SURFACE-BARRIER ANALYSIS FOR RHENIUM FROM PERIODIC DEVIATIONS IN THE THERMIONIC SCHOTTKY EFFECT*

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(Received 27 June 1966)

A precise experimental determination of the Herring-Nichols surface-reflection coefficient μ has been made from periodic deviations in the thermionic Schottky effect for rhenium. The value of $\mu = 0.29\exp(i0.42)$ is in good agreement with a Sommerfeld box model in which the valence electrons of the atoms near the metallic surface are assumed to be free.

In the Richardson-Schottky theory of thermionic emission, the logarithm of the current, $\log j_{RS}$,[1] depends linearly on the square root of the applied electric field:

$$\log j_{RS} = \log j_R + \frac{1}{2.3}\frac{e^{3/2}}{kT}\xi, \qquad (1)$$

where j_R is the zero-field Richardson current and ξ is the square root of the electric intensity ($\xi = E^{1/2}$). Actually, $\log j$ vs ξ oscillates about a straight line, because of interference between reflections which occur at the surface of the metal and at the Schottky motive maximum of the image-force barrier.[2] Herring and Nichols suggested that inasmuch as the electron reflections occur from regions that are well localized and physically separated, the problem could be formulated in terms of two complex reflection coefficients μ and λ, depending, respectively, on the shape of the barrier at the surface of the metal and at the Schottky motive maximum.[3] Subsequent theoretical calculations[4,5] used the image-force[6] and applied-field nature of the barrier at the Schottky motive maximum to evaluate λ and treated μ as a field-independent parameter. The Miller and Good[5] computation of the deviation from Schottky linearity can be written in the form

$$F_2 \equiv \log j - \log j_{RS} \cong 1.6\times10^{-3}\xi^{1.68}\frac{|\mu|}{T} \times\cos\left\{\frac{357.1}{\xi^{0.5}} + 0.9 - (\tfrac{1}{2}\pi - \arg\mu)\right\}, \qquad (2)$$

where T is in °K, and ξ, the square root of the applied electric intensity, is in $(V/cm)^{1/2}$. Thus, the periodic Schottky deviations have been utilized for surface-barrier analysis by determining $|\mu|$ and $\arg\mu$ from experimental data through Eq. (2).

This technique of surface-barrier analysis has been applied to polycrystalline Re. Recent thermionic Schottky data taken on specimens of 5-mil unpolished filament revealed a patch-free region $100 < \xi < 500$ $(V/cm)^{1/2}$, and the periodic deviations were separable with sufficient precision to allow a reliable determination of the complex surface-reflection coefficient μ. Figure 1 is an example of the separated Re data, contrasted with Haas and Coomes[7] measurements on polycrystalline Mo. The experimental amplitude maximum of F_2 taken near $\xi = 200$ from deviation curves for various temperatures is plotted against $1/T$ for both Re and Mo in Fig. 2; the Haas temperature data[7] have been corrected to conform with a more

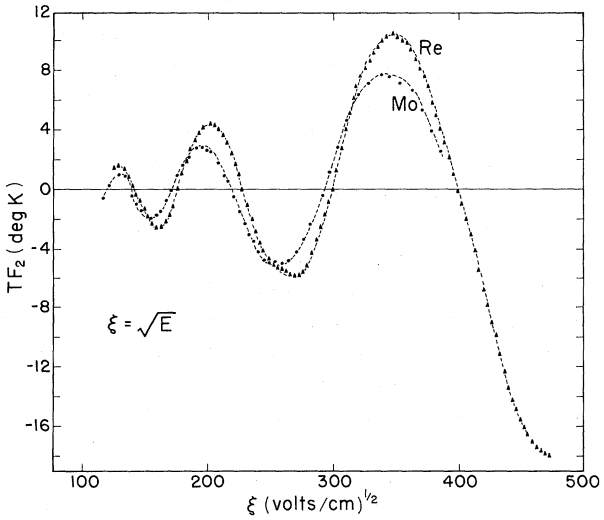

FIG. 1. Typical periodic deviations in the thermionic Schottky effect for rhenium; the closed triangles are experimental points for a polycrystalline Re filament at 1880°K. The closed circles are the data of Haas for molybdenum at 1690°K (see Ref. 7). In order to make a valid comparison, the quantity TF_2 was plotted as a function of ξ. The curves dotted through the experimental points are the Miller-Good theory for reflections from a Schottky motive maximum, and arbitrary complex surface-reflection coefficient μ. See Ref. 5.

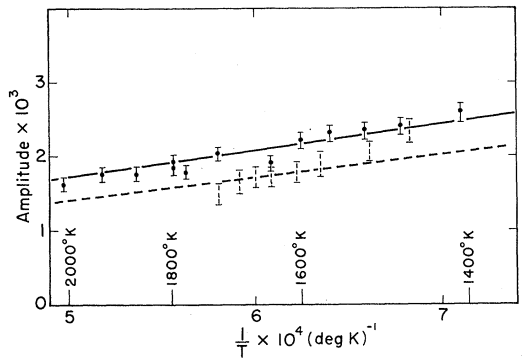

FIG. 2. The $1/T$ dependence of the F_2 amplitude. The closed circles are the experimental data for rhenium at the $\xi \simeq 205$ $(\mathrm{V/cm})^{1/2}$ maximum for the temperature range 1400-2000°K. The solid line drawn through these points has the correct intercept. The molybdenum data of Haas, Ref. 7, have been corrected to conform with a more recent temperature scale (see Ref. 8), and the dotted line is the best fit with correct intercept. The slopes of these lines are used to obtain $|\mu|_{\mathrm{exptl}}$ in Table I.

accurate scale for molybdenum.[8] The $1/T$ lines in Fig. 2 have been drawn to best fit the experimental points and to have intercept required by Eq. (1) simultaneously. The experimental amplitudes of μ recorded in Table I were obtained from the slopes of these lines by making use of the following expression derived from Eq. (2):

$$|\mu|_{\mathrm{exptl}} = 625\,\xi^{-1.68}\left|\frac{dF_2}{d(1/T)}\right|_{\xi=\xi_{\max}} \qquad (3)$$

The experimental values of $\frac{1}{2}\pi$-argμ given in Table I were obtained by requiring the argument of the cosine in Eq. (2) to fit the data in Fig. 1. If the Sommerfeld box model[9] is assumed, both $|\mu|$ and argμ are determined by the single-barrier parameter W_a. The $(W_a)_{\mathrm{exptl}}$ values recorded in the fourth column of Table I are consistent with the corresponding $|\mu|_{\mathrm{exptl}}$ and $(\frac{1}{2}\pi\text{-arg}\mu)_{\mathrm{exptl}}$ through Eq. (42) of Ref. 5.

The electrons associated with a metallic thermionic emitter are usually described by the Sommerfeld model, in which

$$W_a = (\hbar^2/2m)(3\pi^2 f/V)^{2/3} + e\varphi, \qquad (4)$$

where f is the number of free electrons per atom, V is the atomic volume, and $e\varphi$ the work function. When W_a for Re and Mo, obtained from Eq. (4) for $f=1$ together with measured $e\varphi$, are inserted into the Miller and Good[5] calculation, values of $|\mu|$ and $\frac{1}{2}\pi$-argμ obtained are at variance with experiment: Compare the second and third columns of Table II with Table I. Cutler and Gibbons[10] calculated μ for a modified image barrier using the same values of W_a and obtained a better agreement with $(\frac{1}{2}\pi\text{-arg}\mu)_{\mathrm{exptl}}$. See Table II.

Values of W_a in substantial agreement with $(W_a)_{\mathrm{exptl}}$ of Table I are calculated by Eq. (4) if f is assumed equal to the number of valence electrons for the metal. A choice of $f=7$ for Re and 6 for Mo gives $W_a = 28$ and 24 eV, respectively; note that in both cases f is assumed equal to the total number of s and d electrons

Table I. Experimental determination of the complex surface-reflection coefficient μ, obtained by fitting the data of Figs. 1 and 2 to Eqs. (2) and (3), respectively. The W_a correspondence was established through Eq. (42) of the Miller-Good theory, Ref. 5. See also column (4) of Table II.

Metal	$\lvert\mu\rvert_{\mathrm{exptl}}$	$(\frac{1}{2}\pi-\arg\mu)_{\mathrm{exptl}}$	$(W_a)_{\mathrm{exptl}}$ (eV)
Re	0.29	1.1-1.2	27-29
Mo[a]	0.26	1.3-1.5	22-24

[a]Ref. 7.

Table II. Calculations of μ for the Miller and Good mirror-image barrier theory and Cutler and Gibbons modified image-barrier theory with $\eta = 0.068$ Å. The W_a values required in the theories were obtained by Eq. (3); $e\varphi$ was measured. Columns (2) and (3) assume $f=1$, while in column (4) f was chosen equal to the total number of s and d electrons in the unfilled shells.

	Miller and Good[a] $f=1$		Cutler and Gibbons[b] $f=1$		Miller and Good[a] $f=7$ or 6	
Metal	$\lvert\mu\rvert_{\mathrm{calc}}$	$(\frac{1}{2}\pi-\arg\mu)_{\mathrm{calc}}$	$\lvert\mu\rvert_{\mathrm{calc}}$	$(\frac{1}{2}\pi-\arg\mu)_{\mathrm{calc}}$	$\lvert\mu\rvert_{\mathrm{calc}}$	$(\frac{1}{2}\pi-\arg\mu)_{\mathrm{calc}}$
Rh ($e\varphi = 4.9$ eV)	0.20	2.1	0.61	1.5	0.29	1.1
Mo ($e\varphi = 4.3$ eV)	0.19	2.2	0.61	1.5	0.26	1 4

[a]Ref. 5. [b]Ref. 10.

in unfilled atomic shells. On this assumption, the computed values for μ (column 4, Table II), and the experimental values (Table I), are in good agreement.

The bandwidth $W_a - e\varphi$ obtained through band-theory calculations[11,12] and positron-annihilation experiments[13] lead to a lower W_a than found in this experiment, but it is substantially higher than the one-free-electron values used in obtaining Table II. The calculation of Mattheiss[11] yields $W_a \cong 16$ eV for Re, and that of Loucks[12] gives $W_a \cong 13$ eV for Mo. The energy-level sytem of a metal determined for regions deep in the crystal will probably undergo modification at the surface.[14] What the present experiment would indicate is that the electrons at the surface, unlike those in the bulk material, are well represented by the Sommerfeld model, if the Fermi band is chosen wide enough to accommodate all the valence electrons.

The authors appreciate and gratefully acknowledge the interesting and helpful discussions with Professor R. H. Good.

*Work supported in part by Office of Aerospace Research, U. S. Air Force Cambridge Research Laboratories, and in part by U. S. Office of Naval Research.

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OSCILLATING-FIELD-INDUCED MAGNETIZATION IN SOLIDS*

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(Received 29 July 1966)

Recent experiments[1-4] have been performed to study the behavior of a spin system on being irradiated by a near resonant rf magnetic field, and they have been successfully analyzed by using the concept of spin temperature in the rotating frame.[1,5] We report here an experiment[6] describing the behavior of a spin system as it evolves into this thermal equilibrium state, before it is amenable to such an analysis.

It was found that the nonadiabatic application of an off-resonant field to an ordered but demagnetized spin system induced a transient magnetization at a large angle to the effective applied field in the rotating frame, followed by a quasiequilibrium state quite different from full thermal equilibrium in the rotating frame.

Calculations of the dipolar energy of the quasiequilibrium state, based on the assumption that in the rotating frame there is either a complete thermal equilibrium or a complete transfer of nonsecular dipolar energy into Zeeman energy, lead to smaller dipolar energies than were observed experimentally. This was also true for a similar experiment performed on resonance.

All measurements were made on the F^{19} nuclei in a CaF_2 crystal with its 100 axis oriented along a 3375-G constant field (H_{const}). The off-resonance experiment was performed with an irradiating magnetic field (H_{osc}) which was linearly polarized perpendicular to H_{const} and had a peak effective amplitude of 5.2 G in the rotating frame and a frequency 12 kc/sec ($\approx$3