Radiation Damage in Pt Produced by 1.8–3.0-MeV Electrons

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The change in electrical resistivity in Pt, $R(E)=\Delta\rho$/electron cm^2, was measured in the energy range 1.8–3.0 MeV. The experimental values found in this interval are consistent with a displacement threshold of 37 eV, using the Mott equation for relativistically scattered electrons. The resistivity increase per unit integrated flux at 2.0 MeV was found to be 4.6×10^{-26} Ω cm/electron cm^2, which yields 7.5×10^{-4} for ρ_f, the resistivity per unit concentration of Frenkel pairs.

I. INTRODUCTION

ELECTRON bombardment of metals at liquid-helium temperatures can yield information on the effective threshold for atomic displacement, the change in a physical property per unit defect concentration, directional effects of the recoiling atoms, and multiple defect production.

This paper is concerned with the rate of damage production in electron-irradiated platinum at low temperatures. The primary objective of this work was to determine the effective threshold energy for lattice displacement and the resistivity per unit defect concentration.

Specifically, we report here measurements of the change in residual electrical resistivity as a function of bombarding electron energy in the range from 1.8 to 3.0 MeV.[1] All irradiations were done at a temperature of less than 7°K.

A description of the experimental equipment and techniques is given in Sec. II. The experimental results are presented in Sec. III, and a discussion of results in Sec. IV.

II. EXPERIMENTAL

The platinum used in these experiments was obtained from Englehart Industries in the form of polycrystalline foil 0.0004 in. thick. The stated purity before rolling was 99.995%. However, a mass spectrographic analysis of the foil indicated it could contain as much as 0.04% rhodium, and 0.1% carbon. Other impurities were detected but in lesser amounts. The possible effects of impurity atoms causing displacements was investigated by Sherman[2] and found to be entirely negligible for the energies used in this experiment. The foil was cut into strips approximately 0.030 in. wide and 1.5 in. long. The strips were vacuum annealed at 700°C for 4 h prior to mounting.

The sample mount employed is shown in Fig. 1. All parts are machined from beryllium-copper. The main block (B_1) is a single U-shaped piece of copper having an adapter (A) at the bottom of the U for attachment to the cold finger of the Dewar. Small holes (C) are located in the arms of the U to position the potential leads and in the base of the block (D) to hold the foils. The small copper blocks (B_2,B_3) at the ends of the U are electrically insulated from it with a mixture of sapphire granules and GE 7031 calorimeter adhesive baked in place. Potential leads were attached by soldering after the sample and control foils had been soldered into the block. The control foil was shielded from stray electrons with copper plates. The free length of each strip after mounting was 0.6 in. The entire sample mount with foils, was cleaned ultrasonically in a toluene solution. The mount was affixed to the cold finger of the Dewar with Wood's metal.

After mounting the observed resistivity ratio, ($\rho_{293}/\rho_{4.2}$) was found to be 230. The irradiation cryostat has been previously described by the authors.[3]

A Rucibon 6-Dial Thermofree Potentiometer was used to measure the resistance of the sample and control. The current through the specimens was maintained at 0.065 A and monitored with a Leeds and Northrop K-3 potentiometer. Thermal emf's were corrected for by reversing the current. The precision of a typical series of resistivity measurements was $\pm1.1\times10^{-10}$ Ω cm.

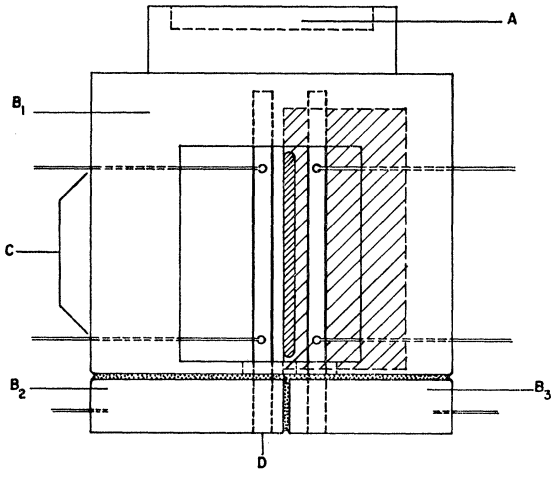

FIG. 1. Sample mount.

[1] A preliminary report on this work was given by the authors in Bull. Am. Phys. Soc. 9, 655 (1964).

[2] C. H. Sherman, Scientific Report No. 5, Contract No. AF19(628)-2419, Parke Mathematical Laboratories, 1965 (unpublished).

[3] L. F. Lowe, C. M. Jimenez, and E. A. Burke, Rev. Sci. Instr. 34, 1348 (1963).

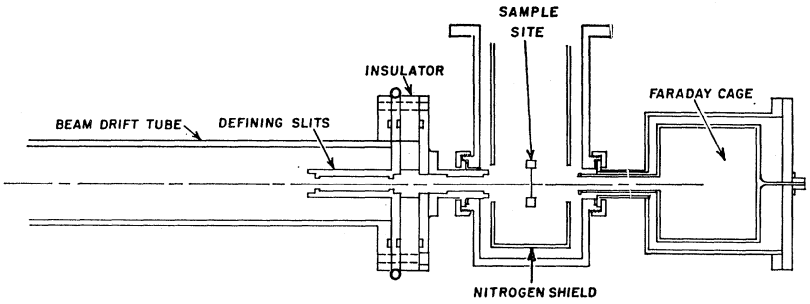

FIG. 2. Final slits, Dewar head and Faraday cup arrangement.

A vertically mounted High Voltage Corp. model KN-3 Van de Graaff was used as the source of electrons. At 3.0 MeV the primary electron-beam spot from the Van de Graaff proved to be too small and nonuniform to use directly. Consequently, after magnetically bending the beam 90°, it was passed through a 0.002-in. aluminum foil, a rough collimating slit and 4.5 feet of drift tube to obtain a spot of reasonable size and uniform intensity. Before entering the irradiation cryostat the beam passed through a defining slit with a 0.1×0.3 in. opening. This was fabricated of 0.04-in.-thick platinum. After passing around and through the sample the electrons were collected in a Faraday cup. The experimental arrangement is shown in Fig. 2.

To ensure beam uniformity a series of defining slits were placed at the entrance to the Faraday cup and the collected current recorded as a function of slit width. No detectable departure from uniformity was observed over the 0.1×0.3-in. opening defined by the entrance slit. The position, uniformity, and cross sectional area of the beam was also checked with polyvinyl chloride film. This was done whenever the irradiation Dewar had been disconnected from the drift tube. Prior to each experimental run the position of the beam was checked with a quadrant positioning slit before bending it through 90°.

The current density at the sample was derived from the known area subtended by the beam at the sample position and readings of total collected current versus total beam current as a function of energy. To correct for electrons scattered away from the collecting cup, calibration runs were made with and without the experimental foil in place. An Eldorado model CI-110 current integrator was used to measure the collected current.

The electron-beam energy prior to and after the series of experimental runs reported here was checked using the Be(γ,n) (1.655 MeV) reaction. These calibrations indicated a voltage variation of less than 0.01 MeV.

The temperature was measured at the point where the irradiated sample was soldered to the small copper block at the bottom of the sample mount. A triple copper-constantan thermocouple was employed in these measurements and referenced to a Rosemount platinum resistance thermometer imbedded in the cold finger of the cryostat. The thermometer was calibrated using the

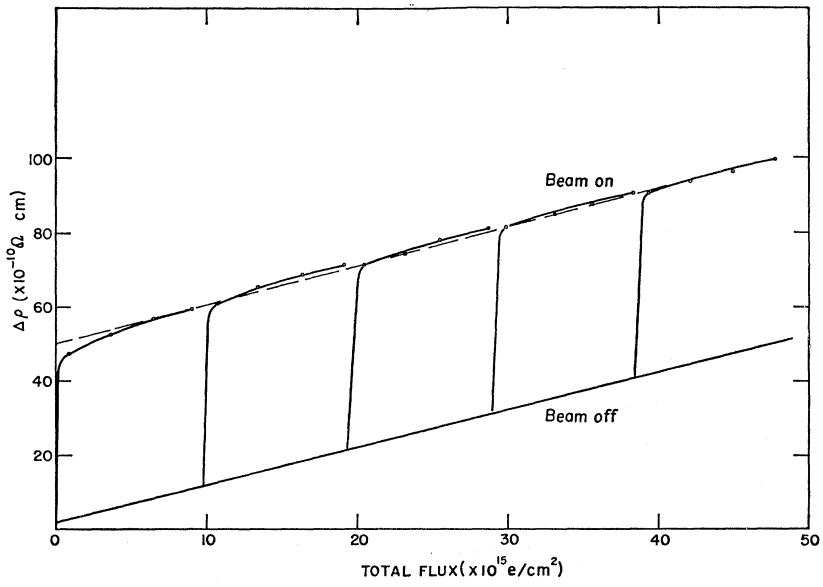

FIG. 3. Effect of beam heating on damage rate.

Corruccini three-point method. For the current densities used in these experiments the maximum temperature at the center of the irradiated sample was estimated to be less than 7°K. This is based upon resistivity measurements with the beam on, together with the temperature indicated by the thermocouples at the base of the irradiated sample.

III. EXPERIMENTAL RESULTS

The damage production rate was determined at each energy both with the beam on and off. The effect of beam heating could be readily observed as shown in Fig. 3. The magnitude of the resistance increase with beam on is consistent with a temperature rise of less than 1.0°K. This estimate takes into account the variation of thermal conductivity with temperature to arrive at a temperature profile for a given beam current. The damage rates for beam on and off measurements are within 8% of one another. The slightly higher damage rates derived from the beam on measurements can be attributed to a decrease in thermal conductivity during bombardment which results in a slight increase in temperature for a fixed beam current. A set of damage-rate determinations is shown in Fig. 4 and in Table I based upon beam-off measurements. The experimental data were corrected for electron energy loss in the aluminum scattering foil and the platinum sample, the increase in average path length due to multiple scattering within the sample, and the surface contribution to the measured resistance.

The effective energy of the beam was determined from the energy distribution at a point half way through the sample. The calculation of the distribution was based upon an extension of Landau's theory[4] to the case of more than one absorbing layer by Parke *et al.*[5] These calculations are approximate since the Landau theory does not include the effects of the angular deviations resulting from scattering. However, it has been shown by Sherman[6] that for thin foils, such as those employed in this experiment, the additional refinement is negligible. The energy correction proved to be 0.03 MeV over the range of electron-beam energies studied in this experiment.

TABLE I. Damage-production-rate data for Pt.

Energy (MeV)	Damage rate $\times 10^{-26}$ [Ω cm/(electron/cm²)]
1.77	2.79±0.005
1.97	4.60±0.210
2.17	6.51±0.193
2.37	7.93±0.078
2.47	8.35±0.158
2.67	9.42±0.292
2.97	10.18±0.021

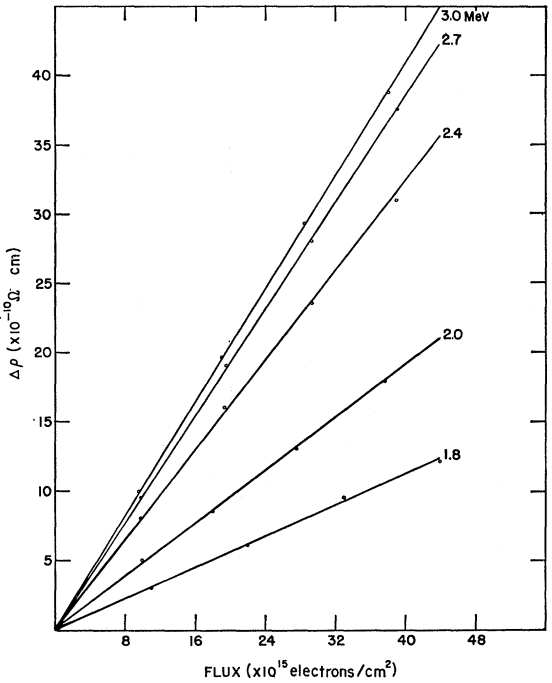

FIG. 4. Resistivity change versus electron flux at various energies.

It is also necessary to correct for the increase in the path length of electrons as they pass through the sample. This has the effect of an increase in the effective flux density with position through the sample. As a result, the damage produced is inhomogeneous and increases as the beam traverses the sample. Previous treatments of the scattering correction[7] have employed Yang's[8] calculation of average path length. However, as pointed out by Sherman[6] the calculation by Rose[9] appears to be in better agreement with the available evidence. This is apparently due to the fact that the Goudsmit-Saunderson theory, upon which Rose's work is based, uses a better small-scattering-angle approximation than the Rossi-Greisen theory which Yang used. Accordingly, Rose's value of average path length was used in the corrections applied here. It is interesting to note that this is roughly equivalent to the values employed by Lucasson and Walker[7] who multiplied Yang's values by $\frac{3}{4}$. Over the energy range employed in these experiments the path-length correction is quite small and is shown combined with the surface correction in Fig. 5.

The surface correction arises from the fact that the samples employed were of a thickness comparable to the mean free path of the conduction electrons. Under these circumstances scattering of electrons from the

[4] L. Landau, J. Phys. (USSR) 8, 201 (1944).
[5] N. G. Parke, W. Williams, and C. H. Sherman, Scientific Report No. 1, Contract No. AF19(628)-2419, Parke Mathematical Laboratories, 1963 (unpublished).
[6] C. H. Sherman, Scientific Report No. 2, Contract No. AF19(628)-2419, Parke Mathematical Laboratories, 1963 (unpublished).
[7] P. G. Lucasson and R. M. Walker, Phys. Rev. **127**, 485 (1962).
[8] C. N. Yang, Phys. Rev. **84**, 599 (1951).
[9] M. E. Rose, Phys. Rev. **58**, 90 (1940).

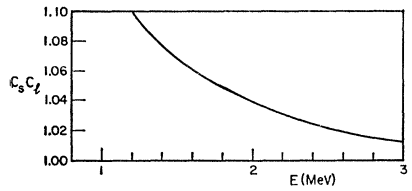

FIG. 5. Path-length and surface-scattering correction.

surfaces results in an increase in the measured resistance. Fortunately, the major part of the surface correction cancels out when we are concerned with changes in resistivity. Sondheimer's theory[10] of the surface effect was employed in these calculations.

The resistivity increase per unit integrated flux as a function of bombarding electron energy is shown in Fig. 6. These results have been derived from damage-rate data as shown in Fig. 4 and include all of the corrections discussed above.

IV. DISCUSSION

In order to derive a value for the effective threshold energy it is necessary to assume that the radiation damage production rates will follow the shape of the Mott-Rutherford (M-R) formula for relativistically scattered electrons in a particular energy range. This energy range must be high enough to avoid directional[11] and subthreshold effects due to dislocations or impurity atoms[12,13] but low enough to avoid complications due to multiple displacements. A computer program for evaluating M-R has been developed at AFCRL[14] which give M-R for any atomic number Z, any energy E, and any angle of scatter θ, where the Rutherford scattering equation does not apply.

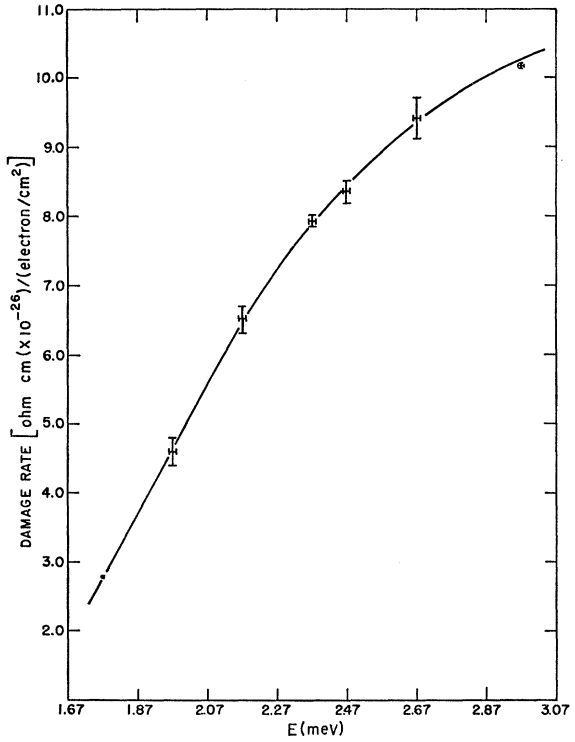

FIG. 6. Damage production as a function of electron energy.

The above assumption may be expressed as follows:

$$R(E,T_d) \propto \int_{\theta_d}^{\pi} P_d(\theta) \frac{d\sigma}{d\Omega}(\theta) \sin\theta \, d\theta, \qquad (1)$$

where $R(E,T_d)$ = rate of damage for electron energy E and threshold T_d, $d\sigma/d\Omega(\theta)$ = differential scattering cross section (M-R), $P_d(\theta)$ = probability displacement function, and θ_d = minimum angle of scatter which can lead to a displacement.

The theoretical curves in Fig. 7 assume that $P_d(\theta)$ is a step function, i.e., all atoms receiving less than an amount of energy T_d are not displaced, and all receiving an energy more than T_d are displaced. As can be seen from Fig. 7 this assumption gives a good fit from 1.8–2.7 MeV for a threshold of 37 eV. This is in good agreement with a value of 36 eV found by Bauer[15] using electrons in the 1.3–2.1-MeV range.

The energy range used in the present work, from 1.8–3.0 MeV, is such that the problem of multiple defects must be considered from roughly 2.5 MeV and up. Using the model of Kinchin-Pease, a calculation has been made[16] of $\bar{\nu}(T)$, the average number of displacements per primary recoil of energy T. This would naturally imply more damage than predicted by M-R in the region above 2.5 MeV. However, the reverse seems to be true as is shown in Fig. 8 where the effect of $\bar{\nu}(T)$ is added to M-R. Although these experiments did not extend very far into the multiple displacement region, the data at 2.7 and 3.0 MeV does indicate a definite drop-off in the increase of damage rate. Possible explanations for this are purely speculative at this time and could be summarized as follows:

(a) "Thermal spike" annealing activated by multiple defect production.

(b) The spatial configuration of the multiple defects might differ enough from that of single defects to yield a lower resistivity per unit concentration of Frenkel pairs (ρ_f).

(c) Systematic experimental errors.

[10] E. H. Sondheimer, Advan. Phys. **1**, 1 (1962).

[11] W. Bauer and A. Sosin, Phys. Rev. **135**, A521 (1964).

[12] K. Kamada, Y. Kazumata, and S. Suda, Japan Atomic Energy Research Institute Memorandum, No. 1639, 1964 (unpublished).

[13] W. Bauer and A. Sosin, J. Appl. Phys. **35**, 703 (1962).

[14] E. A. Burke, N. Grossbard, and L. F. Lowe, Air Force Cambridge Research Laboratories Report No. AFCRL-65-286, 1965 (unpublished).

[15] W. Bauer (private communication).

[16] C. H. Sherman, Parke Mathematical Laboratories TM No. 10, Contract No. AF19(628)-2419, 1964 (unpublished).

The ρ_f from (b) above can be determined by the relationship

$$\Delta\rho = \varphi\sigma_d\rho_f(C_sC_l), \quad (2)$$

where $\Delta\rho$=the experimental change in resistivity, φ=electrons/cm^2, C_s=surface scattering correction, C_l=increased-path-length correction.

Using the data at 1.97 MeV in these experiments leads to a value of $\rho_f = 7.5\times10^{-4}$. (The values of ρ_f in this paper will be expressed in terms of Ω cm/unit concentration of Frenkel pairs.) This compares to 6.0×10^{-4} found by Bauer.[15] The difference can be attributed to the different thresholds reported. If, as suggested by Walker[7] we estimate ρ_f based on the room-temperature resistivities of Pt and Cu, and using the experimentally

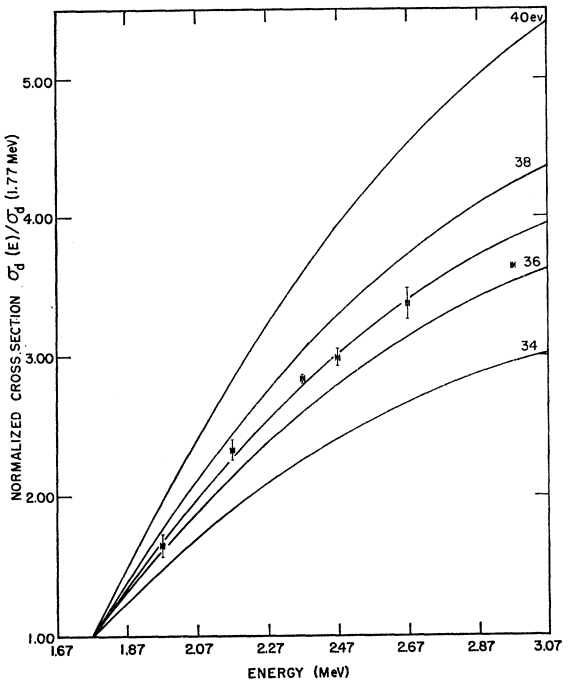

FIG. 7. Experimental data normalized to 1.77 MeV compared to theoretical cross-section curves.

determined value of ρ_f in Cu,[7] we get a value of 7.7×10^{-4} for ρ_f. This agreement indicates that directional effects are about the same in Pt and Cu.

Our data were normalized at 1.77 MeV instead of 2.97 MeV because of multiple defect production at the higher energy. Normalization must be done in a region where there is some knowledge on the shape of the cross section-versus-energy curve. This is true at 1.77 MeV but not at 2.97 MeV.

An alternate method of analyzing damage rate data employed by Bauer and Sosin[11] is shown in Fig. 9. In this case, a value of ρ_f is selected so as to give the best

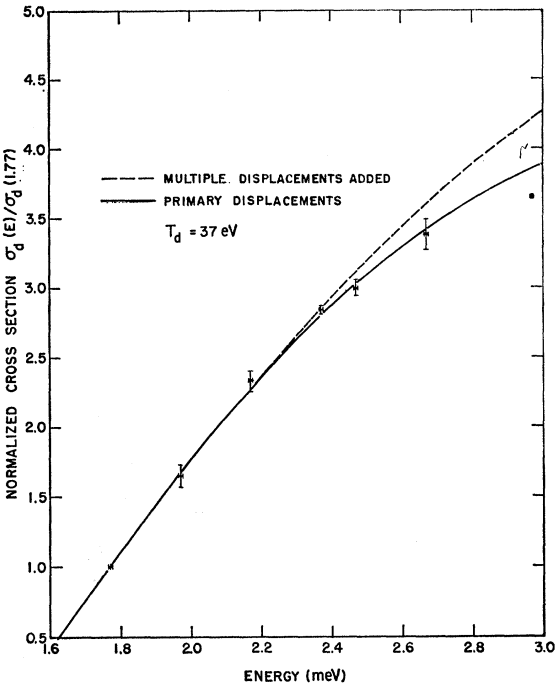

FIG. 8. The effect of multiple defects on the damage production rate at T_d=37 eV.

fit to the theoretical curves expressed in barns. As can be seen from the figure a threshold of 37 eV still yields the best fit.

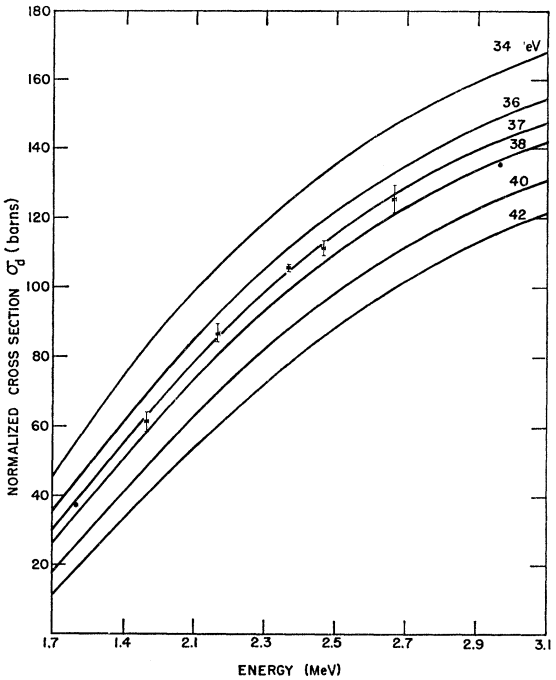

FIG. 9. Experimental data compared with theoretical cross-section curves for $\rho_f = 7.5\times10^{-4}$.

V. SUMMARY

As a result of irradiating Pt at 7°K with electrons in the 1.8–3.0-MeV energy range the following was obtained:

1. An effective threshold for atomic displacements in Pt was found to be 37 eV.
2. The change in electrical resistivity per unit concentration of Frenkel defects, ρ_f, turned out to be 7.5×10^{-4} Ω cm.
3. The damage rate at 3.0 MeV was less than predicted by theory for reasons as yet not understood.
4. A step function for atomic displacements fits the data quite well in the single displacement region (1.8–2.4 MeV).
5. Directional effects appear to have a small role in the displacement process in Pt.

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Low-Temperature Specific Heats of Alloys Based on the Noble Metals, Cu, Ag, Au: ζ-Phase Ag-Sn Alloys*

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Heat-capacity measurements have been made between 1.6 and 4.2°K on a series of Ag-Sn hcp ζ-phase alloys. It is inferred from the results that the density of states at the Fermi surface in this alloy phase is higher than in the preceding α-phase solid solution, and that it has a maximum at about 1.53 electrons per atom. A possible explanation of the data is presented in terms of interactions between the Fermi surface and the Brillouin zone.

INTRODUCTION

RECENT interest in the electronic structure of alloys of the noble metals follows from the determination by means of a number of new techniques of the topography of the Fermi surface in copper, silver, and gold.[1] In all three cases the existence of contact between the Fermi surface and the centers of the hexagonal {111} faces of the Brillouin zone has been demonstrated. In terms of simple models of the band structure,[2] this suggests that the density of states at the Fermi level should decrease initially when the noble metals are alloyed with elements whose addition increases the electron concentration. Since the measurement of electronic specific heat yields a direct measure of the density of states at the Fermi level, this technique has been employed in a number of recent investigations to probe the band structure of the α phases, i.e., the terminal solid solutions of the noble metals. The published results for a number of systems based on copper and silver[3–9] indicate relatively small changes in the density of states on alloying; and a number of interpretations have been suggested to account for the observed trends.[3,4,6,7]

The intermediate phases that follow the terminal solutions are sometimes known as electron phases, and they have either cubic or hexagonal structures.[10] Two such phases have recently been explored in the Cu-Zn system in which the measurement of the electronic specific heat has been reported for the *bcc* β phase[11] and for the complex cubic γ phase.[12] In the present investigation the data on four alloys falling in the phase range of the *hcp* ζ phase in the Ag-Sn system is reported.

EXPERIMENTAL DETAILS AND RESULTS

The apparatus used was a helium-4 cryostat employing a mechanical heat switch. The technique has been described previously.[4] The samples were made from high-purity silver and tin and the sample preparation procedure was the same as that adopted for the α-phase silver-tin[6] alloys with the following modification: since the annealed ζ-phase alloys have poor machining properties, test specimens of required dimensions (0.937 in. in diameter and approximately 2 in. long) were cut directly from the chill-cast ingots. Subsequently,

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[1] See, for example, *The Fermi Surface*, edited by W. H. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960).
[2] J. M. Ziman, Advan. Phys. **10**, 1 (1961).
[3] B. W. Veal and J. A. Rayne, Phys. Rev. **130**, 2156 (1963).
[4] L. L. Isaacs and T. B. Massalski, Phys. Rev. **138**, A134 (1965).
[5] J. A. Rayne, Phys. Rev. **110**, 606 (1958).
[6] T. B. Massalski and L. L. Isaacs, Phys. Rev. **138**, A139 (1965).
[7] B. A. Green, Jr., and H. V. Culbert, Phys. Rev. **137**, 1168 (1965).
[8] H. Montgomery and G. P. Pells, in Conference on The Electronic Structure of Alloys, University of Sheffield, 1963 (unpublished).
[9] J. A. Birch and G. K. White (private communication).
[10] See, for example, T. B. Massalski and H. W. King, Progr. Mater. Sci. **10**, 1 (1961).
[11] B. W. Veal and J. A. Rayne, Phys. Rev. **128**, 551 (1962).
[12] B. W. Veal and J. A. Rayne, Phys. Rev. **132**, 1617 (1963).