

Spectral Reflectivity as a Function of Temperature of β -Brass Type Alloys

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A number of β -brass type alloys undergo reversible color changes as a function of temperature. Normally, yellow β -brass becomes copper-red at about 250°C, the color change taking place gradually. β -AgZn is pink at room temperature; it is silver gray at 300°C. Similar changes have been observed in β -AgCd, β -AuZn, and β -AuCd. Color changes consistent with the above observations have been noted on cooling to liquid nitrogen temperatures. Although disordering takes place in some of these alloys, it is not thought that these color change phenomena are primarily due to disordering or to surface films. Quantitative measurements of reflectivity as a function of wavelength at several temperatures have been made on β -CuZn, β -AgZn, β -AuZn, β -AgCd, β -AuCd, and α -brass. The reflectivity edge for β -brass shifts from 5000 Å at 27°C to 5300 Å at 275°C equivalent to a shift of about -5.6×10^{-4} eV/°C. Edge shifts of this magnitude were not observed with α -brass, copper, gold, Au₃Zn, CuAu, or Cu₃Au. A number of possible explanations of the optical results are discussed; it is believed that these results are primarily due to plasma effects strongly influenced by interband transitions.

INTRODUCTION

COLORING metals have long been produced for jewelry purposes but few quantitative measurements of optical properties have been made in comparison with the extensive studies of insulators and semiconductors. Room temperature measurements have been made of many of the elements and of several copper alloys. As a function of temperature, only copper, silver, and gold have been studied.¹ To the author's knowledge no alloy optical properties have been studied as a function of temperature. Intermetallic compounds such as Mg₂Sn have been studied, but most are semiconductors. Color changes in β -brass have been observed upon heating but were discounted as being due to surface oxidation and hence were never reported. This investigation has shown that strong temperature effects on optical properties are found in most β -brass type (CsCl structure) alloys and are not found in most face-centered cubic metals and alloys.

Observations have been restricted to colored metals for the simple reason that the gross effect, if any, can be observed visually. Thus, gray metals and alloys may undergo some large changes in optical properties in the infrared or ultraviolet spectral regions, but the eye could not observe such changes. Quantitative studies of spectral reflectivity have so far been confined to those alloys showing interesting visual changes.

The colors of these β -brass type alloys may be due to the same mechanism as that proposed to explain the colors of copper and gold (i.e., the internal photoelectric effect).² On the other hand, plasma effects may be the primary cause. It is to be expected that there may be complicated interactions between the various factors in reflectivity. It is to be hoped that these spectral reflectivity experiments will help explain the changes in electron energy bands and plasma oscillations and in

turn upon the band picture as a function of interatomic spacing.

VISUAL OBSERVATIONS

A number of metal and alloy specimens were polished or abraded and were then sealed in glass tubes at forepump vacuum. The tubes were then placed in furnaces and raised to the desired temperatures. They were then removed from the furnaces and observed visually while cooling. In some cases the tubes were quenched in cold water leading to cracking of the glass and rapid cooling. For low-temperature observations, polished alloy buttons were placed in liquid nitrogen. The buttons were assumed to be at the liquid nitrogen temperature after cessation of the violent bubbling. The polished surface could easily be observed either under the liquid nitrogen or above the liquid nitrogen after sufficient liquid had boiled off. In the latter case, the surface was in a dry nitrogen atmosphere. No differences were observed with the specimen surface above or below the liquid nitrogen.

The results obtained are listed in Table I. While it is impossible to describe a color accurately in words, the main trend of color changes is obvious. This trend is given by green \rightarrow yellow \rightarrow red \rightarrow gray. This sequence indicates that the dominant wavelength is moving to longer wavelengths with increasing temperature. The color changes seem to be instantaneous with tempera-

TABLE I. Appearance of alloys at various temperatures.

	-195°C	28°C	300°C (approx)
β -CuZn	Yellow ^a	Yellow gold	Copper-red
β -AgZn ^b	Straw yellow	Salmon pink	Gray
β -AuZn	Red	Pale purple	Gray
β -AgCd ^c	Red	Violet	Gray
β -AuCd ^d	Pale gold	Pale gold	Gray

^a This appeared slightly greener than did the 28°C yellow.

^b This alloy had 3-1/2 at. % gold substituted for silver and will be designated in the text as β -AgZn (3-1/2% Au).

^c This alloy is hcp at temperatures above 240°C and is orthorhombic below about -150°C.

^d This alloy was 52.5 at. % gold.

¹ G. Joos and A. Klopfer, *Z. Physik* **138**, 251 (1954).

² F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. 17, p. 654-656.

ture; quenched specimens go immediately to their new equilibrium colors. Furthermore, if the temperature changes gradually, the color does so also. One may watch β -brass, copper-red at 275°C, pass through orange as it cools to room temperature.

Specimens of copper, gold, α -brass (20% Zn), and Cu_3Au were also heated in evacuated glass tubes and visually examined at temperature. No changes in color were noted but some of the specimen colors were definitely less saturated. This was particularly so with copper and gold which were observed at 600°C. This is in accord with what one should expect from the measurements of Joos and Klopfer.¹ No difference was noted between the appearances of Cu_3Au ordered and disordered.

Irreversible changes in appearance occurred in some of the β -brass type alloys when they were raised to temperatures around 500°C. Presumably dezincification occurred and left a coating of zinc or zinc oxide on the surface. At room temperature these surfaces appeared tarnished and the colors were less evident. Nevertheless, upon subsequent reheating, the same color changes could be seen taking place "underneath" the surface contamination. Keeping specimen temperatures below 350°C prevented such irreversible changes and the polished surfaces maintained their sheen. This does not mean that thin oxide films may not have formed.

There is no question that the presence of oxide usually does deepen the specimen color. Zeta-AgZn (normally gray) was slightly oxidized and it then appeared pale yellow-brown. Since zinc oxide is usually colorless, this is taken to mean that the zinc oxide formed was not stoichiometric in composition. A layer of such a colored oxide over a colored metal would change the apparent color of the metal. Such changes were observed in oxidized β -brass and β -AgZn (3½% Au).

The possibility of interference colors from thin oxide layers will be discussed in a later section.

CRYSTAL STRUCTURES OF THE ALLOYS

Alloys having electron-atom ratios in the vicinity of 3/2 usually crystallize in one of the following forms: disordered body-centered cubic, ordered cubic (CsCl), hexagonal close-packed, or β -Mn. Often martensitic transformations occur at low temperature or are produced by deformation. When the alloys are produced from elements of the periodic table IB and IIB elements, the atomic percentages are 50–50. Such alloys, as has been seen, are often colored.

At room temperature β -brass is fully ordered and has the CsCl structure. Above 480°C the alloy is body-centered cubic disordered. This phase cannot be maintained by quenching. Barrett and Massalski³ have shown that deformation at room temperature may lead

³ C. S. Barrett and T. B. Massalski, *Symposium on Transformations* (Institute of Metals, London, 1955).

to a transformation to either a face-centered cubic or a hexagonal close-packed phase.

The alloy β -AgZn can be produced at room temperature by quenching from above 280°C. It is then ordered (CsCl) and appears salmon-pink. If slowly cooled it is found to have a complex hexagonal structure (ζ) and is silver-gray in appearance. Above 280°C it is disordered body-centered cubic and appears gray. The substitution of at least 3½ at. % of gold for silver suppresses the ζ phase and allows a smooth order-disorder transformation wholly in cubic structures just as in β -brass.⁴

Beta-AuCd undergoes a martensitic transformation from the CsCl ordered structure at temperatures in the range 30 to 80°C (depending upon the composition).⁵ While the color does depend on the composition and temperature, it does not depend on the phase. AgCd forms four equilibrium phases: high-temperature phase—disordered cubic; 450 to 240°C—hexagonal close packed (ζ); 240 to about –150°C—ordered cubic⁶; low-temperature phase—orthorhombic.⁷ Both the ζ and the β ordered phases can be produced at room temperature. In contrast to the AgZn case, both AgCd room temperature phases appear somewhat similar. The ζ phase can again be suppressed by the substitution of gold for silver.⁸

The alloys β -AuCd⁹ and β -AuZn¹⁰ are presumed not to disorder appreciably at temperatures considerably below melting. Furthermore, β -brass is only slightly disordered at 275°C.¹¹ Thus, it is clear that disordering is not the primary factor in these color changes with temperature. Even the phase changes in the AuCd and AgCd have little effect upon the alloy colors. Only in the alloy AgZn is there a striking difference in appearance of the ζ and β phases. This independence of optical properties and crystal structure has been noted for some semiconductors.¹² Apparently, the Brillouin zone structures are not changed very much in some cases of phase transformation.

ELECTRON DIFFRACTION OBSERVATIONS

A number of reflection electron diffraction patterns were taken of the alloy surfaces variously prepared. Abrading usually produced a hexagonal close-packed surface while polishing produced either the hcp or a fcc surface on alloys other than β -AuZn. These were the transformation products observed by Massalski and Barrett¹³ in the deformation of β -brass. Surface color

⁴ L. Muldower, *J. Appl. Phys.* **22**, 663 (1951).

⁵ L. C. Chang and T. A. Read, *Trans. AIME* **189**, 47 (1951).

⁶ L. Muldower, M. Amsterdam, and F. Rothwarf, *Trans. AIME* **197**, 549 (1953).

⁷ D. B. Mason and C. S. Barrett, *Trans. AIME* **212**, 260 (1958).

⁸ L. Muldower, *Acta Met.* **2**, 555 (1954).

⁹ A. Bystrom and K. E. Almin, *Acta Chem. Scand.* **1**, 76 (1947).

¹⁰ E. A. Owens and J. G. Edmunds, *Proc. Phys. Soc. (London)* **50**, 389 (1938).

¹¹ D. Chipman and B. E. Warren, *J. Appl. Phys.* **21**, 696 (1950).

¹² J. Black, E. M. Conwell, L. Seigle and C. W. Spencer, *J. Phys. Chem. Solids* **2**, 240 (1957).

¹³ T. B. Massalski and C. S. Barrett, *J. Metals* **9**, 455 (1957).

changes in some cases were noted as a result of polishing. For this reason, the room temperature spectral reflectivity curves shown in the next section are those obtained after the specimen had been run at high temperature. The room temperature reflectivity curves before and after annealing do show significant differences. A discussion of this phenomenon will be reserved for a later paper.

In some early runs of the alloys at temperature insufficient flushing of the specimen chamber led to surface oxidation. Diffraction patterns taken of β -AuZn, ζ -AgZn, β -AgZn(3½%Au) and β -CuZn clearly showed the presence of ZnO. Electron diffraction patterns of the alloy surfaces immediately after the runs of Figs. 2 through 5 showed some oxide except for β -AuZn which showed none.

It might be well to discuss the depth of penetration of the 50-kV electrons and visible light in these alloys and their oxides. The $1/e$ penetration of visible light in zinc oxide is of the order of millimeters (if ZnO is similar to MgO). However, in these β -brass type alloys the depth of penetration of light varies from 100 to 500 Å. Thus, it is clear why changes may be seen underneath the surface film. Even if the zinc oxide were a defect lattice and its absorption constant were greater by several orders of magnitude, the oxides would be relatively transparent. The depth examined by electron diffraction depends upon the particular substance but there is no sharp difference between oxide and metal. The $1/e$ depth is probably no more than 500 Å in any of the cases under discussion. Cu $K\alpha$ x rays, on the other hand, penetrate to distances of the order of 100 000 Å. Thus, that which is observed by means of electron diffraction is only a small fraction of that which is observed by x-ray diffraction. In practice, this means one does not see the same material at all in these two diffraction techniques. Thus, x-ray diffraction may not see structural changes in the first few hundred angstroms of surface, the region of interest for optical properties. Electron diffraction is to be preferred for the examination of clear metallic surfaces which are being studied optically.

SPECTRAL REFLECTIVITY MEASUREMENTS

The visual observations served a very useful purpose in that interesting phenomena were observed and interesting regions to study were mapped out. For quantitative solid state purposes one would like to have the absorption constant (nk) as a function of wavelength. The index of refraction n and extinction coefficient k are defined through the complex index of refraction: $n^* = n - ik$. Measurements of n and k , however, are quite difficult and time consuming. It was felt that spectral reflectivity data would be sufficiently good to give a quantitative understanding as to what was occurring. Figure 1 shows the relation between (nk) and reflectivity for normal incidence for copper. The values of n

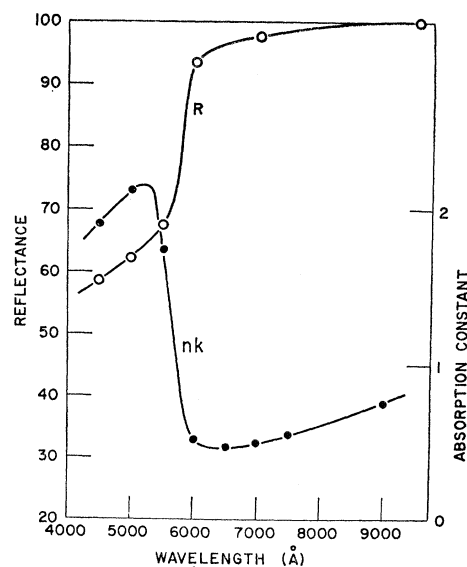


Fig. 1. Reflectivity for normal incidence and (nk) for copper. These are calculated values from the same data for n and k .

and k were obtained from Schulz¹⁴ and Schulz and Tangherlini.¹⁵ It should be noted that there is an edge in both curves and that the edges are at the same wavelength. There is obviously a close connection between the absorption constant (nk) and reflectivity, which for normal incidence is given by

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

The basic apparatus consisted of a Beckman DU spectrophotometer and a simple spectral reflectivity attachment. This reflectivity chamber was placed between the phototube compartment and the main instrument housing. Light reflected from the specimen surface was compared with three reflections from evaporated aluminum mirrors. The angle of incidence was 18° so that conditions of near normal incidence were satisfied. To make reflectivity measurements at elevated temperatures, the chamber was first filled with a dry nitrogen atmosphere and was then heated by a 300-W soldering iron. Heat was conducted to the sample by means of a copper rod in contact with the back surface of the specimen. The specimen buttons were about 3/16 in. thick and 3/8-in. diam and the temperature of the front face was determined by means of an iron-constantan thermocouple at the edge of the face.

During heating and cooling the nitrogen flow was maintained. As a result, little oxidation of consequence occurred even though some was indicated for some of the samples. In the early reflectivity measurements at elevated temperature, a good deal of oxidation was pro-

¹⁴ L. G. Schulz, J. Opt. Soc. Am. 44, 357 (1954).

¹⁵ L. G. Schulz and F. R. Tangherlini, J. Opt. Soc. Am. 44, 362 (1954).

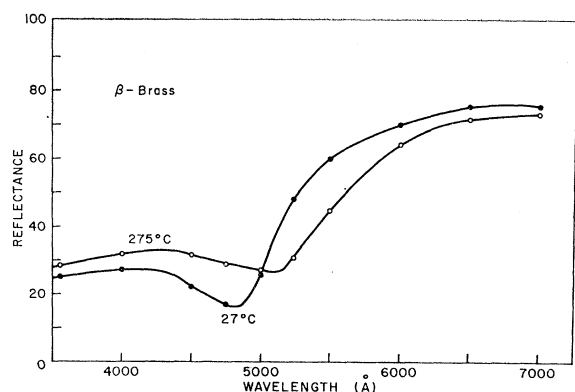


FIG. 2. Beta-brass reflectivity at room temperature and at 275°C.

duced and this was indicated in a number of ways. Electron diffraction photographs showed clear, sharp patterns of well-formed zinc oxide; the colors of the specimens were changed and deepened; and the reflectivities in the blue end of the spectrum were reduced by a factor of 2 to 10. When measured at room temperature after the heating runs in Figs. 2 and 4, there was no reduction in reflectivities in the blue region for β -CuZn and β -AuZn indicating negligible oxidation. A reduction factor in the blue reflectivity of 1.06 was obtained for β -AgCd and β -AgZn ($3\frac{1}{2}\%$ Au) indicating small amounts of oxidation. Such effects did not change the curves in any significant manner.

These reflectivity measurements cannot be considered as absolute values. Imperfections in the polished alloy surfaces and slight variations in the beam position relative to the phototube may readily produce errors which are presumed to be systematic. It is believed that all reflectivities reported here are low. The monochromaticity was fairly good for the region 3600 to 6000 Å. Here, the half-intensity bandwidth is everywhere below 45 Å. For 6500 Å it was 135 Å and for 7000 Å it was 337 Å. It should be noted, however, that

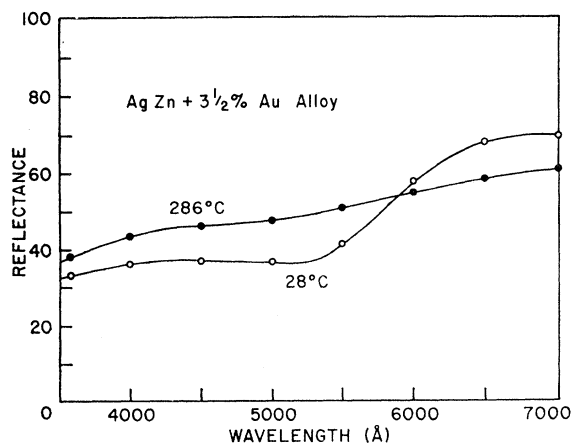


FIG. 3. Beta-AgZn($3\frac{1}{2}\%$ Au) reflectivity at room temperature and at 286°C.

the red region is not one of great interest and that reflectivities usually are slowly varying for the alloys studied.

Figures 2 through 6 show the results of the reflectivity measurements on β -brass, β -AgZn ($3\frac{1}{2}\%$ Au), β -AuZn, β -AgCd and α -brass. Reflectivity curves for freshly polished specimens were always different in character from those which have once been run at elevated temperatures. To check that equilibrium conditions had been obtained after one heating cycle and to check the technique as far as oxidation was concerned, a second set of reflectivity measurements was taken near 250°C and at room temperature. In the several cases where this was done using the technique which produced the data presented here, little or no effect was observed except for the slightly lower values in the blue as discussed above. The presumable explanation for the differences observed for the freshly polished surface is

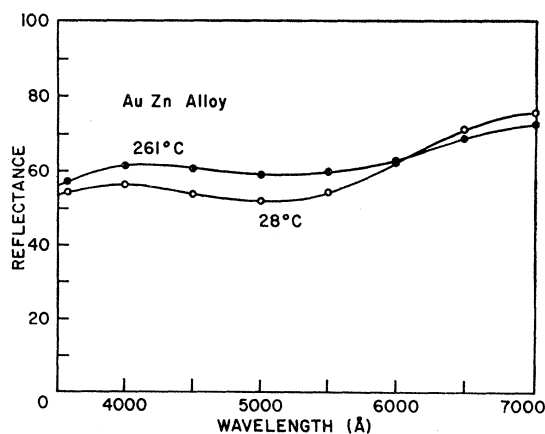


FIG. 4. Beta-AuZn reflectivity at room temperature and at 261°C.

the presence of cold worked layers or transformation products on the surface. Heating of the polished surface caused reversion back to the normal CsCl structure and thus the room temperature runs shown in the figures were those after runs at elevated temperatures. Reflectivity runs were also made for β -brass at 27, 157, 213, and 261°C. The motion of the reflectivity edge was gradual and this corroborated visual observations made earlier.

There are several quantitative features to be obtained from these curves: (1) the position of the edge, (2) the slope of the edge, (3) the difference in reflectivity on either side of the edge, and (4) the depth of the minimum. One cannot be precise in stating these values as is apparent from inspection of the curves. The edge position may be taken as the wavelength for the onset of the linear portion of greatest slope,¹⁶ although the center of the edge is more significant in color specification. The position of the reflectivity minimum is also of physical

¹⁶ P. D. Fochs, Proc. Phys. Soc. (London) **B69**, 70 (1956).

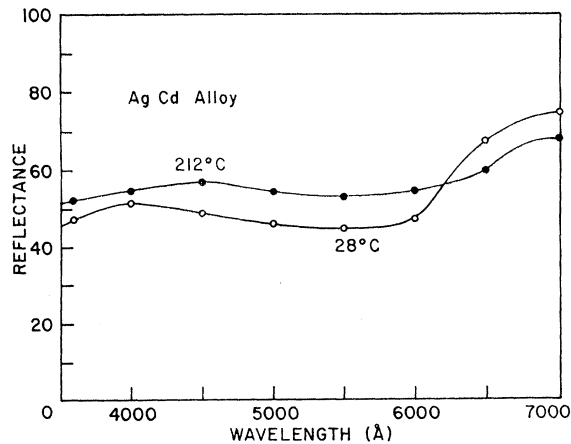


FIG. 5. Beta-AgCd reflectivity at room temperature and at 212°C.

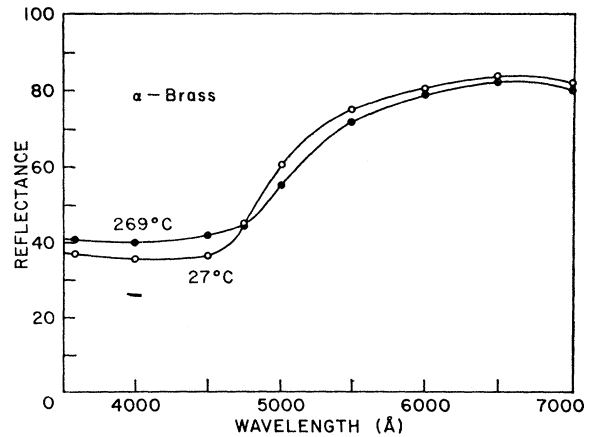


FIG. 6. Alpha-brass (30%Zn) reflectivity at room temperature and at 269°C.

significance; it is well correlated with edge position. The slope of the edge is that for the steepest portion. Table II includes some data from Figs. 2 through 5. The reflectivity difference on either side of the edge is only an average. Included in Table II is a column called apparent gap. This is the energy spacing associated with the main reflectivity edge. Its relation to the electron band structure will be deferred until the discussion.

The general features observed upon heating these alloys are (1) a shift in edge position towards the red, (2) a decrease in the slope of the edge, (3) a decrease in the difference in reflectivity on either side of the edge, and (4) a decrease in the depth of the minimum in keeping with the general smearing of the reflectivity curve. The edge shift for β -brass is about -5.6×10^{-4} eV/°C; no numerical values can be given for the other alloys. Note that these effects are similar to those found for semiconductors. From these curves it is easy to understand the visual observations: the color shift of β -brass and the loss of color of the other alloys. At elevated temperature, the edges for β -AgZn (3½% Au), β -AuZn, β -AgCd become almost imperceptible in agreement with the gray (silvery) appearance.

Significant differences appear when the exact composition in the beta field varies. There are color differences

visible to the eye between 47.5% Cd and 50.0% Cd β -AuCd. However, the changes with temperature are similar. The exact dependence upon composition is currently being studied.

Figure 7 shows the room temperature runs for β -CuZn, β -AgZn (3½% Au), and β -AuZn. From an inspection of edge position, of difference in reflectivity on either side of edge, and of slope of edge, it almost seems that the temperature has increased in going from β -CuZn to β -AgZn to β -AuZn. A similar effect is observed in going from β -AgZn to β -AgCd. There seems to be a strong relation between average atomic weight and an effective temperature as indicated by, say, the slope and position of edge. Debye temperatures, obtained in various ways, are included in Table III. While the exact values of the Debye temperatures (Θ_D) are not important, the trend as one moves to heavier elements is unmistakably to lower values. It may be that the effective temperature (some function of T and Θ_D) is an important variable. This will be further discussed in a later section.

The reflectivity curve for α -brass, Fig. 6, differs greatly from the other curves in that its edge shifts by

TABLE II. Position of reflectivity edge, width of apparent gap, difference in reflectivity on either side of edge, and maximum slope of edge.

	Edge (Å)	Gap (eV)	ΔR (%)	Slope ($\Delta R/\Delta \lambda$)
β -CuZn	5000	2.48	50	0.09
β -AgZn (3½% Au)	5700	2.18	37	0.05
β -AuZn	6000	2.07	22	0.02
β -AgZn (3½% Au)	5700	2.18	37	0.05
β -AgCd	6100	2.03	34	0.04
β -AuCd	6000	2.07	15+	0.01
β -CuZn (27°C)	5000	2.48	50	0.09
β -CuZn (275°C)	5300	2.34	42	0.06

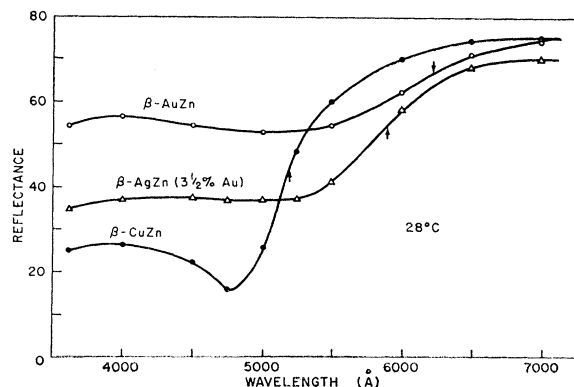
FIG. 7. Room temperature reflectivities of β -CuZn, β -AgZn (3½% Au) and β -AuZn.

TABLE III. Debye temperatures of alloys.

Alloy	Debye temperature	Debye temperature by averaging ^a
β -CuZn	265°K ^b	252°K
β -AgZn		215°K
β -AuZn	190°K ^c	192°K
β -AgCd		174°K
β -AuCd	135°K ^b	164°K

^a Method averaged the Debye temperatures of the component elements (average of $1/\theta_D^3$) and the Debye temperatures listed in R. W. James, *Optical Principles of the Diffraction of X Rays* (G. Bell and Sons, London, 1948), Chap. 5, p. 221.

^b Method utilized elastic constant data.

^c Method used x-ray diffraction temperature factor [M. Schwartz and L. Muldower, *J. Appl. Phys.* **29**, 1561 (1958)].

about 1/4 the shift of β -brass for a corresponding temperature difference. Although there is little edge shift and little change in slope, there is a considerable reduction in the difference in the reflectivity on either side of the edge. This would mean, visually, that the purity of the color would be reduced. This is in agreement with previous visual observations of copper.

THE OXIDE LAYER "EXPLANATION"

It is only natural to question whether some or all of these effects are the result of surface layers of oxide. This was raised by a number of others and will therefore be treated in detail. The first question to be resolved is whether the observed room temperature colors are due to a surface layer. One does not question the colors of copper and gold and certainly gold is quite inactive chemically. Surfaces of β -CuZn and β -AgZn tend to whiten when abraded and then recover their colors with time. This could be interpreted as indicating removal of oxide and then regrowth of oxide. However, it was noted that the colors were recovered under vacuum grease and under dry benzene. Schulz has stated that thin films of these alloys show transmission colors,¹⁷ and such transmission colors may be taken as indicative of bulk properties.

The above discussion has concerned itself with a selectively absorbing oxide film. There is, of course, also the possibility of a transparent interfering film. The observed color changes as a function of temperature could be explained if the optical thickness changed reversibly and appropriately with temperature. A primary objection to this hypothesis is the shape of the reflectivity curves; they are not those expected from interference films. When plotted as a function of wavelength, the long-wavelength slope near the minimum should be less than that on the short-wavelength side.¹⁸ Figure 2 shows just the opposite condition. In addition, observed edge shifts can only be explained on the basis of a 10% change in optical thickness; a coefficient of expansion for ZnO of $10^{-5}/^\circ\text{C}$ would only give a 0.1%

¹⁷ L. G. Schulz (private communication).

¹⁸ P. M. van Alphen, *Philips Tech. Rev.* **19**, 59-67, No. 2 (1957/58).

change even if the index of refraction were to remain constant. Actually, the index usually changes in such a manner as to keep the optical path constant. A reversible increase and decrease in film thickness seems to be out of the question.

Other points against the oxide film theory are (1) no oxide film was observed in the case of β -AuZn, (2) the film thickness would have to be considerably above that readily detected by electron diffraction, (3) changes in color are seen taking place "underneath" the surface oxide, (4) color changes are seen even when the temperature is lowered—this refutes oxide growth and sublimation possibilities, and finally (5) the whole pattern of color changes in the four β -brass type alloys is systematic and unlikely to be produced by random oxidation thicknesses.

DISCUSSION

Mott's explanation of the yellow color of α -brass assumed a band structure unchanged from that of copper.¹⁹ In α -brass there would be a higher Fermi level due to the contribution of two electrons by each zinc atom. A higher Fermi level would mean a larger energy would be required for the onset of the $3d^{10}4s$ to $3d^94s^2$ electron transition, thus shifting the edge from red for copper to yellow for α -brass. The magnitude of the predicted shift with change in composition differs from the observed shift; this has been discussed by Biondi and Rayne.²⁰ The observed shifts for α -brass cannot be extrapolated into the β -brass region; this is to be expected because of differing crystal structures.

In general appearance, the reflectivity curve for silver²¹ resembles that of β -brass although the minimum at 3200 Å is deeper and edge is steeper for silver. Both substances show a broader minimum at shorter wavelengths. Furthermore, the edge shift with temperature for silver, -4×10^{-4} eV/°K, is similar to that for β -brass. Silver differs markedly in its response to temperature variation and in the shape of its reflectivity curve from other basically fcc metals such as copper, gold, CuAu, Cu₃Au and Au₃Zn. Taft and Philipp²¹ have shown that the reflectivity minimum in silver is associated with *both* interband transitions and plasma effects. We should, therefore, be prepared to examine the β -brass alloys with both possibilities in mind.

In a metal having a conduction electron concentration N , effective electron mass m^* , and infinite relaxation time τ , the reflectivity as a function of ω is 100% up to $\omega_p = (4\pi N e^2 / m^*)^{1/2}$, it falls sharply to zero at a slightly higher ω , then rises to an intermediate value.²² As τ decreases, the minimum rises and the general curve becomes more rounded and the edge shifts somewhat.²³ In fact, the reflectivity curves for silver and β -brass re-

¹⁹ N. F. Mott, *Proc. Phys. Soc. (London)* **49**, 354 (1937).

²⁰ M. A. Biondi and J. A. Rayne, *Phys. Rev.* **115**, 1522 (1959).

²¹ E. A. Taft and H. R. Philipp, *Phys. Rev.* **121**, 1100 (1961).

²² B. Lax, *Trans. IRE MTT-9*, 83 (1961).

²³ M. S. Dresselhaus (private communication).

semble such curves greatly. On the other hand, the reflectivity curves for copper and gold do not show a minimum above the edge and the absence of a sharp peak in $nk/(n^2+k^2)^2$ for these metals in the visible shows the absence of significant plasma oscillation effects.²⁴ It might then be suggested that the β -brass reflectivity minimum is associated primarily with a plasma frequency with the possibility that interband transition coupling can play a strong but secondary role.

If the real part of the dielectric constant is zero and damping is negligible, then the reflectivity will be that associated with plasma oscillations. This is the case for silver^{21,24} and recent unpublished results in this laboratory shows that this also is true for β -brass.

The calculated plasma frequency ω_P for β -brass corresponds to an energy of 12.7 eV (970 Å) if the electron mass is assumed to be that of the free electron and the electron density N is assumed to include all outer electrons (one from each copper and two from each zinc atom). This is a good deal below the reflectivity minimum for β -brass. Examination of the situation in silver shows again that the calculated value, obtained using naive values for m^* and N , and the experimental ω_P differ greatly. The experimental value of the plasma energy is 3.75 eV (3300 Å) while the value using naive constants is 9.02 eV (1370 Å). Thus, there is a substantial basis for the β -brass discrepancy. The shift of the plasma frequency from its classical value in both silver and in β -brass is due to the interband coupling in the model used.

The basic model in this discussion is that found in Mott and Jones for silver.²⁵ They show the contributions to the real part of the dielectric constant arising from the conduction electrons, the core electrons, and the interband transitions. For the conduction electrons it is

$$\epsilon_1 = 1 - (4\pi N e^2 / m \omega^2),$$

for the core there is a constant term, while for the interband transitions there is an oscillator type term. In the absence of the interband effects, the zero of ϵ_1 is near the classical value. However, the addition of the interband term drastically shifts the frequency at which $\epsilon_1=0$ to a value close to the observed reflectivity minimum in silver. Ehrenreich has extended this model and has applied it to copper.²⁶ There is some evidence for the conductivity ($nk\nu$) peak expected in this model in β -brass at wavelengths somewhat below the reflectivity edge.

In Table IV a comparison of the classical plasma wavelength in the absence of interband transitions is made with the observed reflectivity minima in several alloys. Included also is the wavelength calculated with

TABLE IV. Plasma wavelengths. (a) Using free electron mass and electron density according to Hume-Rothery. (b) Using N/m^* according to Schulz.²⁷ (c) Estimate of observed minimum in reflectivity curve. Included are the ratios of (c) to (b) and (c) to (a). Values are in angstroms.

Metal	(a)	(b)	(c)	Ratio (c)/(a)	Ratio (c)/(b)
Ag	1370	1350	3300	2.41	2.45
CuZn	970	1640	5000	5.26	3.05
AgZn	1070	1430	5700	5.32	3.99
AuZn	1060		6000	5.10	
AgCd	1170	1560	6100	5.21	3.91

* See reference 27.

the aid of values of N/m^* of Schulz.²⁷ In all cases, there is a large difference in wavelength between calculated classical λ_P and reflectivity minima. This is a measure of the shift produced by the interband transition.

It can be seen that a shift in the absorption band due to interband transitions will have a strong influence on the wavelength at which $\epsilon_1=0$. Furthermore, any broadening of this band as might arise from an increase in temperature would show up in the reflectivity edge. Effects not observed with either a pure plasma edge or a pure absorption edge may be possible.

The main problem is to explain the reflectivity edge shift with temperature. β -brass shows a shift of about -5×10^{-4} eV/°C and the other alloys of this series show similar changes. Semiconductors generally show shifts of this magnitude; for germanium it is -4.4×10^{-4} eV/°C and for Mg_2Sn it is -3.5×10^{-4} eV/°C. CuAu and Au_3Zn show shifts near -1×10^{-4} eV/°C. It is necessary, then, to explain the basis for these differing values for various alloys.

The explanation of the edge shifts in semiconductors follows two main arguments. One, given by Bardeen and Shockley, is based on thermal expansion and corresponding shifts in energy bands.²⁸ It would then be expected that materials having high expansion coefficients could show large changes in gap energy. Such is apparently the case with amorphous selenium with its very large temperature shift of -9.7×10^{-4} eV/°C.²⁹ It may be noted that the expansion coefficients for α - and β -brasses are almost the same; thus, their difference in optical behavior with temperature cannot be attributed simply to a difference in the expansion coefficient. It may be, however, that their response to a given expansion may be significantly different.

A second possibility was given by Fan and involves the explicit dependence of the energy gap on the lattice vibrations.³⁰ He showed that there is a shift of gap width resulting from the virtual emission and absorption

²⁴ H. Frohlich and H. Pelzer, Proc. Phys. Soc. (London) **A68**, 525 (1955).

²⁵ N. F. Mott and H. Jones, *The Theory and Properties of Metals and Alloys* (Dover Publications, New York, 1958), pp. 123-124.

²⁶ H. Ehrenreich (private communication).

²⁷ L. G. Schulz, as reported in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 269.

²⁸ J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950).

²⁹ C. Hilsum, Proc. Phys. Soc. (London) **B69**, 506 (1956).

³⁰ H. Y. Fan, Phys. Rev. **78**, 808 (1950).

of phonons by electrons. In fact Fan indicated that, in some cases, lattice vibrations are more important in producing gap changes than is lattice dilation. Neuringer has shown experimentally that electron-lattice interaction is the major determinant in the thermal shift of gap in silicon and germanium.³¹ It should be noted that this effect is the same as the phonon assisted interband transition of an electron (violation of the selection rule, $k = \text{const}$). If this coupling probability increases with temperature, the apparent gap energy should diminish with increasing temperature. However, such effects may not be very important in metals.

A third mechanism, one which has been little discussed, is the change in relaxation time τ with changing temperature and its concomitant effect upon the position of the plasma edge. The mechanisms discussed above are concerned basically with interband or internal photoelectric effects. This third possibility, while influenced by the interband excitations, is fundamentally different. It should be noted that thermal expansion, through its effect upon N , also affects the plasma frequency. In the case of β -brass, this shift amounts only to about 15% of the observed shift.

It can easily be determined from Tables II and III that a good correlation exists between (a) the Debye temperatures of the alloys and (b) the room temperature values of the position of the reflectivity edge, slope of edge, and ΔR . It is generally true that the Debye temperature goes down as one proceeds to higher atomic weight elements in a given family of compounds; Table III shows that this holds for the β -brass type alloys. Thus, it might well be that the reflectivity curves, for some reason, are functions of an effective temperature which would be something like T/Θ_D . This Debye temperature dependence indicates a strong electron-lattice interaction. However, nothing in this makes allowance for the interband transition.

In intermetallic semiconductors, the gap energy decreases in going from one compound to another where an element has been replaced by a heavier one from the same column of the periodic table. Burstein and Egli explain this observation by the fact that the binding energy of the valence electrons generally decreases with increasing atomic number.³² This would explain the observed gap energies in a series such as Sb_2S_3 , Sb_2Se_3 , Sb_2Te_3 .³² This gap energy decrease can also be seen in the series β -CuZn, β -AgZn, β -AuZn (Table II). The interband transition energy should only be a little above that for the reflectivity minimum. Gap energy here does not mean energy separation of bands but the minimum energy required for a non-phonon assisted electron excitation with the selection rule that the electron momentum $k = \text{constant}$. However, the first ionization energies of copper, silver, and gold are 7.68, 7.54, and

9.18 eV, respectively. Hence, the above simple explanation cannot hold and an alternative must be found.

Another feature of the reflectivity curves for which there are a number of explanations is the decrease in edge steepness with increasing temperature. It is recognized that this is probably closely related to the edge shift. Joos and Klopfer have observed the change in edge slope in copper, silver, and gold.¹ They show that unsharpening of the Fermi distribution can account for the whole of the observed changes. It is assumed that electron interband transitions from an underlying d -band to the top of the Fermi surface or from the surface to the next band are responsible for the edges.

Another possibility for the explanation of the temperature effect on the sharpness of the edge may be found in the Bardeen and Shockley local dilation model.²⁸ They consider the effect of local variations in density arising from thermal vibration upon the energy band spacings. Thus, the higher the temperature, the greater the variations in local density and the greater the variations in gap energy. These variations exist as a function of both time and position in the crystal. The net effect would be to blur the edge in agreement with observed effect.

A third possible explanation involves the decrease in τ with increasing temperature and the effect of this upon the plasma edge.

The concluding remarks will be devoted to considerations of the electron bands for β -brass type alloys. Frank³³ has made measurements of copper, α -brasses, and β -brass from room temperature to almost 600°C. In all cases the coefficient decreases with increasing zinc concentration and rises with temperature. For copper it is $-5.2 \times 10^{-5} \text{ cm}^3/\text{C}$ at 0°C and -5.8×10^{-5} at 550°C which behavior is almost that of free electrons. For β -brass it is -0.6×10^{-5} at 0°C and -1.9×10^{-5} at 550°C. Two things are to be noted: (1) the coefficient for β -brass at room temperature is close to zero; and (2) the rise for β -brass with temperature is more than twice that for copper. Frank believes that the composition effects are due to the increasing distortion of the Fermi surface as it approaches the Brillouin zone as zinc is added. As the Fermi surface rises, the effective mass for transport phenomena decreases and may even become negative in some directions thus reducing the Hall coefficient. Interestingly, the β -brass values of the coefficient continue the trend seen with the α -brasses. β -brass is ordered simple cubic. For β -brass the electron-atom ratio is close to 1.5. When disordered (bcc), the first zone is 3/4 full. Upon ordering, a new zone is created inside this zone with its edges at the surface of the old zone. Thus it is possible, in ordered β -brass, that electron and hole conduction occur in both the first and second zones producing the low coefficient. It would seem likely that temperature effects in such a situation

³¹ L. J. Neuringer, Phys. Rev. **113**, 1495 (1959).

³² E. Burstein and P. H. Egli, in *Advances in Electronics and Electron Physics* (Academic Press Inc., New York, 1955), Vol. VII, p. 20.

³³ V. Frank, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. **30**, No. 4 (1955).

would be more pronounced than in the almost free electron case of copper.

As has already been stated, increasing the temperature increases thermal vibration and expands the lattice both of which decrease energies between bands. Since the energy gap is narrowed, the behavior should be more electronic. The narrowing of the gap and the consequent greater electronic behavior are in accord with Hall data. Such behavior would tend to make the Fermi surface more spherical.

Obviously this has significance for optical behavior. In the model presented above, the change in the gap energy with temperature will be observed in the shift of the reflectivity edge.

The following conclusions may be drawn: (1) the reflectivity edge in β -brass, as in silver, is plasmalike in character, (2) the position of the plasma frequency and the closely associated reflectivity minimum is strongly dependent upon the energy range of the interband transition, (3) the strong temperature effects in β -brass and in silver compared to copper and gold are probably due to the nature of the plasma-interband coupling in the former compared with absorption effects only in the latter, (4) the relation of these reflectivity curves to the Debye temperature is not clear.

Much remains to be done in clarifying the exact nature of the temperature effect and in making quanti-

tative calculations. A theoretical and experimental research program is continuing in this laboratory.

Note added in proof. Ehrenreich and Philipp³⁴ have recently examined the optical properties of silver and copper in terms of free electron effects, interband transitions, and collective oscillations. They have related the plasma resonances to characteristic energy losses and have identified interband transitions with the aid of recent band calculations. Their discussion is very important to the understanding of the optically similar β -brass.

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³⁴H. Ehrenreich and H. R. Philipp, *Phys. Rev.* (to be published).

Interband Transitions and Maser Action

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The possibility of using interband transitions to achieve maser action is considered. The criterion for maser action is presented in a way which allows the most direct use of optical absorption data. The absorption constant for interband transitions, which is negative corresponding to induced emission when a population exists, is related to the normal absorption constant for direct, indirect, and indirect exciton transitions. Using available absorption data, it is shown that in Ge maser action, using either the indirect or indirect exciton transitions, would be prevented by absorption due to free carriers. In GaAs, or other materials with a direct band gap, however, it is entirely possible that maser action could be achieved.

SINCE the initial operation of the ruby maser, there has been considerable speculation concerning the possibility of observing maser action in semiconductors such as Ge and Si. These semiconductors, as well as several of the III-IV and II-VI intermetallic compounds have several interesting features. First, it is possible to prepare relatively pure, homogeneous, single crystals, with reasonably good optical properties. Secondly, it is possible in semiconductors to excite electrons by injection or by avalanche breakdown techniques rather than by optical pumping. Finally, the band structure and optical properties are sufficiently well

known, such that it should be possible to theoretically decide whether or not certain transitions can give rise to maser action.

Opposing these advantages are several characteristics which are usually not present in current laser materials. First, free-carrier absorption of emitted light is possible because of the continuous density of levels to which the carriers may be excited. Free-carrier absorption is, in fact, a sufficiently important dissipative mechanism for photons, such as to overshadow the losses suffered at imperfectly reflecting end surfaces. Secondly, nonradiative recombination through localized