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Optical properties of β'-CoAl

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The optical absorptance of β'-CoAl in the (0.1 – 2.5)-eV region was measured and analyzed by the Kramers-Kronig method. The optical conductivity shows interband features beginning below 0.1 eV, with several structures below 2 eV. These structures agree with those calculated from the energy bands of Moruzzi, Williams, and Gelatt. The experimentally observed systematics in CoAl and NiAl confirm our previous interpretation of the spectra of β'-NiAl, and disagree with other experimental and theoretical attempts to understand the optical properties of these compounds.

I. INTRODUCTION

In a recent paper[1] on the optical properties of β'-NiAl we presented an interpretation of the interband transitions in that intermetallic compound, typical of a number of CsCl-structured transition-metal – Al compounds. Our interpretation disagreed with the previous interpretation[2] in that we assigned most of the transitions to initial states below the Fermi level E_F with final states at E_F. This identification was made using detailed joint density-of-states (JDOS) calculations based on first-principles energy-band calculations for β'-NiAl by Moruzzi, Williams, and Gelatt.[3] The previous work assigned these transitions to initial states at E_F with final states above, the interpretations being primarily based on systematics involving the optical spectra for CoAl.[4–6] In particular, a prominent feature in the imaginary part of the dielectric function, ϵ_2 at 2.5 eV in NiAl was not seen in CoAl. Within a rigid-band model it would then seem plausible that, with one less electron and therefore a lower Fermi level, the initial states for the 2.5-eV feature in NiAl were unoccupied in CoAl. By approximating a JDOS for CoAl (using the NiAl bands), however, we found that the 2.5-eV peak was present but masked by new, allowed transitions.[1] In reviewing the optical experiments for CoAl we concluded that they lacked sufficient low-energy data to detect these new transitions.

Recently, new sets of self-consistent augmented-plane-wave calculations for CoAl and NiAl were used to compare theory with available optical results.[7] In addition to computing the JDOS, the authors approximated the effect of the dipole matrix elements. The results indicated that while the JDOS was a good approximation to the complex dielectric function for NiAl, it was a poor approximation for CoAl. Their results showed that the 2.5-eV feature in NiAl *was not* masked by other allowed transitions as we had postulated, thus agreeing with the previous interpretations.

In this paper we present optical measurements of CoAl showing the dramatic presence of the low-energy optical transitions which have eluded earlier investigators. We find that our optical spectra for CoAl are in better agreement with simple JDOS calculations than with the matrix-element approximation scheme of Eibler and Neckel.[7]

II. METHOD AND RESULTS

The sample was polycrystalline bulk β'-CoAl with about 51 at. % Co produced by electron-beam melting. (Less cobalt gave two-phase samples.) After spark cutting and abrasive polishing the sample was annealed for 12 h at 1100 °C and furnace cooled. It was then lightly electropolished and mounted in the apparatus. The absorptance, $A = 1 - R$, with R the reflectance, was measured in the (0.1 – 2.5)-eV region by a calorimetric technique previously described.[8] The resultant spectrum is shown in Fig. 1. This was analyzed by a Kramers-Kronig (KK) procedure to yield the optical conductivity, $\sigma = \sigma_1 + i\sigma_2$, the absorptive part

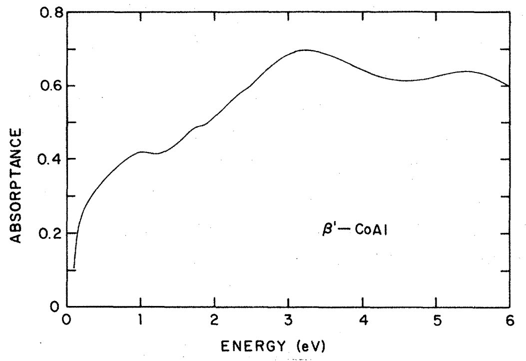

FIG. 1. Absorptance of β'-CoAl at 4.2 K.

of which is shown in Fig. 2. The extrapolation to low energy was achieved by fitting the data at the lowest energy to a Drude term, and to high energy by using the data of Ref. 4 between 2.5 and 6 eV, our data[1] for β'-NiAl to 30 eV, and a power-law extrapolation beyond.

III. DISCUSSION

Previous measurements on CoAl suggested free-electron-like behavior below about 2 eV. A free-electron metal should have a slowly rising absorptance in the infrared, even for rather short relaxation times. This is *not* the case for β'-CoAl, as seen in Fig. 1. There is a strong interband edge beginning below 0.2 eV. This is even more clear in Fig. 2 where we have *not* subtracted the free-electron term used for the KK analysis. The low-energy interband absorption, which was not seen in previous measurements, shows that β'-CoAl is not free-electron-like even below 0.3 eV. These results may be compared easily to our approximate JDOS of CoAl. In Fig. 4 of Ref. 1 the JDOS was divided by E^2 (where E is the transition energy) to show the interband contribution to ϵ_2, neglecting dipole matrix elements. If we plot σ_1 instead of ϵ_2, the interband terms are emphasized with respect to the Drude or free-electron contributions. Thus, in Fig. 2 we give the same JDOS divided by E to show the calculated interband contribution to σ_1. The interband transitions produce a number of structures which appear both in the measured spectra and in the calculation. The strong onset of interband transitions around 0.5 eV is present in both spectra, although the actual onset of transitions is much lower in energy, below 0.1 eV in the calculation. The conductivity peak at 1.2 eV is represented by a double peak in the calculation, but here the electric-dipole matrix elements may play a large role, possibly causing one peak to weaken considerably. The 1.75-eV peak also appears as a doublet in the calculation, again appearing too prominent because of neglected matrix elements. The small shoulder at 2.40 eV is present in both spectra. The small structures remaining in the calculated spectrum above 3 eV do not appear similar in the experimental one, because of matrix-element effects. The transitions above 3 eV have structures which do not depend on the Fermi level, and these would be described equally well or poorly for β'-NiAl and β'-CoAl.

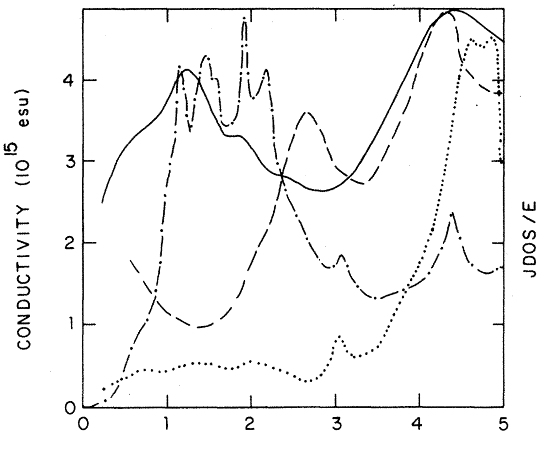

FIG. 2. Real part of the optical conductivity of CoAl obtained by a Kramers-Kronig analysis of the spectrum in Fig. 1 (solid) compared to the calculated JDOS/E from Ref. 1 (dot-dash) and the calculated conductivity from Ref. 7 (dotted). The conductivity of NiAl from Ref. 1 (dashed) is included to highlight the experimental systematics. The scale on the left is for the conductivity of CoAl while the remaining curves are scaled in arbitrary units.

The trends observed in CoAl agree with those expected from our interpretation of the optical properties of NiAl. We include in Fig. 2 our NiAl experimental results for ϵ_2 from Fig. 1 of Ref. 1, scaled by E to compare conductivities. As discussed in Ref. 1, by comparing band calculations of CoAl (Ref. 9) with NiAl (Ref. 3) the 2.5-eV feature in NiAl was expected to shift to lower energy by ~0.5 eV in CoAl and lose its peaklike appearance to new, allowed transitions. By comparing the NiAl and CoAl conductivities in Fig. 2 we see that this is indeed what has occurred.

The remaining puzzle is why the dipole-matrix-element approximations of Eibler and Neckel,[7] which agreed quite well with the conductivity for

NiAl, should show such poor agreement with CoAl. In Fig. 2 we reproduce their calculated ϵ_2 scaled by E to compare with the conductivities. The feature near 4 eV in CoAl and NiAl is similar in both theory and experiment since it involves the same states. The 2.5-eV structure is present in their theory and in our experiments for NiAl but is absent in their calculation for CoAl while evident (but shifted and masked) in our data. The observed trends indicate that the changing character of the *final states* near E_F is primarily responsible for the evolution of optical features in going from NiAl to CoAl. Apparently this region, where hybridization character is changing rapidly as E_F approaches the d bands, is not adequately treated by a basis consisting of atomic d orbitals and plane waves.[7] Following this reasoning, the agreement of their calculation with experiment for NiAl is seen as an accident arising from overly unfavorable matrix elements for transitions *to* E_F being compensated by the overly favorable matrix elements for transitions *from* E_F. Though matrix-element effects are more important for CoAl than for NiAl, we find that, as postulated in Ref. 1, interband transitions make a very important contribution to the low-energy optical spectra of CoAl.

ACKNOWLEDGMENTS

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