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New Kind of Surface State in Nearly-Free-Electron Metals*

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We show that for a (2,0,0) surface of a bcc crystal there exist not only the Goodwin surface states in the (1,0,0) energy gap but also a new kind of surface state in the $(\frac{1}{2},\frac{1}{2},0)$ energy gap. Although the Goodwin state exists only when V_{200} is negative, these new surface states exist for either sign of V_{110}.

It has been a third of a century since Goodwin[1] showed the existence of surface states on the (ijk) surface of a nearly-free-electron metal. These states have an energy within the $(\frac{1}{2}i, \frac{1}{2}j, \frac{1}{2}k)$ energy gap and exist only if V_{ijk} [i.e., the (ijk) Fourier transform of the crystal potential] is negative. Goodwin used a model in which the potential was identical to the bulk-crystal potential up to the surface plane and zero beyond the surface plane so that negative V_{ijk} means that the surface plane must be chosen to be at the point where $V(\vec{r})$ is a minimum.[2] In this paper we show, using Goodwin's model, that (2, 0, 0) surface states exist in bcc metals in the $(\frac{1}{2}, \frac{1}{2}, 0)$ energy gap and that their existence is independent of the sign of V_{110} and in all likelihood independent of where in the surface unit cell the surface plane is chosen. Although the discontinuous model potential is not very physical, these facts indicate that they should exist in real metal surfaces. A simple generalization of the following derivation shows that this kind of state exists for an (I, J, K) surface if there exists a set of degenerate energy gaps $(\frac{1}{2}i, \frac{1}{2}j, \frac{1}{2}k)$, $(\frac{1}{2}i', \frac{1}{2}j', \frac{1}{2}k')$, etc. such that $(i+i', j+j', k+k') = (I, J, K)$.

Consider the following wave function inside the crystal (i.e., for $x \leq 0$):

$$\psi = e^{iky}(e^{i\pi z/a} + \beta e^{-i\pi z/a})(e^{i(\pi x/a+\varphi)} + e^{-i(\pi x/a+\varphi)})e^{qx}. \tag{1}$$

This is a Bloch function in the (k_y, k_z) plane with $k_y = k$, assumed to be small compared to π/a, and $k_z = \pi/a$. Consideration of the continuity of the two-dimensional energy bands, as well as detailed numerical calculations,[3] shows that if Eq. (1) is a surface state at $(k, \pi/a)$ there will also exist surface states at $(k, \pi/a - \delta)$, where $\delta \ll \pi/a$. However if $\delta \neq 0$, the functional form of the surface state becomes much more complicated than Eq. (1) and our simple derivation cannot be made. The Hamiltonian within the crystal is

$$H = -\nabla^2 + V(\vec{r}), \tag{2}$$

where we take the pseudopotential

$$V(\vec{r}) = V_0 + V_{110}(e^{i\chi}e^{2\pi i(x+z)/a} + e^{-i\chi}e^{-2\pi i(x+z)/a} + e^{i\chi}e^{2\pi i(x-z)/a} + e^{-i\chi}e^{-2\pi i(x-z)/a}). \tag{3}$$

Because the pseudopotential of a nearly-free-electron metal is very weak,[4] we are able to neglect all other Fourier transforms of $V(\vec{r})$ which mix plane waves of much higher kinetic energy into Eq. (1). This is the reason we require $k \ll \pi/a$. The surface plane is taken to be at $x = 0$ but its location with respect to the crystal lattice is determined by χ. Note that in the surface plane, $V(\vec{r}) = V_0 + V_{110} 4\cos\chi \cos 2\pi z/a$. Therefore, we expect our results to be independent of the sign of V_{110} because a change in the sign of V_{110} is equivalent to replacing z by $z + \frac{1}{2}a$ which is of no physical consequence. This differs from the case considered by Goodwin[1] where V_{200} was the important contributor to $V(\vec{r})$; thus $V(\vec{r})$ was a constant in the $x = 0$ plane making the sign of V_{200} of paramount importance.

Inserting (1) into the Schrödinger equation, removing the common factor $e^{iky}e^{qx}$, multiplying through by $e^{\pm i\pi x/a}e^{\pm i\pi z/a}$, and integrating over x and z yield four equations which reduce to the following two if we assume $\beta = \pm 1$:

$$[k^2 + (\pi/a)^2 + (\pi/a - iq)^2 + V_0 - E]e^{i\varphi} + V_{110}\beta e^{-i(\varphi+\chi)} = 0, \tag{4}$$

$$[k^2 + (\pi/a)^2 + (\pi/a + iq)^2 + V_0 - E]e^{-i\varphi}$$

$$+V_{110}\beta e^{i(\varphi+\chi)}=0\ . \qquad (5)$$

Setting the determinant of the coefficients of $e^{i\varphi}$ and $e^{-i\varphi}$ equal to zero we obtain

$$E-V_0=k^2+2(\pi/a)^2-q^2\pm[V_{110}^2-4(\pi/a)^2q^2]^{1/2}. \qquad (6)$$

The wave function outside the crystal ($x>0$) is

$$\psi_0=e^{iky}(e^{i(\pi/a)z}+\beta e^{-i(\pi/a)z})$$
$$\times\exp\{-[k^2+(\pi/a)^2-E]^{1/2}x\}\,, \qquad (7)$$

and applying the boundary condition

$$\psi^{-1}\frac{\partial\chi}{\partial x}\bigg|_{x=0}=\psi_0^{-1}\frac{\partial\psi_0}{\partial x}\bigg|_{x=0}\,, \qquad (8)$$

we obtain

$$-[k^2+(\pi/a)^2-E]^{1/2}=q-(\pi/a)\tan\varphi\ . \qquad (9)$$

At this point we restrict ourselves to $\chi=0$, i.e., the surface plane is chosen to be a plane of maximum potential variation. Adding and subtracting Eqs. (4) and (5) yields

$$\sin 2\varphi=-2q(\pi/a)/\beta V_{110} \qquad (10)$$

and

$$\cos 2\varphi=\pm[V_{110}{}^2-4(\pi/a)^2q^2]^{1/2}/\beta V_{110}\,, \qquad (11)$$

where we have used Eq. (6). Equations (10) and (11) can be combined to give

$$(2\pi/a)q\tan\varphi=-\beta V_{110}\pm[V_{110}{}^2-4(\pi/a)^2q^2]^{1/2}\ . \qquad (12)$$

We note that a solution to Eq. (9) exists only if $\tan\varphi$ is positive but Eq. (12) shows this to be the case if βV_{110} is negative. Since we are free to choose β to be either 1 or -1, we can always make βV_{110} negative and always get a surface state. Squaring Eq. (9) and substituting from Eqs. (6), (10), and (12) we find

$$q=[\beta V_{110}/(V_0+\beta V_{110})][-V_0-\beta V_{110}-(\pi/a)^2]^{1/2}\,, \qquad (13)$$

where V_0 must be sufficiently negative to make the square root real and we have discarded a second solution which is the negative of Eq. (13) because q must be positive. Substitution of Eq. (13) into Eq. (6) yields two values of the energy, one of which fails to satisfy (and arose from squaring) Eq. (9). The remaining value of the energy is

$$E=V_0+k^2+(\pi/a)^2+(\pi/a)^2[V_0/(V_0+\beta V_{110})]^2$$
$$-\beta V_{110}V_0/(V_0+\beta V_{110}). \qquad (14)$$

We may also solve for q, φ, and E in the opposite limit, where $\chi=\frac{1}{2}\pi$, i.e., when the surface plane is chosen to be a plane of zero potential variation. The algebra is much simplified if we take V_{110}/V_0 and $V_{110}/(2\pi/a)\ll 1$, which is always the case for a nearly-free-electron metal. From Eqs. (4) and (5) we obtain

$$\sin^2\varphi=\tfrac{1}{2}+(\pi/a)q/\beta V_{110}\,, \qquad (15)$$

$$\cos^2\varphi=\tfrac{1}{2}-(\pi/a)q/\beta V_{110}\,, \qquad (16)$$

$$\tan\varphi=\left(\frac{\beta V_{110}+2(\pi/a)q}{\beta V_{110}-2(\pi/a)q}\right)^{1/2}\,, \qquad (17)$$

where we have used Eq. (9) to discard the negative square root in (17). Squaring (9) and substituting from (6), (16), and (17) yields

$$2\beta V_{110}(\pi/a)^2+V_0[\beta V_{110}-2(\pi/a)q]$$
$$=\beta V_{110}[V_{110}{}^2-4(\pi/a)^2q^2]^{1/2}\,, \qquad (18)$$

where we have taken the negative square root in (6), the positive square root yielding an equation for q whose solution fails to satisfy (9). The right-hand side of (18) is smaller than the left-hand side by a factor of V_{110}/V_0. Therefore, we solve (18) by iteration to second order in V_{110}/V_0 obtaining

$$q=\frac{\beta V_{110}}{(2\pi/a)}\bigg(1+\frac{2(\pi/a)^2}{V_0}-\frac{(2\pi/a)}{V_0{}^2}$$
$$\times\beta V_{110}[-V_0-(\pi/a)^2]^{1/2}\bigg). \qquad (19)$$

Note that βV_{110} must be positive for q to be positive. We emphasize again that the sign of V_{110} is of no physical importance; had we chosen $\chi=-\frac{1}{2}\pi$ instead of $\frac{1}{2}\pi$, we would have obtained Eq. (19) with βV_{110} replaced by $-\beta V_{110}$. Substituting (19) in (6), we find to first order in V_{110}/V_0:

$$E=V_0+2(\pi/a)^2+k^2-\frac{2\beta V_{110}(\pi/a)}{V_0}$$
$$\times[-V_0-(\pi/a)^2]^{1/2}\ . \qquad (20)$$

Thus we have demonstrated the existence of (2, 0, 0) surface states in the ($\frac{1}{2}$, $\frac{1}{2}$, 0) energy gap of nearly-free-electron bcc metals with a step discontinuity in the potential at the surface plane. The surface states have been shown to exist whether the discontinuity is taken at a point of maximum or zero potential variation in the plane and undoubtedly exist for any intermediate choice. Their existence for more realistic, continuous, surface potentials therefore seems likely and indeed has been demonstrated elsewhere[3] by detailed numerical calculations. If one adjusts the zero of energy in band calculations[5] for Li and Na so that the Fermi energy is equal to minus the work function, one finds that the (1, 0, 0) gap lies in the positive energy range so that Goodwin surface states cannot exist.[6] On the other hand the ($\frac{1}{2}$, $\frac{1}{2}$, 0) gap lies in the negative energy range so the surface states described in this paper should be present. They are of course unoccupied, lying above the Fermi level. They should be observable with high-resolution electron transmission through thin films,[7] with inelastic low-energy-electron diffraction (LEED), and as resonances of elastic LEED.[8]

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Effect of Pressure on Vacancy Concentrations in Platinum[†]

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The excess electrical resistivity quenched into platinum as a function of pressure (up to 6 kbar) and of quench rate has been measured. The activation volume for the formation of vacancies was found to be 6.4 ± 0.7 cm^3/mole (0.70 atomic volume). Preliminary results on fractional vacancy loss during quench as a function of quench rate are consistent with previous conclusions that vacancy clustering is negligible in platinum.

I. INTRODUCTION

The mechanism for the low-temperature recovery of excess electrical resistivity in platinum after a quench from high temperature is much simpler than in the noble metals or aluminum.[1] As a preliminary to studying the loss mechanism during the quench, we have measured the excess electrical resistance quenched into platinum from a fixed high temperature as a function of pressure and of quench rate. Since the basic theory, apparatus, and techniques have been described earlier,[2] only the relevant differences and the results will be presented here.

II. EXPERIMENTAL

Specimens were fabricated from 0.075-mm-diam reference-grade platinum wire supplied by the Sigmund Cohn Corp., Mt. Vernon, N. Y. Since it was impractical to make electrical-resistance measurements at liquid-helium temperature, changes in the specimen resistance relative to a reference specimen were measured with standard bridge arrangement.[3] Potential leads of 0.013-mm-diam platinum wire, resistance welded to the larger wire, defined the specimen and reference regions. The roughly 3 cm lengths of the specimen and reference regions were within 0.5% of each other.

The specimen and reference were given the cleansing heat treatment in air described by Jackson,[4] with one exception. The specimen mount precluded the water quenches and aqua-regia etch after the 1500 °C anneal. The mount also made it impossible to determine the liquid-helium-temperature resistance of the specimen after the cleansing heat treatment. Room-temperature to liquid-helium-temperature resistance ratios measured for samples taken from the same section of stock wire as the specimen and prepared in the same way were about 3300. A spectrographic analysis of the stock wire by Jarrell-Ash, Waltham, Mass., is listed in Table I.

After the initial heat treatment, the specimen resistance was measured in air at atmospheric temperature and pressure. The values, corrected to 0 °C, were typically 0.5 Ω. The specimen mount was placed in the high-pressure vessel where it remained for the duration of the experiment. The pressure medium was either ultra-high-purity (UHP) argon or UHP argon–5% oxygen. The reference pressure of the system was 1700 psi, at