RECEIVED BY DTIE OCT 4 1967

MASTER

C00-1198-479

CESTI PRICES

COLOR CHANGES IN THE COMPOUND AuAl_2
INDUCED BY IMPERFECTIONS

H.C. \$ 3.00; MN .65

Han C. Shih
Department of Mining, Metallurgy and Petroleum
and
Materials Research Laboratory
University of Illinois, Urbana, Illinois

August 1967

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

This research was supported in part by the U. S. Atomic Energy Commission under Contract AT(11-1)-1198, Contract Number C00-1198-479. This report is based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Metallurgy in the Graduate College of the University of Illinois, 1967.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

The intermetallic compound AuAl_2 has a brilliant purple color and the crystal structure of CaF_2 with $a_0 = 6.00\text{\AA}$. This eta-phase has a higher melting point than that of Au, is quite brittle, and is completely unworkable at room temperature. The unusually strong attraction between Au and Al atoms results in large negative deviations from Vegard's law; much heat evolution when Au and Al are mixed; a small range of homogeneity; and very little solubility of Au in Al. All these suggest that the bonding is not purely metallic, but has considerable ionic and covalent character.

Distinct color changes when cold-worked samples of AuAl_2 are annealed have been established. They have been demonstrated as shifts of the spectral absorption edge which moves toward shorter wavelengths during the annealing of a heavily deformed crystal. The amount of the shift depends on the annealing temperature and time. Similar results were obtained for powdered specimens and evaporated thin-films. No such effect is observed for the pure component metals.

Two modes of investigation were used for high temperature reflectivity studies of AuAl_2 . That is, isothermal measurements were made, as well as changes as a function of constantly increasing temperature. As the temperature rises the absorption spectrum gradually flattens.

ACKNOWLEDGMENT

The author wishes to express his deepest appreciation to Professor John J. Gilman, University of Illinois, for suggesting the problem, and for his continued advice, guidance, and encouragement throughout this research.

TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION	1
A. Historical	1
B. Purpose of Present Investigation	3
C. Choice of Specimen Composition	3
II. EXPERIMENTAL PROCEDURES	5
A. Preparation of Specimens	5
B. Preparation of Specimens for Optical Reflectance Measurements	6
C. Optical Systems for Reflectivity Measurements	7
D. Another Method	8
E. Measurement of Reflectivity	9
III. EXPERIMENTAL RESULTS	11
A. Reflectivity Curves	11
B. X-ray Studies	13
C. Hardness Test	14
IV. DISCUSSION AND CONCLUSIONS	15
V. TABLES	17
VI. GRAPHS	21
APPENDIX	44
LIST OF REFERENCES	45

I. INTRODUCTION

A. Historical

The present material was first studied by Roberts-Austen in 1890.¹ He was attempting to correlate alloy properties with atomic volumes, and he described the purple compound AuAl_2 , noted its high melting point, and the fact that it formed with a large evolution of heat. Marked changes in color caused by plastic deformation of Ag-Au alloys were noticed by Tammann in 1919.² He reported that whitish-green alloys (in the composition range 60-70 % Au) became yellowish when they were heavily cold-rolled. This effect is more pronounced with some ternary alloys of Ag, Au, and Cu; and its magnitude increases with increasing deformation. Lipson, Burstein, and Smith³ observed that the spectral absorption edge of germanium shifts towards longer wavelengths when it is plastically deformed from 3% to 15% at about 700°C.

Boas⁴ prepared an alloy of about 52 wt.% Au, 22 wt.% Ag, and 26 wt.% Cu, which had a reddish tint in the fully annealed state. An ingot of this alloy was cold-rolled from a thickness of 3 mm. to 0.25 mm.; and a part of it was then annealed in nitrogen for 1/2 hr. at 450°C. The two strips had different colors, with the rolled one being more yellow than the annealed one. He drew attention to the influence of the Fermi energy on the position of the absorption band and its possible variation as a result of expected plastic deformation.

Philipp and Taft⁵ determined the optical constants of Ge from measurements of reflectivity over a broad wavelength range, 0.6 ev to 11.3 ev. The real part of refractive index, n , has maxima of 5.5 at 2.07 ev and 4.2 at 3.2 ev. The extinction coefficient, k , shows maxima of 2.0 at 2.5 ev and 4.2 at 4.4 ev.

Fumi⁶ proposed that the main contribution to the formation energy of a vacancy comes from the change in the Fermi energy of a metal. A somewhat smaller but similar change in the Fermi energy is expected at the core of an edge dislocation.

Cardona and Sommers⁷ studied the 2.1- and 4.4-ev peaks in the reflectivity spectrum of Ge as a function of temperature. They found that the temperature coefficient for the $L_3' - L_1$ gap, is -4.2×10^{-4} ev/ $^{\circ}\text{K} \pm 10\%$; or the same as that of the thermal gap, and of the direct absorption edge.

Yates⁸ examined the effect of deformation on reflectivity in single-phase binary alloys of Ag and Au. His annealed samples appeared visually to be more white (or less yellow) than his deformed samples, and his reflectance measurements showed that annealing caused the absorption edges of heavily deformed samples to move about 5-4 $\text{m}\mu$ toward shorter wavelengths.

Philipp, Dash, and Ehrenreich⁹ studied the reflectance peaks of Ge and Si below 5 ev in crystals subjected to four-point elastic bending. The effect of uniaxial elastic stresses along various directions measures changes of band

edges induced by hydrostatic pressure; and in principle, measures deformation potential constants.

B. Purpose of Present Investigation

Since a strong absorption band occurs for AuAl_2 in the visible region (545 m μ) of the spectrum, an observable change in color might result from plastic deformation of it. Therefore, a survey has been made of changes in the absorption edge as a function of annealing temperature and time for plastically deformed AuAl_2 . The process of annealing out dislocations markedly affects the reflectivity of this intermetallic compound. This behavior may be used as a means for probing the electronic structures of dislocations.

C. Choice of Specimen Composition

The particular composition of interest in the Au-Al alloy system is the intermetallic compound AuAl_2 because of its unique purple-color. Such a highly colored metal is quite unusual. Like most intermetallic compounds, AuAl_2 is very brittle and hard and completely unworkable at room temperature. It has the CaF_2 structure of eta-phase and so is analogous to other compounds like Mg_2Si , Mg_2Ge , etc. It resists the action of dilute acids and alkalies. It becomes ductile only at an elevated temperature, and it deteriorates by spontaneous cracking when it is exposed to laboratory air for a few weeks.

After plastic deformation the color of a cold-worked sample changes visibly to a less intense purple color (more

grayish). Similar color changes are induced when annealed samples are heated above room temperature. This change is reversible, as are changes to a more reddish-purple color that is induced by cooling the compound to 78°K. It may be concluded that the electronic structure of AuAl_2 is particularly sensitive to the influence of temperature.

The reflectivity curve of AuAl_2 shows a minimum (absorption maximum) at 545 m μ . Its high reflectivity for red and blue light causes its purple coloration.

II. EXPERIMENTAL PROCEDURE

A. Preparation of Specimens

Specimens (33.33 at.% Au, 66.66 at.% Al) were prepared from zone-refined Al [0.3 ppm Fe, 0.3 ppm Cu] and Au [0.000X (low) Ag, 0.000X (low) Cu] in a graphite mold (or alumina crucible) by melting in an induction furnace with an argon atmosphere at a temperature of about 1200°C. The system was evacuated to $< 5 \times 10^{-3}$ Torr. with a mechanical pump, and fluxed with dry argon (99.996+%) several times to reduce the air in the system to a minimum. Very little weight loss was observed (a max. of 0.0031 grams in a total charge of 15.2292 grams, or 0.009%) after this process. It was necessary to cool the compound very slowly in order to relieve the solidification stresses. Some of the specimens burst into fragments after they were removed from the mold. Homogenizing anneals were done by sealing the ingots in quartz tubes under vacuum for 24 hrs. at 300°C.

Monocrystals of AuAl_2 were grown using the Bridgeman technique (Figure 1). A weighed piece of AuAl_2 was placed inside a 7/16 in. I.D. graphite mold, evacuated to a pressure of 2×10^{-6} Torr. in a quartz tube and sealed off. The cold ampule was attached to a quartz rod, held by a Nichrome wire that was connected to a pulley driven by a synchronous motor; and lowered at about 1 cm/hr. through the furnace.

The temperature was about 150°C above the melting point of AuAl_2 in the center of the furnace.

Laue back reflection photographs were taken at three different points along the ingot axis to make sure that they were really monocrystals.

B. Preparation of Specimens for Optical Reflectance Measurements

1. Bulk crystals for reflectivity measurements

Clean ingots (11 mm. dia.) of AuAl_2 were carefully compressed to reduce their thickness by 81% at approximately 400°C using a small hydraulic press. This was done inside a furnace containing an argon atmosphere. Polished cylinders of Alumina were used as platens as shown in Figure 2.

Both diamond-abrasive slicing and spark cutting were found satisfactory for cutting this hard and brittle substance into pieces. These were then ground by a series of Emery papers, followed by two stages of vibrational polishing using an aqueous slurry containing 0.3μ and 0.05μ Alumina powder abrasives. The polished surfaces were cleaned with acetone and deionized water, and baked to remove any oil-film traces. Since the amplitude of a surface reflection is a "surface property", it may depend on precisely how the surface is made.

2. Evaporated thin films for reflectivity measurement

Thin films of AuAl_2 can be produced by evaporation from its liquid phase followed by condensation of the vapor onto a substrate. In the present work the evaporation heater

was a double tungsten wire in the form of conical basket, and the condensation substrate was at room temperature. AuAl_2 evaporates rapidly in vacuo when its temperature produces a vapor pressure in excess of 2×10^{-7} Torr. The actual evaporation process lasted about 10 min.

For each evaporation, four sets each containing four glass plates were placed at distances of 15, 20, 25, and 30 cm respectively from the filament. This allowed the comparison of films deposited under the same condition of evaporation.

The glass plates were of good optical quality, precisely plane and parallel, and $1 \times 3 \text{ in.}^2$ in size. The plates were previously washed in dilute nitric acid, then rinsed with deionized water, and dried in an oven.

In the aging experiments, the specimen plates were kept in a desiccator to protect them from dust, tobacco smoke, flames, and chemical fumes.

3. Powdered specimens for diffuse reflectance measurements

Since AuAl_2 is very brittle at room temperature, it can be pulverized in an agate mortar and sieved (325 mesh in this case). The grinding operation made the crystallites imperfect and portions of the powder were annealed under vacuum at various temperatures and times. The powdered specimens were used for X-ray diffraction pattern studies.

C. Optical Systems for Reflectivity Measurements

Two systems were used: an integrating sphere type; and a reflection type. See Figure 3. The integrating

sphere type was used for measuring diffuse reflectance in conjunction with a Beckman DK-2 Spectrophotometer. The reflection type was used for measuring specular reflectivity.

A specimen R, whose reflectivity is to be measured, is mounted (Figure 4) on a spectrometer table with the axis of rotation perpendicular to the reflecting plane. The holder plate has a rectangular aperture Q of 0.374 in. x 1.875 in. which allows large incidence angle measurements (as shown in Figure 5). The tungsten light source L is mounted on a movable arm of the optical bench. An EGG Spectroradiometer (Model 580/585) is located in a fixed position where it is used as a monochromator and detector. The elements of this instrument are shown in Figure 4. (F is the filter, M is the monochromator, D is the PbS photodiode, and I is the indicator unit). In position 1, the photodiode receives light passing from shutter S through Q directly when sample R is removed, or after passage through the sample when this is inserted. In position 2, it receives light from R at several different angles of interest (45° , 60° , 70° , 80°). This light can be considered to be coming from the virtual image S of the source. Filters were used to eliminate the lower harmonics of the wavelengths reflected by grating in the monochromator housing.

D. Another Method

One pair of specimens was examined with a Beckman DK-2 Spectrophotometer fitted with a reflection attachment

consisting on an integrating sphere. Magnesium Oxide was used as the reference, and the specular reflectivity curve was obtained as a function of wavelength. The results were essentially the same as those obtained with the system as described above. An extension of the reflectivity curve into the infrared region was also made (out to 2500 $m\mu$).

E. Measurement of Reflectivity

The specular reflectivity, R , was measured by means of the system described in Section C where the intensity of the incident radiation (I_0) and that of the reflected radiation (I) from the specimen were measured. The value of R equals the ratio of I to I_0 ; i.e., $R = I/I_0$.

Reflectivity values as a function of wavelength from 350 to 800 $m\mu$ are given in Figure 6 for an incidence angle of 45° . The value of R depends on the incidence angle as shown in Figure 7 for 60° , 70° , and 80° . Both bulk crystals and evaporated films were studied. Two components: R_p , the reflectivity for incident light vibrating parallel to the incidence plane; and R_s , the reflectivity for incident light vibrating perpendicular to the incidence plane, were measured with the aid of a polarizer. R_p and R_s also depend on the incidence angle as shown in Figures 8(a),(b).

The powdered specimens were placed on a segment of an integrating sphere coated with MgO and the diffuse reflectance was measured with reference to that of MgO . The reflectance attachment for a Beckman DK-2 Spectrophotometer was used.

A tungsten filament served as the light source for the region 350-800 m μ . Checks were frequently made by comparing a deformed specimen with an annealed one (Figure 9). The resulting curves give the reflectivity (relative to that of MgO) as a function of wavelength (Figure 10).

III. EXPERIMENTAL RESULTS

A. Reflectivity Curves

1. Specular reflectivity measurements

The reflectivity versus wavelength in the visible region is given in Figure 6 which shows that there is an absorption band at 545 m μ . For longer wavelengths, the reflectivity increases abruptly and reaches about 95% in the far infrared region (3-10 μ). This was determined by means of a Beckman Infrared Spectrophotometer with an Al mirror as the reference (see Figure 11). The reflectance attachment is shown schematically in Figure 12. Bulk crystals, powdered specimen, and evaporated films all yielded reflectivity curves of the same shape, but with different absolute reflectivities. The data are illustrated in Figures 6, 10, and 14, and are summarized in Table I.

The color change of AuAl₂ that occurs upon plastic deformation was studied by means of the shift of the absorption edge of the green band. A pair of typical spectral reflectivity curves for a deformed (81%) and an annealed (550°C) specimen is shown in Figure 13(a). The effect of deformation is to decrease the depth of the green absorption band and increase broad band U.V. absorption. This results in overall graying or decrease in the intensity of the purplish

coloration. Differences in the reflectivities of the specimens can be summarized by giving the minimum reflectivity at approximately 545 m μ (2.28 ev) and the half-breadth of the absorption band (1900A for cold-worked, and 1790A for annealed as shown in Figure 13(b)).

The rate of change of reflectivity with respect to wavelength was calculated graphically from the curves over the region 550-650 m μ . Curves of this rate were plotted (Figures 18(a),(b)) and the maximum occurred at 595 m μ for an annealed specimen and at 615 m μ for a deformed one (see also Table II).

The reflectivity spectra of an evaporated film had the same shapes as those of bulk crystals as shown in Figure 14. The film thickness was approximately 3600A, and its reflectivity in the annealed state was lower than that of the freshly evaporated material. Numerical data is given in Table III. These results were confirmed by the Beckman DK-2 Spectrophotometer (see Figure 15).

The reflectivity of AuAl₂ is strongly dependent on temperature. Isothermal curves were measured at 25°C, 250°C, and 400°C. Figure 16 shows that the green absorption band broadens and decreases in depth as the temperature increases. The change of the minimum reflectivity with temperature is shown in Figure 17.

2. Diffuse reflectance measurements

Since diffuse reflectance involves the penetration of a portion of the incident light flux into the interiors of the specimen particles, its measurement helps to verify

that bulk properties (rather than surface ones) are being measured. It is assumed that the specimen is composed of small crystallites statistically distributed at all possible angles with respect to the macroscopic surface; the combined specular reflection from all such surfaces being responsible for the scattering of the incident radiation.

The diffuse reflectance curves for AuAl_2 have the same shapes as those of specular reflectance (Figure 10) although the numerical values are somewhat lower. See Figure 19 for more detailed curves, as well as Table IV.

B. X-ray Studies

X-ray diffraction spectra of cold-worked and annealed powders were made photographically and with a recording powder spectrometer. The photographs showed that the broad diffuse lines for cold-worked specimens became sharp (the $\text{CuK}\alpha_1$ and $\text{CuK}\alpha_2$ doublet which was clearly resolved) after annealing.

The spectrometer curves also showed broad peaks for cold-worked specimens, and well-resolved doublets after annealing. Spectrometer curves were also made for the high angle (331) and (420) reflections at elevated temperatures (up to 600°C at intervals of 100°C). There were no changes in the shapes of the curves, and the diffracted intensities remained about the same.

C. Hardness Test

Vickers Hardness Numbers were measured for both deformed and annealed specimens. For as-deformed material the VHN is 556^{+6} and after annealing at 600°C it drops to 379^{+9} . It decreases as the annealing temperature increases as shown in Figure 20.

IV. DISCUSSION AND CONCLUSIONS

The reflectivity of AuAl_2 is unusual for a metal because it has a deep minimum at $545 \text{ m}\mu$, followed by unusually high reflectivity for wavelengths greater than $1150 \text{ m}\mu$. Polished crystals, powders, and evaporated films all show this same reflectivity minimum.

For the absolute reflectivity measurements, the specimen surface must be very carefully prepared, because oxide layers or oil films might cause reflectivity changes. In the present study surface contamination has not had significant effects because:

- (i) different annealing environments did not affect the result;
- (ii) both specular and diffuse reflectance gave the same result;
- (iii) a plastically deformed specimen that was examined before and after annealing gave the same result as an annealed specimen before and after the compression;
- (iv) X-ray diffraction patterns showed no evidence of oxidation, phase transformation, or order-disorder transformation;
- (v) evaporated films gave results similar to those for powdered specimens and bulk crystals;
- (vi) freshly cleaved specimens had the same colors inside and out.

It may be concluded that crystal imperfections produce the observed color changes. Annealing tends to remove the imperfection to an extent that depends on the annealing temperature and time. Yates¹⁰ concluded that the color change in AuAg is independent of annealing time and temperature; but this is not the case for AuAl₂. Not only the optical behavior but also the hardness decreases considerably as annealing temperature increases. When this occurs the strong absorption band in the green narrows and strengthens. The sharpening of the X-ray diffraction maxima also indicates that annealing removes strains and defects from the crystals.

TABLE I
REFLECTIVITY DATA FOR FULLY ANNEALED AuAl₂

WAVELENGTH (microns)	BULK CRYSTAL (45° incidence angle) (percentage)	POWDERED SPECIMEN (particle size 325 mesh) (percentage)	EVAPORATED FILM (thickness 3600A) (percentage)
0.35	0.571	0.286	0.321
0.40	0.514	0.210	0.289
0.45	0.468	0.175	0.243
0.50	0.366	0.250	0.174
0.55	0.281	0.110	0.147
0.60	0.334	0.160	0.225
0.65	0.454	0.240	0.348
0.70	0.530	0.302	0.436
0.75	0.570	0.341	0.470
0.80	0.610	0.362	0.568

TABLE II
ANALYSIS OF REFLECTIVITY CURVES FOR AuAl₂

MATERIAL	COLD-WORKED SPECIMENS			ANNEALED SPECIMENS		
	Wavelength at point of intersection (mμ)	Slope $\Delta R/\Delta \lambda$ (mμ ⁻¹)	Wavelength at point of inflection (mμ)	Wavelength at point of intersection (mμ)	Slope $\Delta R/\Delta \lambda$ (mμ ⁻¹)	Wavelength at point of inflection (mμ)
Bulk Crystal	670.0	0.203	615.0	654.0	0.410	595.0
Powder	678.8	0.134	625.0	667.5	0.196	614.0

TABLE III
REFLECTIVITY DATA FOR ANNEALED EVAPORATED-FILMS OF AuAl_2

WAVELENGTH (m μ)	ANNEALING TEMPERATURE		
	200°C (percentage)	400°C (percentage)	500°C (percentage)
350	0.426	0.361	0.325
360	0.397	0.396	0.320
380	0.381	0.353	0.303
400	0.358	0.342	0.289
420	0.343	0.321	0.272
440	0.315	0.297	0.356
460	0.285	0.266	0.231
480	0.246	0.231	0.198
500	0.216	0.199	0.174
520	0.201	0.178	0.158
540	0.189	0.170	0.148
560	0.225	0.180	0.151
580	0.261	0.213	0.175
600	0.310	0.271	0.225
620	0.346	0.334	0.281
640	0.410	0.388	0.329
660	0.450	0.432	0.366
680	0.480	0.471	0.402
700	0.499	0.509	0.436
720	0.501	0.510	0.428
740	0.530	0.540	0.448
760	0.545	0.535	0.463
780	0.559	0.557	0.482
800	0.565	0.566	0.499

TABLE IV

DIFFUSE REFLECTANCE OF POWDERED AuAl_2

WAVELENGTH (μ)	PLASTICALLY DEFORMED (room temperature) (percentage)	ANNEALED (300°C/24hr.) (percentage)	ANNEALED (500°C/24hr.) (percentage)
400	0.262	0.221	0.175
450	0.201	0.180	0.140
500	0.144	0.125	0.086
550	0.121	0.104	0.180
600	0.162	0.182	0.262
650	0.230	0.263	0.320
700	0.283	0.308	0.350
750	0.321	0.350	0.373
800	0.350	0.370	0.402
850	0.364	0.390	0.415
900	0.383	0.401	0.402
950	0.399	0.410	0.406
1000	0.410	0.416	0.425
1050	0.420	0.421	0.435
1100	0.430	0.430	0.430
1200	0.432	0.436	0.439
1250	0.435	0.437	0.440
1300	0.440	0.440	0.450
1350	0.442	0.442	0.442
1400	0.443	0.442	0.443
1450	0.445	0.444	0.445
1500	0.446	0.444	0.444
1550	0.444	0.440	0.443
1600	0.442	0.418	0.441
1650	0.442	0.418	0.440
1700	0.443	0.440	0.440
1750	0.444	0.441	0.442
1800	0.445	0.442	0.442
1850	0.447	0.450	0.443
1900	0.462	0.455	0.456
1950	0.461	0.453	0.454
2000	0.461	0.450	0.453
2050	0.450	0.450	0.461
2100	0.462	0.455	0.461
2150	0.466	0.460	0.464
2200	0.484	0.473	0.466
2250	0.484	0.480	0.480
2300	0.444	0.480	0.482
2350	0.446	0.482	0.482
2400	0.502	0.490	0.484
2450	0.520	0.492	0.500
2500	0.526	0.500	0.516
2550	0.542	0.530	0.533
2600	0.546	0.540	0.540
2650	0.568	0.563	0.580
2700	0.598	0.622	0.640

FIGURE 1. CRYSTAL GROWTH FURNACE.

FIGURE 2. APPARATUS FOR COMPRESSION OF HEATED SPECIMENS.

FIGURE 3. BASIC ARRANGMENT OF REFLECTIVITY MEASURING INSTRUMENTS. (a) REFLECTION TYPE. (b) INTEGRATING SPHERE TYPE.

FIGURE 4. SCHEMATIC DIAGRAM OF THE OPTICAL SYSTEM.

FIGURE 5. SPECIMEN HOLDER WITH HEATING UNIT.

FIGURE 6. SPECULAR REFLECTIVITY CURVES FOR POLY-AND MONO-CRYSTALLINE SPECIMENS.

FIGURE 7. SPECULAR REFLECTIVITY OF AN EVAPORATED FILM WITH DIFFERENT INCIDENCE ANGLES.

FIGURE 8. DEPENDENCE OF SPECULAR REFLECTIVITY ON INCIDENCE ANGLE FOR PLANE POLARIZED LIGHT. (a) R_p AND R_s . (b) RATIO OF R_p TO R_s .

FIGURE 9. DIFFUSE REFLECTANCE OF POWDERED SPECIMENS WITH FULLY ANNEALED STATE AS REFERENCE.

FIGURE 10. DIFFUSE REFLECTANCE OF POWDERED SPECIMENS WITH MgO AS THE REFERENCE.

FIGURE II. INFRA-RED SPECULAR REFLECTIVITY OF AuAl₂.

FIGURE 12. REFLECTANCE ATTACHMENT FOR BECKMAN INFRARED SPECTROPHOTOMETER.

FIGURE 13. (a) SHIFT OF ABSORPTION EDGE OF GREEN BAND.
(b) COMPARISON OF HALF-BREATH OF ABSORPTION BANDS.

FIGURE 14. SPECULAR REFLECTIVITY OF AN EVAPORATED FILM (3600 Å THICKNESS).

FIGURE 15. TOTAL REFLECTANCE SPECTRA OF AN EVAPORATED FILM
(OBTAINED WITH INTEGRATING SPHERE TYPE OF INSTRUMENT)

FIGURE 16. ISOTHERMAL SPECULAR REFLECTIVITY CURVES.

FIGURE 17. DEPENDENCE OF SPECULAR REFLECTIVITY AT $545 \text{ m}\mu$ ON TEMPERATURE OF MEASUREMENT.

FIGURE 18. SLOPES OF REFLECTIVITY CURVES AS A FUNCTION OF WAVELENGTH.
(a) SPECULAR REFLECTIVITY FROM CRYSTAL.
(b) DIFFUSE REFLECTANCE FROM POWDER.

FIGURE 19. DIFFUSE REFLECTANCE OF POWDERED SPECIMANS.

FIGURE 20. HARDNESS OF AuAl₂ AFTER ANNEALING AT VARIOUS TEMPERATURES.

APPENDIX

Crystal Structure of AuAl₂

AuAl₂ is a compound of the type RX₂ with the structure of calcium fluoride (CaF₂). The unit cube contains four molecules with atoms in the following positions (space group O_h⁵):

Au: 000; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$.

Al: $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}\frac{3}{4}$; $\frac{3}{4}\frac{1}{4}\frac{3}{4}$; $\frac{3}{4}\frac{3}{4}\frac{1}{4}$; $\frac{3}{4}\frac{3}{4}\frac{3}{4}$; $\frac{1}{4}\frac{1}{4}\frac{3}{4}$; $\frac{1}{4}\frac{3}{4}\frac{1}{4}$; $\frac{3}{4}\frac{1}{4}\frac{1}{4}$.

A projection upon a cube face of the unit cell of the AuAl₂ arrangement. The smaller circles are Au atoms and the larger circles are Al atoms.

A perspective drawing of the unit cube of AuAl₂. Au atoms are darkened and the Al atoms are left blank.

The density of AuAl₂ was theoretically calculated by using $a_0 = 6.00\text{\AA}$ ^{11,12} and CaF₂ structure. In general, the real value (7.61 g/cm³) is found to be lower than the theoretical value (7.73 g/cm³).

LIST OF REFERENCES

1. W.C. Roberts-Austen - Proc. Roy. Soc. 49, 347 (1891); 50, 367 (1892); Phil. Trans. Roy. Soc. 179A, 339 (1888).
2. G. Tammann - Z. anorg. u. allgem. Chem. 107, 115 (1919).
3. H.G. Lipson, E. Burstein, and P.L. Smith - Phys. Rev. 99, 444 (1955).
4. W. Boas - "Dislocations and Mechanical Properties of Crystals." p. 406. (Wiley: New York.)
5. H.R. Philipp, and E.A. Taft - Phys. Rev. 113, 1002 (1959).
6. F.G. Fumi - Phil. Mag. 46, 1007 (1955).
7. M. Cardona, H.S. Sommers - Phys. Rev. 122, 1382 (1961).
8. E.L. Yates - Aust. J. Phys. 16, 40 (1963).
9. H.R. Philipp, W.C. Dash, and H. Ehrenreich - Phys. Rev. 127, 762 (1962).
10. E.L. Yates - Private Communication.
11. C.D. West, and A.W. Peterson - Z. Krist. A88, 93 (1934).
12. E. Zintl, A. Harder, and W. Hauke - Z. Physik. Chem. B335, 354 (1937).