states by the LDA in the band calculation. It can lead to enhanced hybridization of the $4f$ -states with the valence states (Ce/La $5d$ and Sn $5p$), producing larger $4f$ -character near E_F . It also can lead to the overestimation of the electric-dipole matrix elements through the enhanced overlap of the $4f$ -states with the $5d$ -states. These two factors might contribute to exaggerate the transition strengths involving $4f$ -character for both compounds. The discrepancies in the positions of the structures between the experimental spectra and the calculated results for both compounds might be due to the final-state effect caused by the transitions involving correlated $4f$ - $5d$ -states.

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