

# ELECTRON ENERGY-LOSS SPECTRA OF THE ALLOYS Al-Mg, Cd-Mg, AND Cu-Ni\*

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## Abstract

Characteristic electron energy-loss spectra of the alloys Al-Mg, Cd-Mg, and Cu-Ni are presented. These spectra are interpreted in terms of expected changes in the band structures of the pure metals on alloying.

## I. INTRODUCTION

The electron energy-loss spectra and optical properties of materials can be interpreted in terms of a complex dielectric constant  $\epsilon(k, \omega)$  which depends on both the wavevector  $k$  and the frequency  $\omega$ . For isotropic materials in the long wavelength limit the  $k$  dependence of the dielectric constant may be neglected, and a direct comparison of optical constants and electron energy-loss spectra is possible. For electromagnetic radiation the rate of loss of energy is determined by the imaginary part of the dielectric constant,  $\epsilon_2(\omega)$ , but the rate of loss of energy from an electron beam is proportional to the imaginary part of the reciprocal dielectric constant,

$$-\text{Im}(1/\epsilon(\omega)) = \epsilon_2/(\epsilon_1^2 + \epsilon_2^2).$$

The complex dielectric constant can be calculated in a variety of ways representing different approximations to the electron states in the material. A convenient phenomenological representation is given by the Drude-Sellmeier formula

$$\epsilon(\omega) = 1 + \frac{4\pi N e^2/m}{-\omega^2 + i\omega g_0} + \sum_j \frac{4\pi F_j e^2/m}{\omega_j^2 - \omega^2 + i\omega g_j}.$$

This formula can be conveniently viewed as being made up of two parts. The first part is the dielectric constant due to the free electrons, i.e.

$$\epsilon(\omega)_{\text{free}} = 1 + \frac{4\pi N e^2/m}{-\omega^2 + i\omega g_0},$$

where  $N$  is the density of free electrons and  $g_0$  the damping constant for the electrons. For small damping, this part yields a plasma frequency  $\omega_p^2 = 4\pi N e^2/m$  and a surface plasma frequency  $\omega_s = \omega_p/\sqrt{2}$ . The second part is the dielectric constant due to the

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single-electron oscillator strengths  $F_j$  with frequency  $\omega_j$  and damping constant  $g_j$ , which is given by

$$\epsilon(\omega)_{\text{bound}} = \sum_j \frac{4\pi F_j e^2 / m}{\omega_j^2 - \omega^2 + i\omega g_j},$$

and can change the energies of the free electron plasma resonances. The oscillator strengths  $F_j$  of the single-electron transitions satisfy the Thomas-Reiche-Kuhn sum rule

$$\sum_j F_j = n,$$

where  $n$  is the total number of electrons per atom (see e.g. Seitz 1940).

The above relationships have been used extensively for analysis of the optical properties of metals and semiconductors, where good agreement is found for the simpler metals at least (see e.g. Abeles 1966). In particular, the optical data for aluminium can be fitted very well with a free electron part and an intraband transition part of the dielectric constant (Ehrenreich, Philipp, and Segall 1963). In general the electron energy-loss measurements also agree closely with measured dielectric constants and energy-loss functions, but in practice it is difficult to reduce the energy-loss spectra to values of dielectric constants (Hartley 1969).

There have been some attempts to relate the energy-loss spectra of alloys to the expected forms of their dielectric constants. Staib and Ulmer (1969) show that the electron energy losses of their Rh-Pd and Pd-Ag alloys are what might be expected from the measured optical properties of the elements. Cook and Cundy (1969) have analysed the expected energy-loss spectra of Al-Zn alloys in terms of a free electron dielectric constant modified by one strong interband transition. Their analysis should be applicable to the similar system of Cd-Mg treated in the present work. Other workers who have measured the energy-loss spectra of alloys make no attempt to relate the observed changes in the spectra to changes in the dielectric constants of the component elements on alloying (e.g. Powell 1960; Klemperer and Shepherd 1963; Fujimoto and Sueoka 1964; Sueoka 1965; Sueoka and Fujimoto 1965; Spalding and Metherell 1968).

In the present work measurements of the electron energy-loss spectra of the alloys Al-Mg, Cd-Mg, and Cu-Ni show some features which can be explained in terms of the optically measured dielectric constants of the pure elements. Possible changes due to modification of the band structures on alloying and the presence of ordered alloys are described. Some evidence for such changes is revealed in the measurements on the Al-Mg system of alloys.

## II. INTRABAND TRANSITIONS IN ALLOYS

The energy-loss spectra of materials can be deduced by computing the relative strengths of the free electron and intraband transition contributions to the dielectric constant. The relative contributions depend critically on the band structure of the particular material. It follows that the principal difficulty in understanding the electron energy-loss spectra of alloys is in calculating the possible changes which occur in the band structure of the elements on alloying (see also Friedel 1954).

The changes in the band structure of elements on alloying may be of three types.

- (1) If the elements making up the alloy have different valences, the Fermi level in an alloy may be different from that in the element because of the different average number of electrons per atom. This will change the filling of the levels near the Fermi surface and hence alter the strengths of intraband transitions. A uniform change in the free electron density due to the different valences of the components should produce a linear change in plasmon energy with composition, in the absence of intraband effects and if Vegard's (1921) law is obeyed.
- (2) The alloy may crystallize into a different structure, obviously affecting the intraband transition spectrum. For example, in the Al-Mg alloy system the existence of large unit cells in the  $\beta$  and  $\gamma$  phases may introduce a rather complicated band structure with the possibility of secondary zones inside the fundamental Brillouin zones of the primitive lattice (see e.g. Sato and Tooth 1962).
- (3) The disordered array of atoms in an alloy may tend to broaden the allowed energy states particularly near zone boundaries and symmetry points of the zone scheme (Edwards 1961). It might be expected that the existence of large unit cells and the disordered arrangement of atoms would tend to lower the energies of certain intraband transitions since these effects would tend to reduce the effective band gap of the alloys.

The grain size may also affect the measured electron energy losses in alloy systems which have two phase regions. Sueoka (1965) has shown in eutectoids of aluminium with germanium, tin, and beryllium that, if the grain size is larger than 60 Å, energy losses can be measured which are different for each component of the two phase mixture. If the grain size is smaller than this, however, the energy losses are the same for each phase. Spalding and Metherell (1968) have used this fact to distinguish the energy losses of each phase in the two phase regions of the Al-Mg alloy system.

### III. EXPERIMENTAL PROCEDURE AND ALLOY PREPARATION

The apparatus used in the work and the method of processing the data have been described previously (Swan 1964; Hartley and Swan 1966). No significant changes in experimental techniques have been made for this work.

The Al-Mg alloys were prepared by melting the pure materials under an atmosphere of argon. The ingots were cooled quickly from the melt and subsequently annealed for 10 to 14 days, at a temperature suitable for each alloy composition. Finely ground powder from each alloy was investigated by X-ray powder methods to determine the presence of each component phase.\* The analysis of these samples is summarized in Table 1.

The Cd-Mg alloys were prepared from the pure material by melting the constituents under a flux. The alloy ingots were cooled quickly from the melt and

\* The authors are indebted to Mr. R. K. Dimond for his work on the X-ray powder analysis of these alloys.

annealed for 10 to 14 days under 0.5 atm of argon at a temperature 10–20°C below their respective melting temperatures.

The Cu–Ni alloys were prepared from pure constituents. The alloys were cooled quickly from the melt and subsequently annealed at temperatures near the respective melting points to ensure uniformity of composition.

TABLE 1  
PROPERTIES OF ALUMINIUM–MAGNESIUM ALLOYS

Specimen No.	Mg (at. %)	Atoms in Component Phases (%)		Plasmon Energy (eV)	
				Calc.	Obs.
Al	0	—	100 $\alpha$	15.8	15.30
1	7.7	—	100 $\alpha$	15.4	15.19
2	15.0	74 $\alpha$	26 $\beta$	15.0	14.83
3	23.5			14.6	14.22
4	30.0	23 $\alpha$	77 $\beta$	14.2	14.14
5	38.0	—	100 $\beta$	13.8	14.00
6	41.5	84 $\beta$	16 $\gamma$	13.6	13.64
7	49.7	38 $\beta$	62 $\gamma$	13.3	13.15
8	53.7	—	100 $\gamma$	13.1	13.14
9	57.2	—	100 $\gamma$	12.8	12.80
10	59.9	—	100 $\gamma$	12.7	12.64
11	68.2			12.3	11.76
12	72.7			12.1	11.52
13	83.4			11.6	11.20
14	84.8	66 $\delta$	34 $\gamma$	11.6	11.07
15	90.0	80 $\delta$	20 $\gamma$	11.4	10.97
Mg	100	—	100 $\delta$	10.9	10.80

For each set of alloys, targets were cut from the samples and scraped in vacuum to ensure that the energy-loss spectra were representative of clean surfaces; no detectable difference was found in the spectra of targets cut from different parts of the same sample. Spectra of the Cu–Ni alloys were obtained at room temperature and also at about 400°C, in order to investigate whether any effect associated with changes in magnetic properties could be detected in the high nickel content alloys.

#### IV. RESULTS AND DISCUSSION

##### (a) *Aluminium–Magnesium Alloys*

The energy-loss spectra of some of the Al–Mg alloys are shown in Figure 1. The spectra of the alloys are similar to those of the pure metals and there is a uniform change from magnesium to aluminium. The peaks in the energy-loss spectra are interpreted as surface or volume plasmon losses and sums and multiples of these losses (Powell 1960).

The measured volume plasmon energies are listed in Table 1, together with the calculated plasmon energies found by assuming a contribution of three free electrons per atom from aluminium and two free electrons per atom from magnesium. The densities of the alloys were measured using a density balance and were also calculated from a knowledge of the lattice parameters measured by X-ray powder

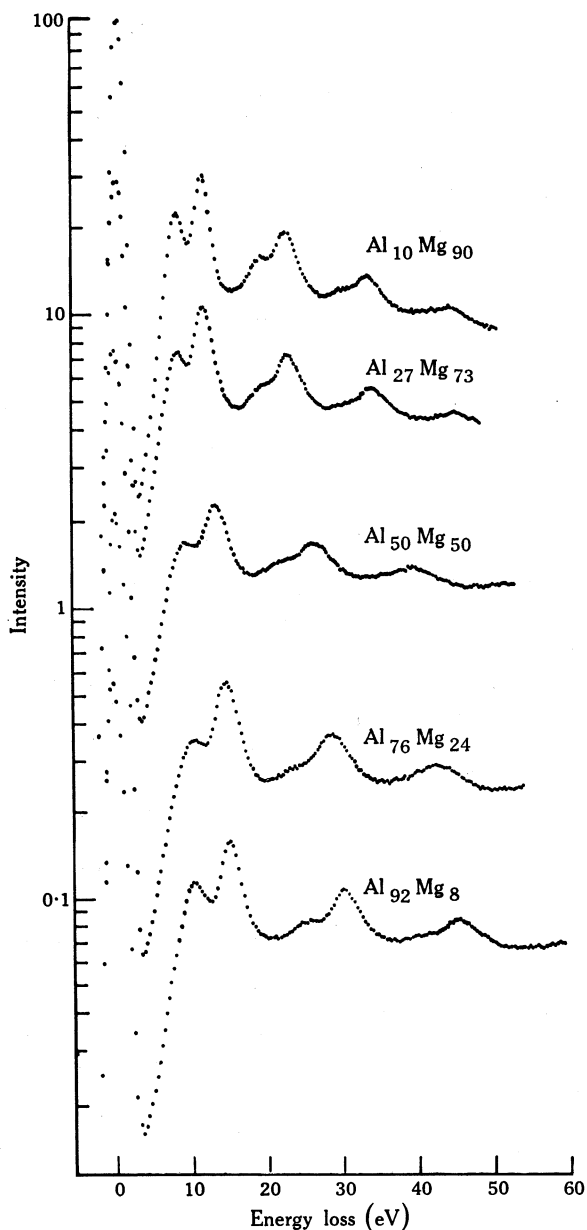


Fig. 1.—Experimental energy-loss spectra for sample Al-Mg alloys.

analysis. The measured densities showed a slight departure from Vegard's law and were used to calculate a theoretical plasmon energy for each alloy.

The results of the measurements of the Al-Mg alloy series are shown in Figure 2. Figure 2(a) shows the measured and calculated plasmon energies plotted against specimen composition. The calculated plasmon energies for the alloys in the mid

range of composition are generally lower than the expected linear variation, owing to a reduced density of these alloys indicating a small departure from Vegard's law. The experimentally measured plasmon energies ( $\Delta E_p$ ) are generally lower than the calculated plasmon energies ( $\hbar\omega_p$ ) except in the mid range of composition, in agreement with the measurements made by Spalding and Metherell (1968).

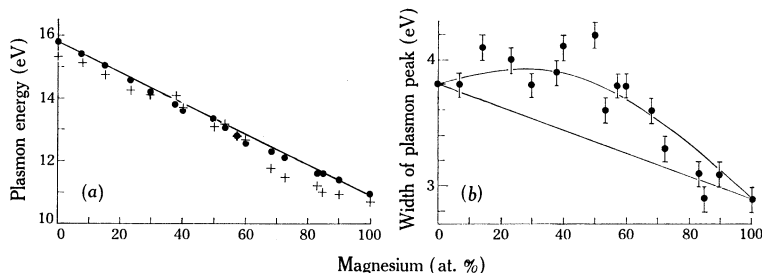


Fig. 2.—Plasmon energies for the Al-Mg alloys: (a) comparison of measured (+) and calculated (●) energies and (b) measured widths of the first volume plasmon peak plotted as functions of specimen composition. The plasmon energies were calculated for (a) assuming three free electrons contributed from aluminium and two from magnesium and using a density determined from the lattice constants measured by X-ray diffraction.

This rather unusual behaviour may be explained by considering the possible structures of these alloys. Reference to the phase diagram (Hansen 1958) shows that the mid-composition range contains a mixture of the large unit cell  $\beta$  and  $\gamma$  phases. According to the principles described above these large unit cells, together with possible disordering of the structure, could lead to a lowering of the energies of intraband transitions, which would result in the values of  $\epsilon_1$  in the plasmon region tending towards the free electron value. Possible changes in the damping term caused by the disordered structure should not significantly affect the plasmon frequency.

The widths of the first volume plasmon peak are shown plotted against composition in Figure 2(b). As would be expected the widths of the peaks for the alloys are greater than the widths of the peaks for the pure metals, since the plasmon energy as measured is an average of those for the different phases present. This follows from the work of Spalding and Metherell (1968), who used a microprobe technique to distinguish the plasmon energies of the separate alloy phases. The widths of the peaks measured in the present work, however, are much less than those measured by Powell (1960) or Klemperer and Shepherd (1963); these workers used evaporated samples of alloys and it is possible that the broadenings of the plasmon peaks ( $\sim 3$  eV) correspond to plasmons excited in a number of layers with different average composition.

In the present work the surface plasmon loss was apparently affected slightly by contamination so that the measured widths of these peaks show no consistent trend.

#### (b) Cadmium-Magnesium Alloys

The Cd-Mg alloy system forms a complete series of solid solutions crystallizing in a hexagonal lattice. The two pure metals have a different  $c/a$  ratio which is nearly

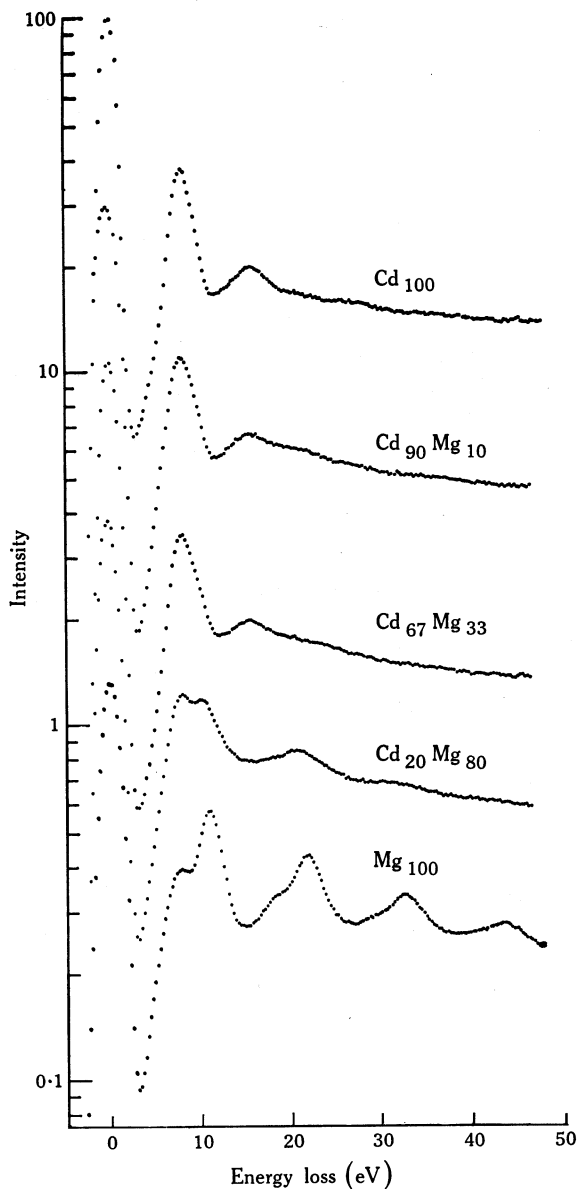


Fig. 3.—Experimental energy-loss spectra for sample Cd-Mg alloys.

ideal for magnesium (1.62) but not for cadmium (1.88). The variation in the lattice parameters in the alloys is not expected to substantially alter the energy-loss spectra.

The energy-loss spectrum of magnesium is interpreted as consisting of volume plasmon and surface plasmon losses at close to their theoretical free electron values (Powell 1960). In the spectrum of pure cadmium the first peak (7.8 eV) is interpreted as containing unresolved components of the volume and surface plasmon losses whilst the peak at about 15 eV is interpreted as arising from ionization of the  $N_{IV,V}$

level of cadmium with a threshold of 9.3 eV. The plasmon energy in cadmium is lowered from the free electron values of 10.2 eV by the presence of these intraband transitions (Jelinek *et al.* 1966). Since the free electron plasmon energies for magnesium and cadmium are nearly the same, the varying strength of these interband transitions should have a major effect on the energy-loss spectra in the alloys. The plasmon energy is not expected to vary linearly with composition, and small amounts of cadmium in magnesium should change the magnesium spectrum rapidly to a cadmium-like spectrum (Cook and Cundy 1969).

This effect is seen in the energy-loss spectra of the alloys in Figure 3. The Cd<sub>20</sub>Mg<sub>80</sub> alloy has a spectrum quite different from that of pure magnesium. The volume plasmon energy is lowered and the surface and volume plasmons are closer in energy. The volume plasmon peak is also broadened and the multiple losses are not distinct. The Cd<sub>67</sub>Mg<sub>33</sub> alloy is nearly identical with the pure cadmium and Cd<sub>90</sub>Mg<sub>10</sub> alloys, the only significant difference being the smaller relative intensity of the ionization peak at 15 eV and the slightly broader peak near 7.6 eV in the alloys. It is difficult to measure the plasmon energies for the cadmium-rich alloys since the surface and volume components are superimposed.

#### (c) *Copper-Nickel Alloys*

The Cu-Ni alloys form a single phase system, with the ferromagnetic transition as the only discontinuity in the nickel-rich alloys. This transition is not expected to affect the energy-loss spectra in any significant way, particularly as any changes would occur at low values of energy loss, i.e. < 4 eV, and the instrumental resolution is insufficient to distinguish such changes.

The measured electron energy-loss spectra of some of the Cu-Ni alloys are shown in Figure 4. The main energy losses measured are summarized in Table 2. It is observed that the energy-loss spectra of the pure metals and alloys are quite similar but that there is a gradual change in the spectra from nickel to copper. The only consistent variation with alloy composition was that observed in the region at about 4 eV. This low energy loss is quite clear in copper but reduces in intensity as the nickel composition increases. This structure was also found to be temperature dependent, being broadened at high temperatures. The energy losses measured for the two peaks at higher energy were smaller at high temperatures than at room temperature in each alloy, but no consistent variation of the 8 eV peak with temperature was observed.

The optical properties of copper and nickel have been measured by Ehrenreich and Philipp (1962), Ehrenreich, Philipp, and Olechna (1963), Beaglehole (1965), and Vehse and Arakawa (1969). None of these measurements extend into the energy region of the 28 eV peak. While optical measurements may give reliable information about the absorption spectrum, they are frequently not very helpful in identifying plasma resonances. The calculation of  $\epsilon_1$  and  $\epsilon_2$  from reflectivity measurements requires the extrapolation of the reflectivity to high energies; also, in the region between 4 and 20 eV, where  $\epsilon_1$  varies slowly, a small absolute error in  $\epsilon_1$  can cause large errors in the predicted plasma oscillation frequency. As the different optical measurements yield different energy-loss functions, it is not surprising that none of these agree very well with the energy-loss spectra reported here.



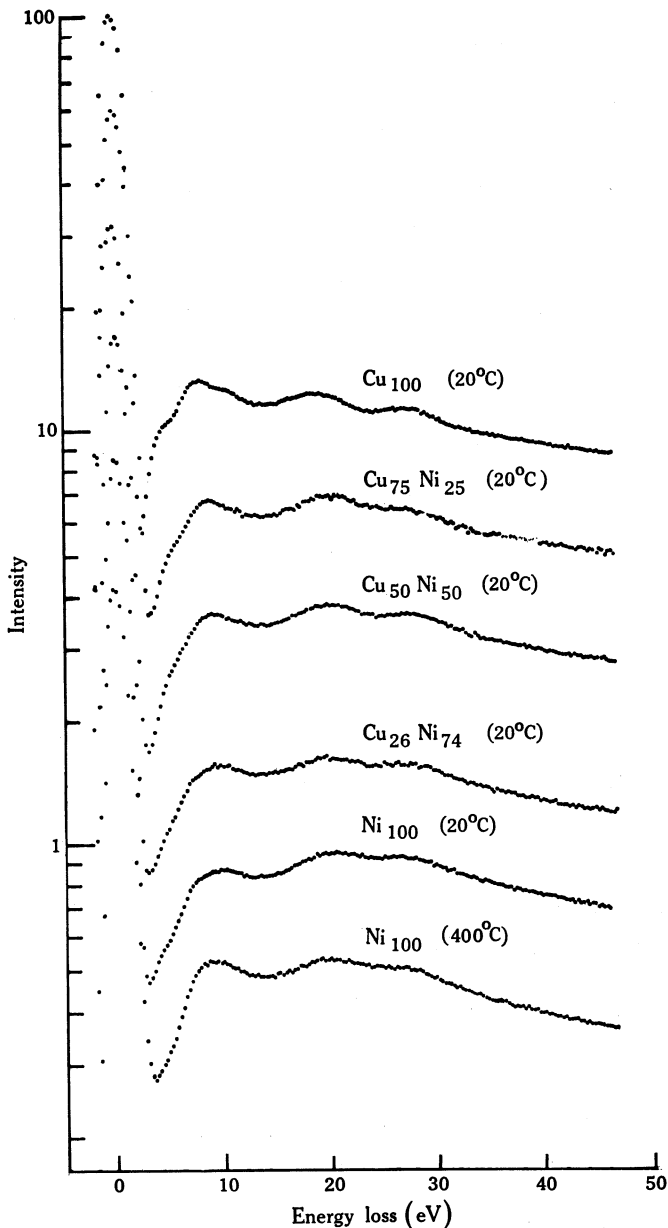


Fig. 4.—Experimental energy-loss spectra for sample Cu-Ni alloys.

The energy loss at about 8 eV measured in each of the alloys is probably due to the excitation of the low energy intraband transitions together with surface plasmon losses. While the peaks at 19 eV had been previously ascribed principally to volume plasmon excitation (Robins and Swan 1960), the availability of optical measurements now supports an interpretation solely in terms of interband transitions.

A peak due to the volume plasmon cannot be identified with certainty from the optical data, and it is suggested that the high energy peak at 28 eV represents excitation of this mode. This interpretation is made mainly on the basis of the absence of the similar peak in the energy-loss spectrum of the adjacent element, zinc (Robins 1961). The marked difference in the electron energy-loss spectra between

TABLE 2  
MEASURED ENERGY LOSSES IN COPPER-NICKEL ALLOYS AT 20°C AND 400°C

Sample Composition		Temperature (°C)	Measured Energy Losses (eV)		
Ni (%)	Cu (%)		1	2	3
100	0	20	8.10	19.61	27.68
		400	7.89	19.23	27.29
74	26	20	7.98	19.46	27.51
		400	8.37	19.33	27.35
63	37	20	7.94	19.49	28.12
		400	7.88	19.08	27.82
50	50	20	7.89	19.60	28.20
		400	8.15	19.14	27.50
75	25	20	7.85	19.61	28.10
		400	7.80	19.25	27.92
81	19	20	7.92	19.47	28.02
		400	7.68	19.07	27.91
89	11	20	7.93	19.31	27.77
		400	8.07	19.19	27.48
0	100	20	7.53	19.19	28.09
		400	7.69	18.95	27.77

these two elements appears to be the result of the volume plasmon energy occurring below the interband threshold in zinc (Jelinek *et al.* 1966). Measurements of the optical absorption spectrum of copper at high energy are needed to clarify the interpretation of peaks in that energy range.

## V. CONCLUSIONS

Whilst the changes in the band structure of alloys from those of the pure metals are expected to influence the optical absorption and electron energy-loss properties of the alloys, only indirect evidence of these changes can be seen. For the Al-Mg alloy spectra, observations of the low energy losses with high resolution may show some evidence of complicated intraband transitions. The energy loss spectra of the Cd-Mg alloys can be reasonably explained in terms of the free electron and bound electron contributions to the dielectric constant. The Cu-Ni alloys did not show any significant changes from the energy losses expected from a simple band structure picture. It is possible that high resolution measurements of the nickel-rich alloys could reveal evidence of changes in electronic structure at the Curie temperature.

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## VII. REFERENCES

- ABELES, F. (Ed.) (1966).—"Optical Properties and Electronic Structure of Metals and Alloys." (North Holland: Amsterdam.)
- BEAGLEHOLE, D. (1965).—*Proc. phys. Soc.* **85**, 1007.
- COOK, R. F., and CUNDY, S. L. (1969).—*Phil. Mag.* **20**, 665.
- EDWARDS, S. F. (1961).—*Phil. Mag.* **6**, 617.
- EHRENREICH, H., and PHILIPP, H. R. (1962).—*Phys. Rev.* **128**, 1622.
- EHRENREICH, H., PHILIPP, H. R., and OLECHNA, D. J. (1963).—*Phys. Rev.* **131**, 2469.
- EHRENREICH, H., PHILIPP, H. R., and SEGALL, B. (1963).—*Phys. Rev.* **132**, 1918.
- FRIEDEL, J. (1954).—*Adv. Phys.* **3**, 446.
- FUJIMOTO, R., and SUEOKA, O. (1964).—*J. phys. Soc. Japan* **19**, 2069.
- HANSEN, M. (1958).—"Constitution of Binary Alloys." 2nd Ed. (McGraw-Hill: New York.)
- HARTLEY, B. M. (1969).—*Phys. Status Solidi* **31**, 259.
- HARTLEY, B. M., and SWAN, J. B. (1966).—*Phys. Rev.* (144) **1**, 295.
- JELINEK, T. M., HAMM, R. N., ARAKAWA, E. T., and HUEBNER, R. H. (1966).—*J. opt. Soc. Am.* **56**, 185.
- KLEMPERER, O., and SHEPHERD, J. P. G. (1963).—*Br. J. appl. Phys.* **14**, 89.
- POWELL, C. J. (1960).—*Aust. J. Phys.* **13**, 145.
- ROBINS, J. L. (1961).—*Proc. phys. Soc.* **78**, 1177.
- ROBINS, J. L., and SWAN, J. B. (1960).—*Proc. phys. Soc.* **76**, 857.
- SATO, H., and TOOTH, R. S. (1962).—*Phys. Rev. Lett.* **8**, 239.
- SEITZ, F. (1940).—"The Modern Theory of Solids." (McGraw-Hill: New York.)
- SPALDING, D. R., and METHERELL, H. J. F. (1968).—*Phil. Mag.* **18**, 41.
- STAIB, P. H., and ULMER, K. (1969).—*Z. Phys.* **219**, 381.
- SUEOKA, O. (1965).—*J. phys. Soc. Japan* **20**, 2212.
- SUEOKA, O., and FUJIMOTO, F. (1965).—*J. phys. Soc. Japan* **20**, 569.
- SWAN, J. B. (1964).—*Phys. Rev.* **135**, A1467.
- VEGARD, L. (1921).—*Z. Phys.* **5**, 17.
- VEHSE, R. C., and ARAKAWA, E. T. (1969).—*Phys. Rev.* **180**, 695.

