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SURFACE DEBYE TEMPERATURES OF THE (100), (111), AND (110) FACES OF PLATINUM

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Surface Debye Temperatures of the (100), (111), and (110) Faces of Platinum.

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ABSTRACT

The intensity of back-diffracted low energy electrons (15-400 ev) from the clean (100), (111), and (110) surfaces of platinum single crystals was measured. From the temperature dependence of the (00)-reflection in the range of 25-700°C, the Debye-Waller factor and the mean displacements of surface atoms perpendicular to the surface planes were determined. The measured mean displacement, $\bar{u}_z$, was found to be a sensitive function of electron energy. The properties of the surface planes were determined from the intensity data taken at the lowest electron energy. Using the Debye model in the high temperature approximation, the Debye temperatures, the frequencies of lattice vibration, and the surface heat capacities were calculated. The mean displacement of surface platinum atoms perpendicular to the surface plane is about twice as great as that in the bulk. This effect gives rise to surface Debye temperatures which are much smaller (107-108°K) than the bulk value (234°K), and greater surface heat capacities.

Creation of a surface by cleaving an infinite crystal parallel to one of its planes, can greatly effect the properties of the solid near the surface plane. Such perturbation of the lattice periodicity gives rise to electronic surface states[1,2] and space charge effects.[3] Changes in the arrangements of surface atoms[4,5] as a function of temperature and changes in the lattice constants[6,7] were found to occur with respect to the bulk of the solid which decreases in magnitude as a function of distance perpendicular to the surface plane.[8] Thus, the phonon excitation spectrum of atoms at the surface is different from that in the unperturbed bulk. Giauque and Archibald[9] have found that the heat capacity of small crystallites of MgO with large surface area is greater than that of large single crystals. It is expected that the thermodynamic parameters of the solid at the surface and, in general, all properties which are a function of the phonon excitation spectrum would be different from that of the bulk of the solid.

Low energy electron scattering and diffraction (Leed) proves to be a powerful tool to study the structure of solid surfaces and many parameters which can describe the dynamics of the crystal lattice at the surface. It has been shown by Farnsworth[10,11] that electrons in the 5-300 ev range do not penetrate appreciably beyond the first two to three atomic layers at metal surfaces. Germer and MacRae[12] have measured the Debye-Waller factor at the (110) face of a nickel single crystal using low energy electrons and have found a Debye temperature,

θ_z, which was appreciably lower than the corresponding bulk value. MacRae[13] has found differences between the in-plane and out-of-plane vibrations, using Leed.

In this paper we report on the studies of the Debye-Waller factor of the clean platinum (100), (110), and (111) surfaces using low energy electron diffraction. For all crystal faces the measurements were carried out at high temperatures ($T > \theta_z$) and were so designed that atomic displacements which are perpendicular to the corresponding surface plane contributed only to the measured Debye-Waller factor. In order to obtain accurate data on the properties of the surface atoms, the Debye temperatures were determined as a function of electron energy.

THEORY

When the crystal lattice is thermally excited, its atoms are displaced from their equilibrium position. The position of each atom, which behaves as a scattering center for the impinging electrons is given by[14]

$$\underset{\sim}{r}(t) = \underset{\sim}{r} + \underset{\sim}{u}(t) \qquad (1)$$

where $\underset{\sim}{r}$ is the equilibrium position of the scattering center and $\underset{\sim}{u}(t)$ is the displacement vector. The intensity of elastically scattered electrons, $I_{\underset{\sim}{k}}$, in the direction of the vector, $\underset{\sim}{k}$, is given by:[15]

$$I_{\underset{\sim}{k}} = \left| \sum_{\ell,\ell'} \left\{ \exp i \frac{2\pi}{\lambda} (\underset{\sim}{k}-\underset{\sim}{k}_o)\cdot[\underset{\sim}{r}_\ell-\underset{\sim}{r}_{\ell'}] + i \frac{2\pi}{\lambda} (\underset{\sim}{k}-\underset{\sim}{k}_o)\cdot[\underset{\sim}{u}_\ell-\underset{\sim}{u}_{\ell'}] \right\} \right|^2 \qquad (2)$$

where the summation is over all pairs of scattering centers, ℓ, ℓ',

λ is the electron wavelength, $\underset{\sim}{k}_o = (2\pi/\lambda)\underset{\sim}{s}_o$ and $\underset{\sim}{k} = (2\pi/\lambda)\underset{\sim}{s}$ fare vectors in the direction of the incident and scattered electron beam, $\underset{\sim}{s}_o$ and $\underset{\sim}{s}$ are the unit vectors in the directions of $\underset{\sim}{k}_o$ and $\underset{\sim}{k}$, respectively. Equation (2) may be expressed in more familiar terms as:

$$I_{hk\ell} = |F_{hk\ell}|^2 \left| \sum_{\ell,\ell'} \exp\{i \tfrac{2\pi}{\lambda}(\underset{\sim}{k}-\underset{\sim}{k}_o)\cdot[\underset{\sim}{u}_\ell-\underset{\sim}{u}_{\ell'}]\} \right|^2 \qquad (3)$$

The term $|F_{hk\ell}|^2$ gives the scattered intensity from a stationary lattice in a particular direction (h,k,ℓ). The remaining exponential term arises from scattering due to lattice vibrations.

The displacement vector, $\underset{\sim}{u}(t)$ could be expressed in terms of the cartesion coordinates. It is more useful, however, to express this vector in terms of normal mode coordinates,

$$\underset{\sim}{u}_\ell(t) = \sum_{j,q} \underset{\sim}{u}_{qj} \cos(\omega_{qj}t-\underset{\sim}{q}\cdot\underset{\sim}{r}_\ell-\psi) \qquad (4)$$

where the summation is over all lattice modes, q, and polarizations, j. The phonon has a frequency, ω_{qj}, a wave vector, $\underset{\sim}{q}$, and an arbitrary phase angle, ψ. Substitution of (4) into (3) and averaging over time gives the mean intensity,

$$I_{hk\ell} = |F_{hk\ell}|^2 \exp\langle \sum_{j,q} (\tfrac{2\pi}{\lambda})^2 \overline{[(\underset{\sim}{k}-\underset{\sim}{k}_o)\cdot\underset{\sim}{u}_{qj}]^2}\{1-\cos[\underset{\sim}{q}(\underset{\sim}{r}_\ell-\underset{\sim}{r}_{\ell'})]\}\rangle \qquad (5)$$

The exponential part can thus be broken up into a term which gives rise to the Debye-Waller[16] factor while further analysis of the $\cos[\underset{\sim}{q}(\underset{\sim}{r}_\ell-\underset{\sim}{r}_{\ell'})]$ term leads one to the properties of thermal diffuse scattering. In this work we measure the total

intensity of the diffraction maxima and separately, the intensity due to the thermal diffuse scattered background. Thus, we can determine the scattered intensity due to the Debye-Waller factor by subtracting the background intensity from the total intensity.

If we disregard the thermal diffuse term in Eq. (5) and define the scattering angle, 2ϕ, as the angle between the vectors, $-\underset{\sim}{k}_o$ and $\underset{\sim}{k}$, then $|\underset{\sim}{k}-\underset{\sim}{k}_o| = |(4\pi/\lambda)\cos\phi|$ and Eq. (5) can further be simplified[17] to give

$$I = |F_{hk\ell}|^2 \exp\left(\frac{-16\pi^2\cos^2\phi}{\lambda^2} \sum_j \sum_q \underset{\sim}{u}^2_{qj\Delta k}\right) \qquad (6)$$

where $\underset{\sim}{u}_{qj\Delta k}$ is the displacement component of $\underset{\sim}{u}_{qj}$ in the direction of $(\underset{\sim}{k}-\underset{\sim}{k}_o)$.

From the equations thus far developed one can see that only those components of lattice displacements will affect the scattered intensity which are parallel to the scattering vector, $(\underset{\sim}{k}-\underset{\sim}{k}_o)$. Figure 1 shows that in the case of the specular reflection (00-reflection) only, the scattering vector, $(\underset{\sim}{k}-\underset{\sim}{k}_o)$, is perpendicular to the surface plane. Therefore, the intensity of the (00)-reflection will be a function of only that component of lattice vibration which is perpendicular to the surface. Higher order diffraction maxima will be a function of a mixture of "in-plane" and "out-of-plane" components of lattice vibrations.

Using the Debye model to describe the phonon excitation spectrum in the high temperature limit, we obtain for the mean square displacement

$$\langle\bar{u}\rangle^2 = \frac{3N\hbar^2}{Mk}\,\frac{T}{(\theta^\infty)^2} \tag{7}$$

where θ^∞ is the Debye temperature, M is the atomic weight and T is the temperature of the vibrating solid, k and $\hbar$ are the Bolzman and Planck constants, respectively, and N is Avogadro's number. Substitution of Eq. (7) into (6) gives

$$I_{hk\ell} = |F_{hj\ell}|^2\, e^{-2W} \tag{8}$$

where the Debye-Waller factor, exp(-2W) is given by

$$\exp(-2W) = \exp\left[-\frac{12N\hbar^2}{Mk}\left(\frac{\cos\phi}{\lambda}\right)^2 \frac{T}{(\theta^\infty)^2}\right] \tag{9}$$

For a given electron wavelength and scattering angle, a plot of the logarithm of the scattered intensity as a function of temperature, T, should yield a straight line. From the slope, in the high temperature limit ($T > \theta^\infty$), we obtain the mean displacement of atoms in the surface and the surface Debye temperature. From the intensity change of the (00)-reflection the mean displacement, $\bar{u}_z$, in the direction perpendicular to the surface plane is obtained with the corresponding surface Debye temperature, θ_z^∞. The Debye frequencies, $\bar{\nu}_z$ can also be evaluated from the relationship, $\bar{\nu}_z = k\theta_z^\infty/h$.

EXPERIMENTAL

The low energy electron diffraction system by Varian was used in the measurements. The measurements were made in the temperature range 25-700°C. The platinum single crystals

of highest purity* were x-ray oriented to less than 1°, were

*The platinum single crystals were obtained from Materials Research Corporation.

cut, polished, and etched. The samples (6 mm diameter, ~1 mm thick disk) were spot welded to the tantalum strip holder which also served to heat the crystal. A thermocouple was attached to the back face of the crystal which was used to determine the temperature of the specimen. The crystals were ion bombarded (ultra-high purity xenon and argon) and annealed until a sharp diffraction pattern of the substrate unit mesh was obtained. The presence of stable surface structures on clean platinum surfaces which form above and below 700°C was reported.[5] Care was taken in all of the experiments to avoid the formation of these surface structures during the intensity measurements. It was found that the presence of these stable surface structures could alter the intensity of the reflections from the substrate unit mesh. The reproducibility of the intensity measurements can also be improved by using crystals which were annealed thoroughly and showed sharp diffraction features. The ambient pressure was in the range of $2\text{-}5\times10^{-10}$ torr for all the measurements. The specimens were heated by A.C. or D.C. current applied across the tantalum holders.

In the experiments which are reported in this paper the intensity of the specularly reflected electron beam, i.e., the (00)-reflection was measured as a function of temperature. These studies were carried out two ways: (a) by a transient method and (b) steady state measurements. The first method consisted of heating the crystal to 700°C and then turning off the heating current. The intensity of the (00)-reflection was measured as a function of temperature while the crystal was cooling to room temperature. The output of a small angle spot-photometer which was used to monitor the intensity of the (00)-reflection, and the thermocouple e.m.f. was displayed continuously on an x-y recorder. With this technique we could avoid inaccuracies in the measurements which are due to the interaction of the electron beam with the electric field applied to the crystal for heating purposes. Studies using several thermocouples indicated that the temperature is uniform throughout the specimen within ±5°. The heating current has affected the measurements at only low electron beam energies ($E < 50$ ev).

The second technique used regulated d.c. heating to reach the desired temperature steady state in the range 25-550°C. The intensity of the (00) reflection was measured with a spot photometer. The results obtained by these different techniques using a given electron beam energy were the same within the accuracy of the measurements.

Three platinum single crystal samples of each orientation were used in the experiments. The measurements were made using

15-350 ev electrons. The particular beam voltage which was preferred for our studies, was chosen, in general, at an intensity maxima of the (00)-reflection.

The intensity of the fluorescent screen background was also monitored at different distances from the (00)-reflection.

RESULTS

A typical trace of the intensity of the (00)-reflection as a function of temperature, as obtained by the transient method, is shown in Fig. II. The decrease of the intensity of the reflected electron beam of well-defined energy with increasing temperature, is clearly displayed. The lower curve in Fig. I shows the background intensity as a function of temperature. We have found no detectable temperature dependence in the total intensity of elastically scattered electrons at different electron beam energies within the energy resolution of our electron beam (± 0.2 ev). In order to obtain accurate data for the intensity of the (00)-reflection as a function of temperature, the background intensity has been subtracted.

A typical plot of the logarithm of the intensity as a function of temperature for a given electron beam energy, is shown in Fig. 3. We obtain a straight line of different slope than that which was computed from the known Debye temperature of bulk platinum ($\theta = 234 \pm 6°K$). There is no detectable curvature to the slope.

We have found that for all three faces of the platinum single crystals the slopes obtained from the log I vs. T curves were strongly dependent on the electron beam energy. For even such a high electron density matrix as platinum a certain fraction of electrons will penetrate beyond the first layer of atoms at the surface.[10] This fraction should increase with increasing electron energy. Calculations predicting lattice expansion at the surface of face-centered cubic crystals[18] indicate that the mean square amplitude of atoms is larger in the surface layer but approaches the bulk value rapidly. Since the measured mean square displacement using low energy electrons is an average over those atoms which contribute to the scattering, the effect of atoms below the surface plane could be appreciable even at relatively low electron energies. Therefore, the observed Debye-Waller factor and the calculated mean displacement are not the property of the surface layer itself but have strongly been affected by the motion of atoms in the underlying planes.

In order to obtain accurate surface Debye temperatures the measurements should be carried out as a function of electron energies and may be extrapolated to zero electron energy. The results of these measurements on the (100), (110), and (111)-faces of clean platinum surfaces are shown in Fig. 4. Here, we have plotted the Debye temperatures, θ_z^∞ as a function of electron energy. These Debye temperatures were obtained from the slope of the ln I vs. T plots at a given energy. θ_z^∞ was calculated using Eq. (9). At high electron energies the

curves approach the bulk value $\theta_{bulk} = 234 \pm 6°K$. This value for platinum was determined from Mossbauer experiments by Harris et al.,[19] and it agrees well with the theoretical prediction for θ^{∞}_{bulk} of Feldman and Horton.[20] At low electron beam energies the curves drop sharply. The lowest electron beam energy at which data was taken with the techniques presently employed was E = 15 ev.

The experimental points were taken at the intensity maxima of the (00) reflection and are the averages of 6-15 determinations by the two different methods described in the previous section. If we assume that the experimental values of θ^{∞}_{z} determined at the lowest electron beam energy employed in our experiment (E = 15 ev) are the effective surface Debye temperatures, we obtain values for all three surfaces which are listed in Table I. Here, we tabulate, along with θ^{∞}_{z} the values of the surface root mean square amplitudes and frequencies of vibration perpendicular to the surface plane, $\bar{u}_z$, and $\bar{\nu}_z$, and the corresponding bulk values.

DISCUSSION

The amplitude of surface atom vibration perpendicular to the surface plane was found to be much larger than the corresponding bulk value for all three faces of platinum which were studied. The mean displacement at the surface is about 7.6% of the lattice parameter of platinum (a = 3.916 Å) while the mean displacement in the bulk is about 3.8% in the temperature range of interest. This result is in good agreement with the values

predicted by Clark, Herman and Wallis[8] for face-centered cubic crystals. It is expected that atom displacements which are perpendicular to the surface undergo the greatest change with respect to the bulk value. Those components of the mean displacement which are parallel to the surface plane are to be affected to a lesser extent[8] [with the exception of the (001) direction on the (110)-face]. The atoms in the (110) crystal face of platinum show a somewhat larger mean square displacement than the other faces. This surface has the lowest atomic density among the three faces studied. This result is also in good agreement with the calculations of Wallis[8] using central forces and taking into account only nearest neighbor interactions.

Care was taken to avoid the formation of surface structures which were found to exist on the clean platinum surfaces in the different temperature ranges.[5*] The presence of such

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*Surface structures, in addition to those reported[21] have been found to exist on the (111) and (100) faces of platinum by the authors. Analysis of these surface structures will be reported in the near future.

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surface structures, ordered or disordered, could effect the mean displacement of atoms in the surface. Open surface structures, such as the domain structure[5] which were found to exist on the (100)-face of platinum in the temperature range 300-500°C, occupy only a small fraction of available surface sites and

would not exert great influence on the atomic displacement of surface atoms in the substrate unit mesh. However, study of the mean square displacement of atoms in the different surface structures which depends on the number of its nearest neighbors may help to verify the position of those atoms on the surface. Studies of the mean displacement of platinum surface atoms about their equilibrium position in the presence of an absorbed gas and the mean displacement of the absorbed gas atoms on the different platinum surfaces, are in progress.

In the last several years experimental evidence has been accumulating[4-8] which indicates that there exists a surface phase in solids with physical properties which are distinctly different from that of the bulk.[22] This surface phase has lattice parameters and a phonon excitation spectrum which are different from that in the bulk. The surface phase itself may undergo "phase transformations," reversible or irreversible rearrangements, order-disorder transitions at temperatures which cause no such effects in the bulk.[23] In short, physical-chemical properties which are a function of lattice dynamics, thermodynamic or kinetic in nature, may be different in the surface phase from that in the bulk phase. The presence of surface plasmons with characteristic frequencies which are markedly different from that of the bulk plasma oscillations, was reported recently.[24] The observation that electron-electron interactions are different in the surface makes it likely that physical properties which are a function of electron-phonon interactions, such as thermal and electrical conductivity may also be different in the surface phase.

It would be useful to determine the thermodynamic parameters, such as surface heat capacity, compressibility, surface entropy and surface free energy, etc. of such surface phase in order to characterize its equilibrium or thermal properties. The determination of the surface Debye temperature from studies of low energy electron scattering allows one to calculate these quantities within the constraints of the harmonic approximation. θ_z^∞, as determined by the Debye-Waller factor measurements, is temperature sensitive to a lesser extent than the Debye temperature, $\theta_c(T)$ as determined by heat capacity measurements.[25] Although the two measurements yield Debye temperatures which reflect different averages over the true phonon spectrum, $\theta_c(T)$ can, in general, be evaluated from θ_z^∞.[25,26]

In order to calculate the surface heat capacity of platinum from our data one needs to know, in addition to $\bar{u}_z$, the other components of the mean atomic displacement which are due to lattice vibrations parallel to the surface plane. These have not yet been determined by experiments. Clark et al.,[8] have calculated however, the mean square displacements of surface atoms in a face-centered cubic lattice both parallel and perpendicular to the (100), (111), and (110) surfaces. Since there is a good agreement between our experimental values of $\bar{u}_z$ and the theoretical results obtained by Clark, Herman and Wallis,[8] we have used our values of $\bar{u}_z$, and their calculated values for $\bar{u}_x$ and $\bar{u}_y$ to evaluate the respective Debye temperatures θ_z^∞, θ_x^∞, and θ_y^∞. Thus, the surface heat capacity, C_v,

using the Debye model, is given by

$$\overline{C}_v = C_v(z) + C_v(x) + C_v(y) = Rf(D)\left[\left(\frac{T}{\theta_z^\infty}\right)^3 + \left(\frac{T}{\theta_x^\infty}\right)^3 + \left(\frac{T}{\theta_y^\theta}\right)^3\right] \quad (15)$$

f(D) is the Debye function,[27] θ_x^∞ and θ_y^∞ are the Debye temperatures calculated from the atomic displacement parallel to the lattice plane in x and y directions, respectively. For the (100) and (111) crystal faces $\overline{u}_x = \overline{u}_y$. The (110) face shows anisotropy ($\overline{u}_x \neq \overline{u}_y$) which has been taken into account.

The surface heat capacity of the clean (100) face of platinum is given in Fig. 5 as a function of temperature along with the bulk heat capacity. The data is plotted for the temperature range $T \geq \theta_z^\infty$ at which appreciable temperature dependence of θ_z^∞ is not expected. The larger surface heat capacity is clearly displayed.

In order to characterize the surface phase it is of primary importance to determine by experiments (a) the extent of the surface, i.e., how far the effect of the presence of a surface extends into the bulk of the crystal; and (b) how rapidly the bulk properties are approached. Theoretical predictions of (a) and (b) have been made for face-centered cubic crystals[8,18] and calculations are also available for molecular[28] and ionic[29] crystals. The strong electron beam energy dependence of θ_z^∞, as shown in Fig. 4 for all three faces of platinum, indicates that the mean displacement, $\overline{u}_z$, rapidly approaches the bulk value within a few atomic layers below the surface. Comparison of such θ_z^∞ vs. E curves for different solids of similar crystal

structure but different electron density and binding energy, should give quantitative information as to how rapidly the bulk properties of the solids are approached.

The mean displacements, $\bar{u}_z$, and other parameters which describe surface atom vibrations reported in this paper, were obtained within the framework of the harmonic approximation. Anharmonic effects such as thermal expansion may play an important role in our high temperature measurements. There is an appreciable volume change for platinum in the temperature range of our measurements (the linear expansion coefficient $\alpha \simeq 9.0 \times 10^{-6}$ deg^{-1}). Fortunately, the Debye-Waller factor for an harmonic crystal can still be represented by Eq. (8) to a very good approximation.[30] This may be the reason why the experimental data in the temperature range of this study could be represented by a straight line in Fig. 3. The presence of anharmonic effects may increase the mean square displacement by 10-15% for the bulk atoms in face-centered cubic crystals.[8,30] The experimental values in Table I may, therefore, reflect both the harmonic and the anharmonic contributions to the mean displacements of the surface atoms of platinum.

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Table I

	θ_z^∞ (°K)	$\bar{u}_z$ (Å)	$\bar{\nu}_z x10^{-12}$ (sec^{-1})
(100)	118±10	0.30±.04	2.4
(111)	111±10	0.32±.04	2.2
(110)	107±10	0.33±.04	2.1
bulk	234±6	0.15	4.7

Figure Captions

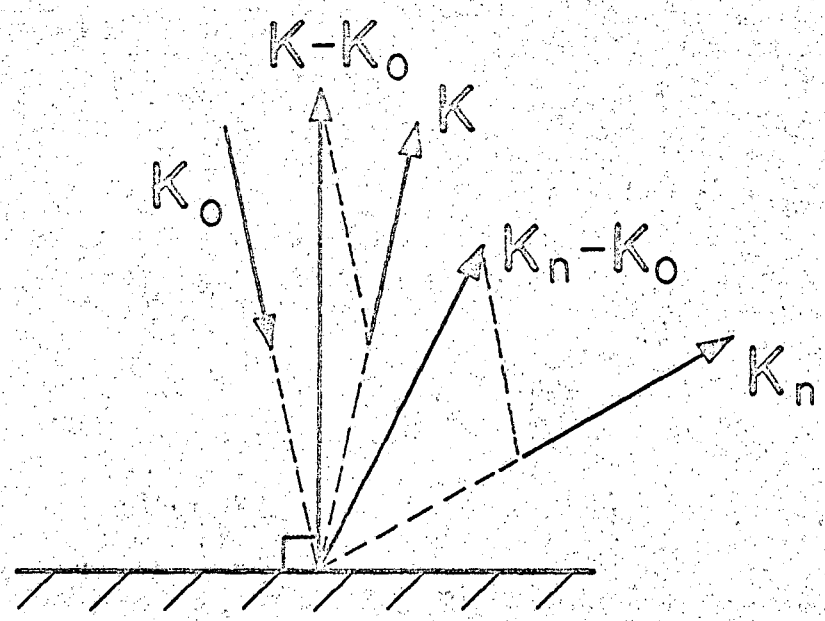
Fig. 1. Vector diagram for elastic scattering of electrons. For the (00) reflection, the scattering vector, $\underset{\sim}{k}-\underset{\sim}{k}_o$, is perpendicular to the surface plane.

Fig. 2. The intensity of the (00) reflection and that of the background scattering from the (111) face of platinum as a function of temperature at a beam voltage of 35 ev.

Fig. 3. Plot of log I vs. T for the data in Fig. II. The dotted line calculated for $\theta_{bulk} = 234°K$ is shown for comparison.

Fig. 4. The effective Debye temperatures of the (100), (111), and (110) faces of platinum as a function of electron energy.

Fig. 5. Plot of the surface and bulk heat capacities of platinum, $C_v/3R$, as calculated from the Debye temperature of the (100) face and from θ^{∞}_{bulk}.



MUB-8766

Fig. 1

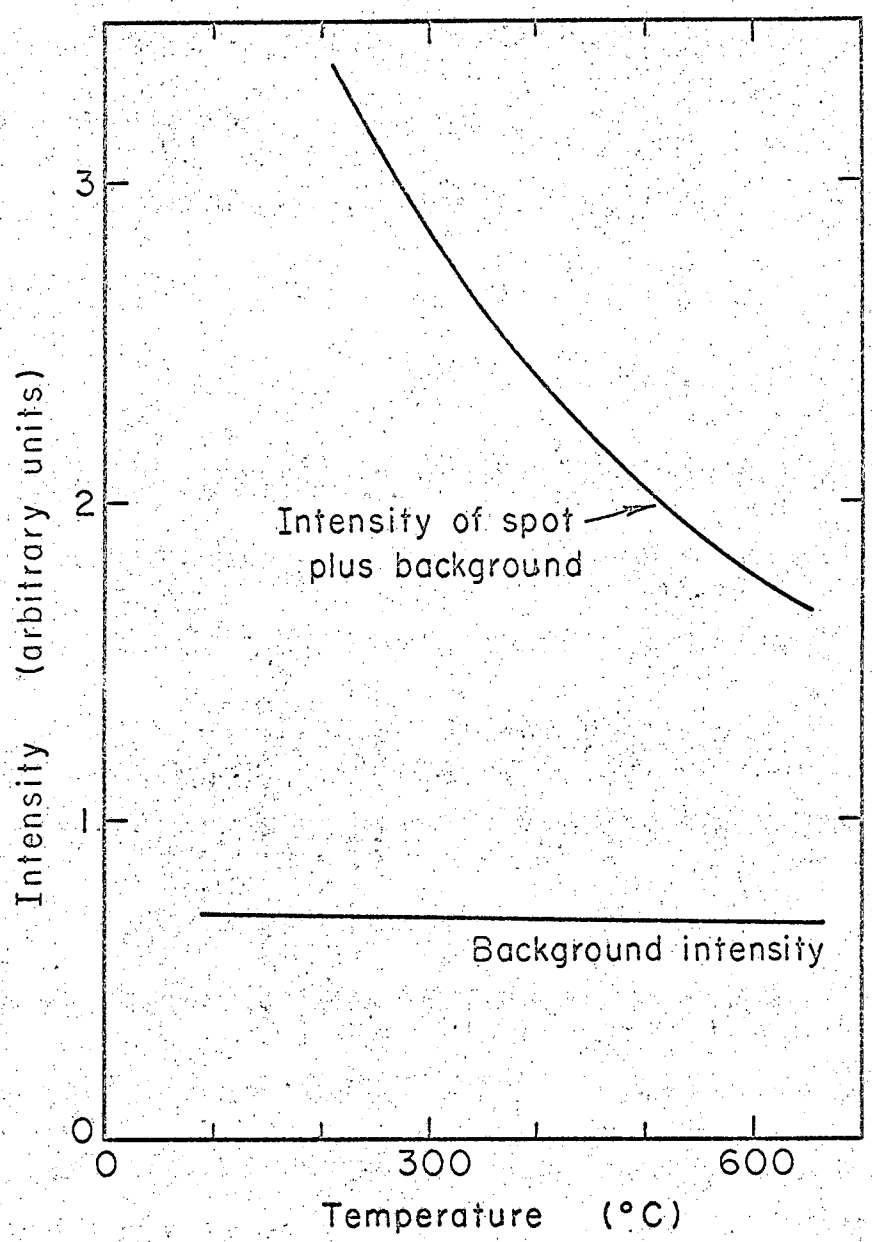


Fig. 2

MUB-8767

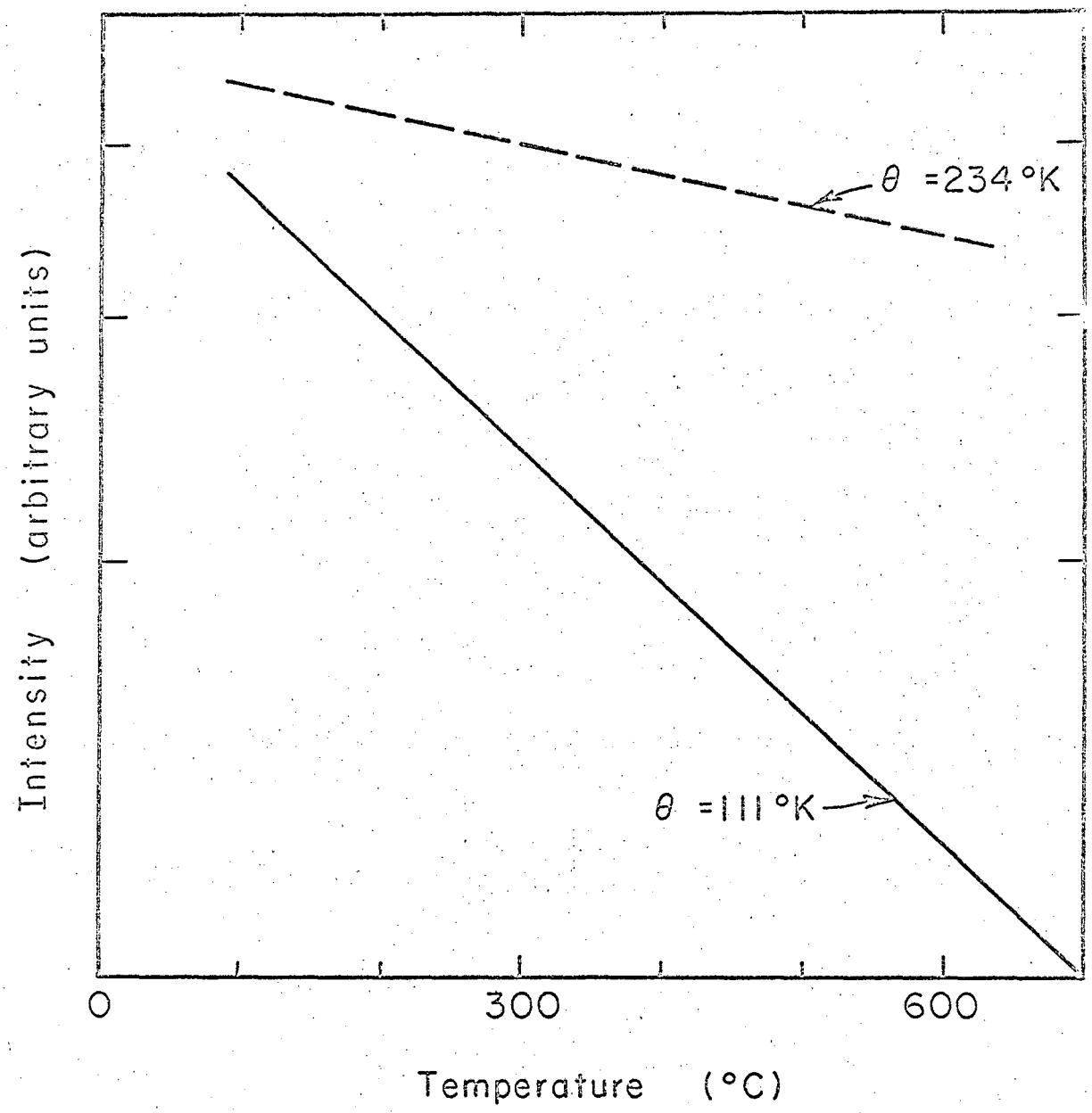
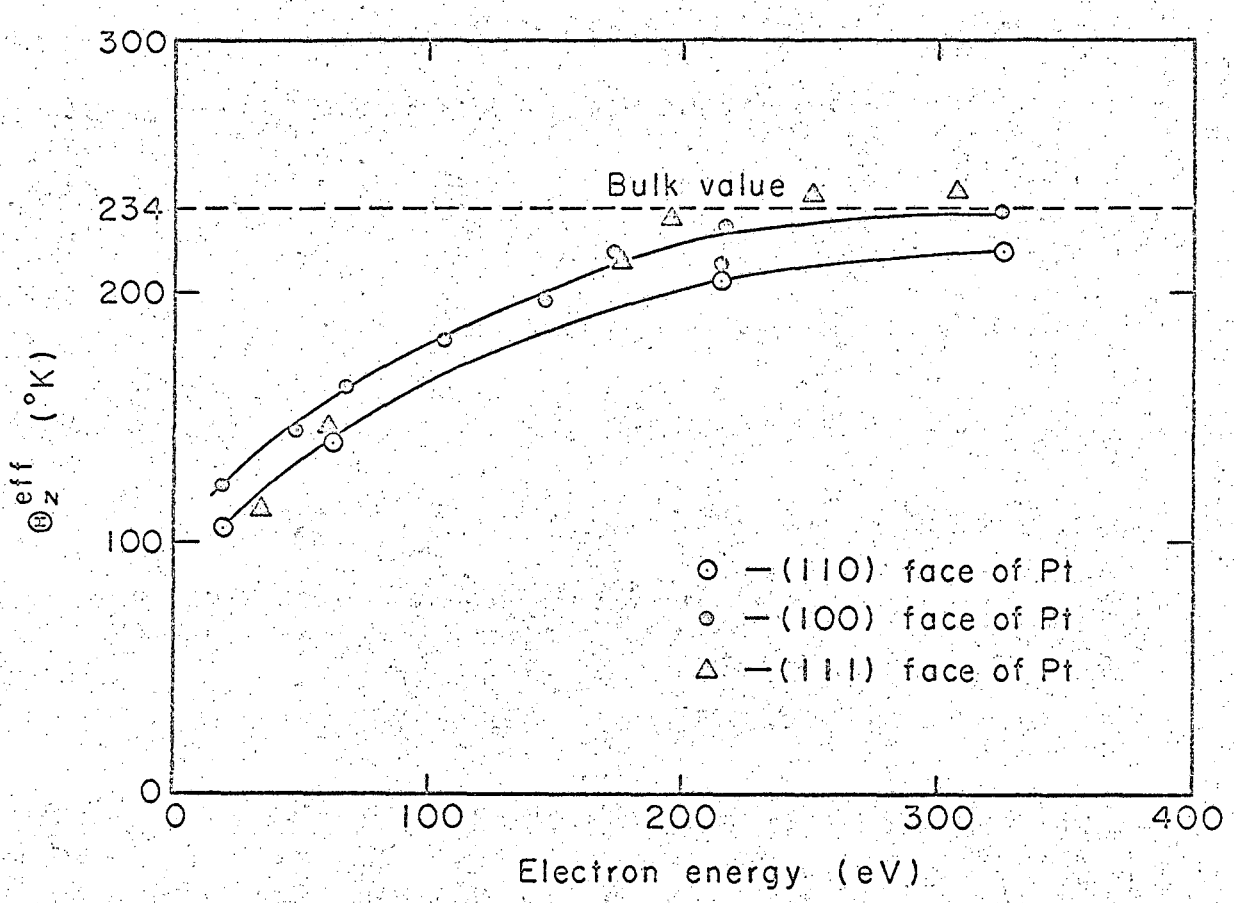


Fig. 3

MUB-8769



MUB-8156

Fig. 4

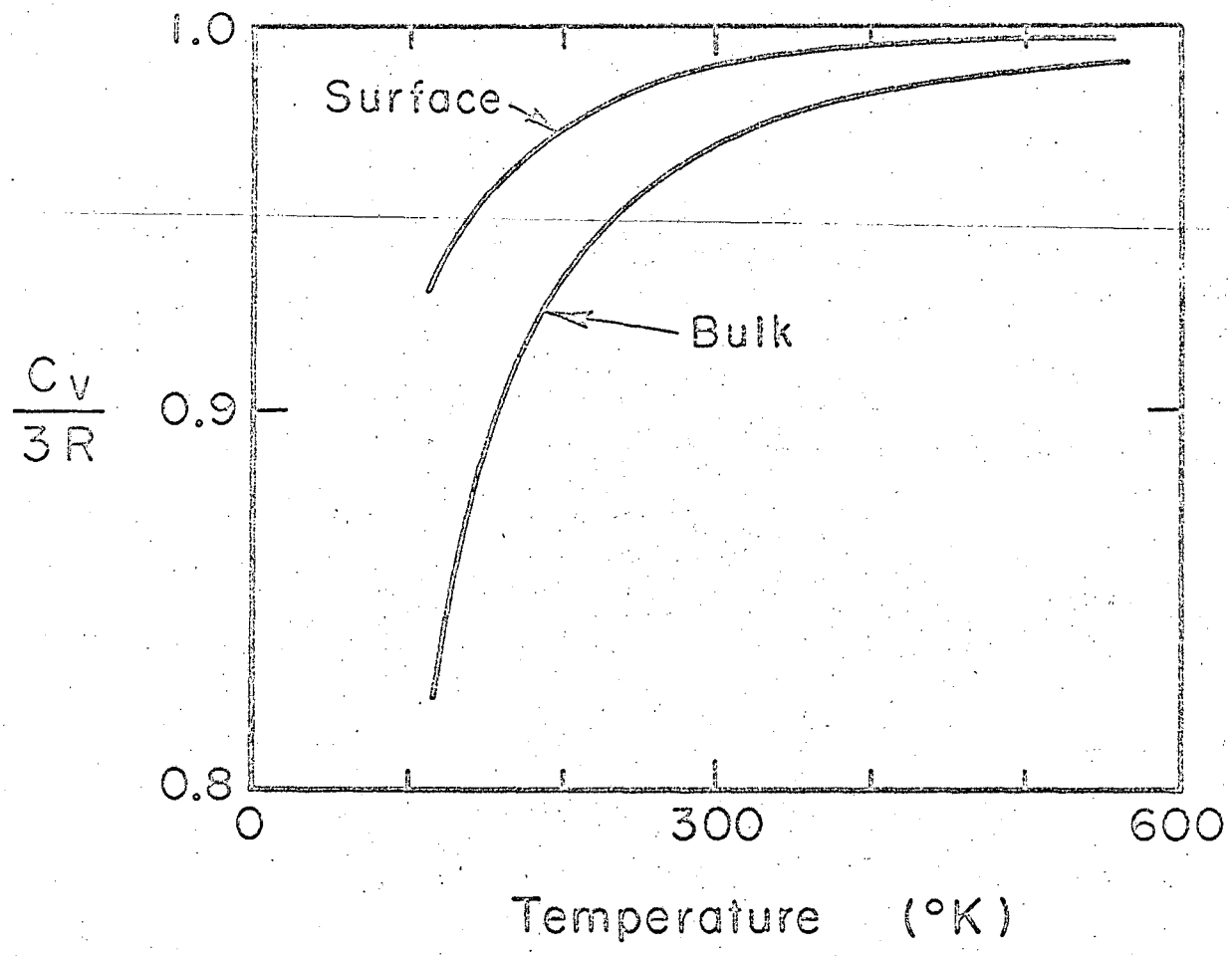


Fig. 5

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