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Thermal shift in the binding energy of bulk W $4f_{7/2}$

H.-S. Tao and T. E. Madey*

Department of Physics and Astronomy and Laboratory for Surface Modification, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08855-0849

J. E. Rowe† and G. K. Wertheim‡

Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974-2070

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High-resolution photoelectron spectroscopy using synchrotron radiation is used to measure the binding energy of the W $4f_{7/2}$ core level associated with bulk atoms of a W(111) crystal in the temperature range from 80 to 780 K. As temperature increases the lattice expands and the binding energy of bulk W $4f_{7/2}$ decreases. A total shift of -45 meV is measured at 780 K with respect to the binding energy of bulk W $4f_{7/2}$ at 80 K. The mechanism responsible for this shift can be understood quantitatively in terms of a Friedel model, in which the narrowing of the *d* band as well as the shift of the center of the *d* band relative to the bottom of the conduction band due to the lattice expansion play dominant roles in shifting the binding energy toward lower energies. [S0163-1829(97)03135-4]

I. INTRODUCTION

Thermal shifts of core electron binding energies have recently been examined in high-resolution photoelectron spectroscopy studies of alkali metals and other *sp* metals.[1] It was found that the binding energies of the shallow core electrons shift to higher binding energy for alkali metals as temperature increases. This is due to a change in the valence-band density as the lattice expands. Based on Hedin and Lundqvist's formalism for calculating the binding energies of alkali metals,[2] the thermal shift of core levels of these free-electron-like metals is made up of three contributions due to change in the lattice constant as the crystal contracts or expands. The first two contributions are initial-state effects: (i) a change in the Fermi level as the density of the conduction-electrons changes, which decreases the binding energy as temperature increases, and (ii) a change in the electrostatic potential for the core electrons due to the change in the density of the conduction electrons, which increases the binding energy as temperature increases. The third contribution is a final-state effect and is (iii) a change in the relaxation energy as the screening length changes, which increases the binding energy as temperature increases. Good quantitative agreement is obtained between experiment and theory for this model.[1] The mechanism responsible for the thermal shifts of core levels is believed to have the same electronic origin as that for surface-atom core-level shifts. It is argued that the change in the electrostatic potential (which shifts the binding energy to higher energy) should also play a role in the surface-atom core-level shift for *d*-band metals,[1] although this was believed to be a small effect in the past.[3] Thermal shifts of core electron binding energies are expected to be observable for *d*-band metals since the valence-band density will change as lattice expands. However, no detailed studies of *d*-band metals have been carried out to investigate the temperature dependence of the core electron binding energies. The relative importance of the *s* band and the *d* band on the binding energies as the lattice expands is not known.

In this study, the temperature dependence of the binding energy of the W $4f_{7/2}$ photoemission from subsurface, bulk W atoms was examined with high-resolution core-level photoelectron spectroscopy using synchrotron radiation. An oxidized W(111) sample has been used in this study, and the binding energy of W $4f_{7/2}$ of the surface oxide is shifted by ~1 eV from bulk W $4f_{7/2}$ (cf. Fig. 1), so the bulk W atoms are clearly distinguished from the surface oxide. The binding energy of bulk W $4f_{7/2}$ is found to shift to a lower binding energy as temperature increases. This is opposite to that observed for alkali metals.[1] For a temperature change of ~700 K, a total shift of -45 meV is measured with respect to the binding energy of bulk W $4f_{7/2}$ at 80 K. The bulk W $4f_{7/2}$ binding energy is determined, with respect to the Fermi level, to be 31.430 eV with a precision of ± 0.010 eV at 80 K. The thermal shift is also found to scale with the bulk thermal linear expansion. Using a simple Friedel model of the valence-band structure,[4] the contributions to the thermal shift from the *s* band and the *d* band are examined, and agree well with the measured value.

II. EXPERIMENTS

The experiments are carried out on beamline U4A at the National Synchrotron Light Source of Brookhaven National Laboratory using a 6-m toroidal grating monochromator. The photoemission data are taken with a 100-mm mean radius VSW hemispherical energy analyzer of 5° angular resolution operating with a pass energy of 2 eV, which gives a nominal resolution of 40 meV. The photon energies used in this study are 75 and 90 eV with a nominal resolution of 50 meV, so that the total instrumental resolution is 64 meV. At each temperature, two photoemission spectra are measured: the W $4f_{7/2}$ core level and the Fermi level. The temperature is monitored by a pair of W5%Re-W26%Re thermocouple wires, which is calibrated by an optical pyrometer. The sample is a W(111) single crystal. The oxidized W(111) is prepared by heating the crystal in 2×10^{-6} torr O_2 at a tem-

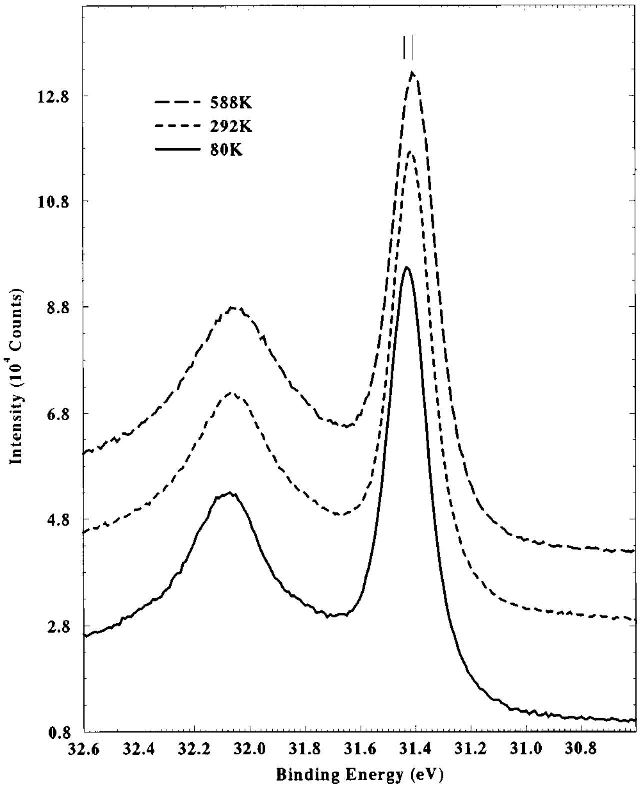

FIG. 1. The photoemission spectra of oxidized W(111) were taken with $h\nu = 75$ eV and collected in a direction 13° off the surface normal. The data indicated by the solid line are taken at 80 K, the short-dashed line at 292 K, and the long-dashed line at 588 K.

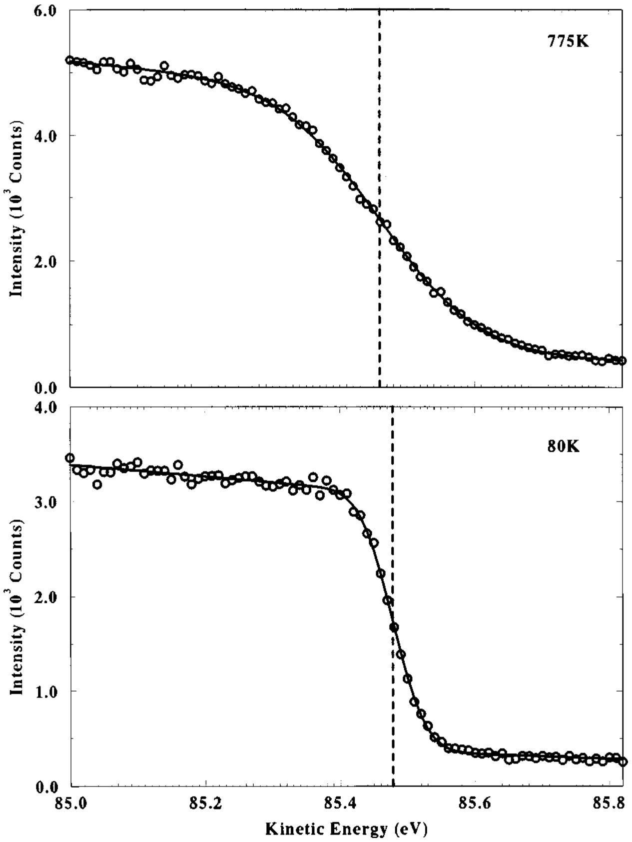

FIG. 2. The Fermi level of oxidized W(111). The solid lines are Gaussian-convoluted Fermi functions determined by nonlinear least-squares fit. The vertical lines are the positions of Fermi level determined by the fit. The shift is due to the thermal *emf* of W wires.

perature of 1000 K for 5 min, after which a low-energy electron-diffraction measurement shows the surface covered with {211} facets.[5] In vacuum better than 1×10^{-10} torr, this surface is very stable for days. No change in the W $4f_{7/2}$ and valence-band spectra can be detected. The sample is heated by radiation from a filament behind the crystal, which is also used for electron-beam heating to clean the sample.

III. RESULTS AND DISCUSSION

A. Thermal shifts of W $4f_{7/2}$

Selected W $4f_{7/2}$ spectra are shown in Fig. 1 to illustrate the temperature dependence of the binding energy of bulk W $4f_{7/2}$ for the oxidized W(111) surface measured with 75-eV photons. The broad photoemission feature at higher binding energy is the oxidized W $4f_{7/2}$ and the sharp photoemission feature at lower binding is the bulk W $4f_{7/2}$. As the temperature increases, both photoemission features broaden and shift to lower binding energy.[6] A total shift of -45 meV for the binding energy of bulk W $4f_{7/2}$ is measured for a temperature range of ~700 K. This binding energy shift is not an artifact due to sample position drift as a result of heating, as verified by measurements at different sample positions. The broadening of the photoemission features is attributed to an enhanced core electron-photon coupling at higher temperature in a Frank-Condon transition model of the core-level phonon broadening.[7]

The W $4f_{7/2}$ binding energy, referenced to the Fermi level, is determined at each temperature in the following way. First, the Fermi level is determined by fitting the Fermi-level spectrum with a model function consisting of a Gaussian-convoluted Fermi function and a slowly varying linear background as shown in Fig. 2. The shift is attributed to the thermal *emf* of the grounding tungsten thermocouple wires.[8] This effect has been observed for a sample supported by constantan,[9] and has been suggested as a way to determine the absolute thermal *emf* of metals. Then, the position of the W $4f_{7/2}$ core level is determined by fitting the W $4f_{7/2}$ spectrum with a model function consisting of a bulk W $4f_{7/2}$ line, oxide W $4f_{7/2}$ lines, and a power-law background. The oxide W $4f_{7/2}$ has a Gaussian line shape. The bulk W $4f_{7/2}$ has a Doniach-Šunjić line shape[10] and is constrained to have a singularity index of 0.03 and a lifetime width of 84 meV.[11] The Gaussian width and the position of each W $4f_{7/2}$ line are free parameters, which depend on temperature. In this analysis, the square of he Gaussian width of the bulk W $4f_{7/2}$ has a linear dependence on temperature above the Debye temperature [cf. Fig. 3(a)], which is in accord with a previous study.[11]

The absolute thermal shift of the binding energy of bulk W $4f_{7/2}$, referenced to the binding energy of bulk W $4f_{7/2}$ at 80 K, is plotted against the W thermal linear expansion[12] as shown in Fig. 3(b), where the data can be fit by a straight line. Similar relations between thermal linear expansion and the thermal shift of binding energy have been observed for alkali metals in a previous study.[1] This suggests that the temperature dependence of the binding energy is related to

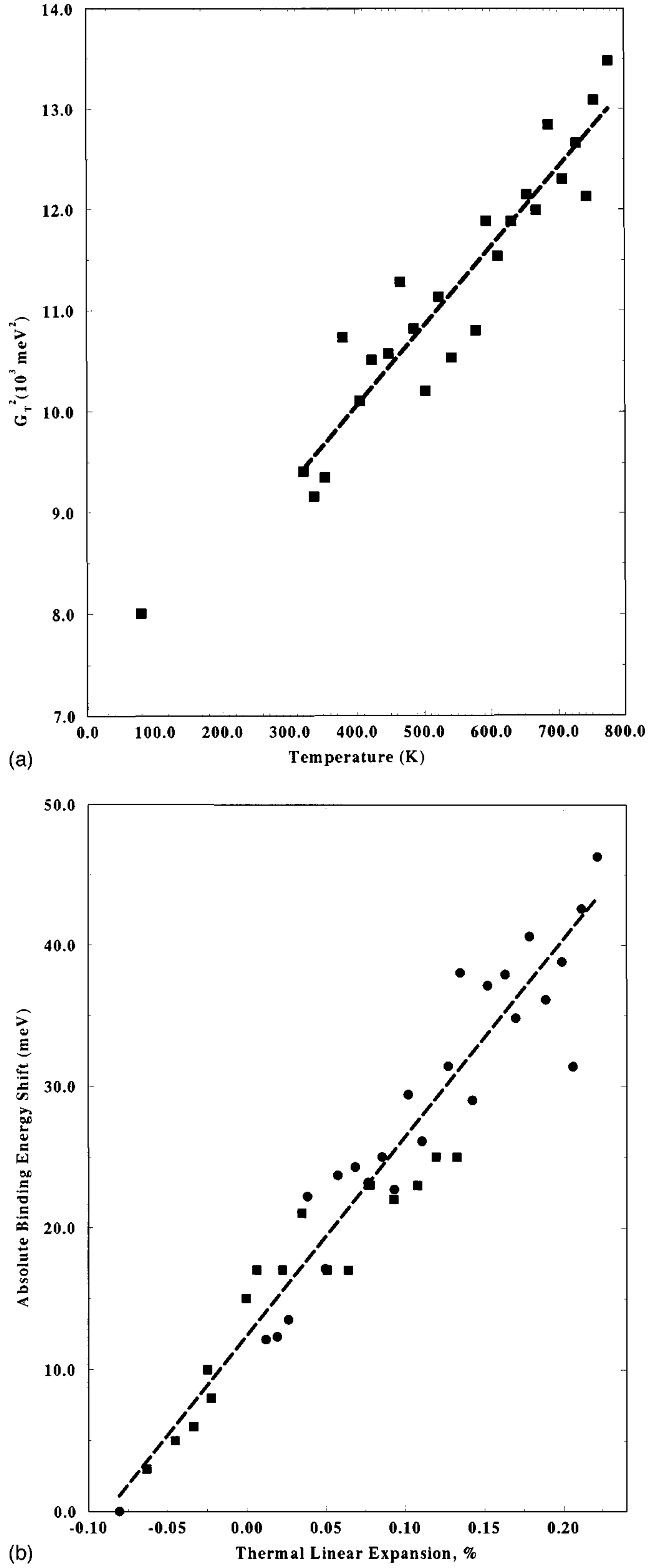

FIG. 3. (a) The square of the Gaussian width obtained from nonlinear least-squares fit is plotted against the temperature (the data are taken using 90 eV photons), and (b) the absolute thermal shifts of binding energy of bulk W $4f_{7/2}$, with respect to the bulk W $4f_{7/2}$ binding energy measured at 80 K, which are obtained by 75 eV (filled squares) and 90 eV (filled circles) photons, are plotted against the bulk thermal linear expansion of W taken from Ref. 12.

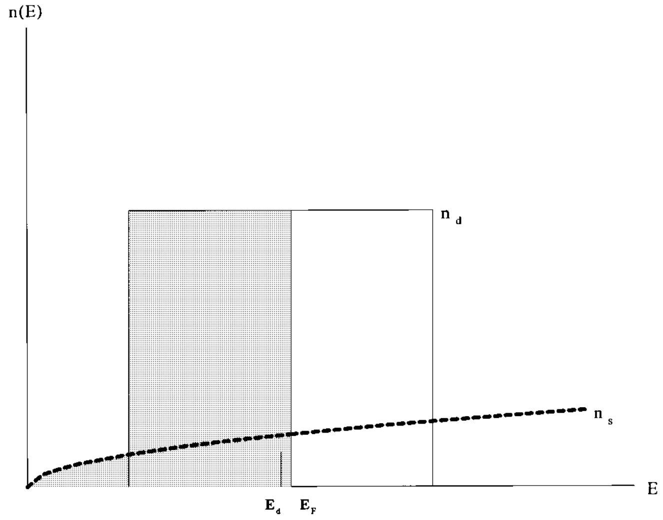

FIG. 4. Friedel model of transition metals (Ref. 13).

the thermal expansion of the lattice, which is about 0.3% over the temperature range of this experiment [cf. Fig 3(b)]. This dependence is a consequence of the fact that the lattice constant affects the valence-band density, which in turn influences the core-level binding energies. Following Ref. 1, we use a Friedel model to examine the bulk W $4f_{7/2}$ core-level thermal shift. In this model, the density of states is assumed to be a linear superposition of two subsets: the *s* band and the *d* band.[4] The mixing or the hybridization of the *s* band and the *d* band is not included.

B. Analysis

Using a simplified Friedel model which is described in detail by Harrison,[4,13] the density of states is made up of two contributions as shown in Fig. 4. The first is due to the *s*-like states whose density n_s is approximated by

$$n_s = n_s(r)\sqrt{E}, \tag{1}$$

with

$$n_s(r) = \frac{2}{3\pi}\left(\frac{2mr^2}{\hbar^2\left(1+\dfrac{5r_d^3}{\pi r^3}\right)}\right), \tag{2}$$

where m is the mass of the electron, r is the atomic sphere radius, and r_d is a characteristic atomic length for each transition metal.

The second is due to the d-like states whose density n_d is approximated by

$$n_d = \begin{cases} \dfrac{10}{W_d} & \left(E_d - \dfrac{W_d}{2} < E < E_d + \dfrac{W_d}{2}\right) \\ 0 & \text{otherwise,} \end{cases} \tag{3}$$

where W_d is the bandwidth of the whole d band (including both occupied and unoccupied states) and E_d is the center of the band relative to the bottom of the s band. E_d and W_d depend on the atomic sphere radius in the following way:

TABLE I. The contributions from the s band to the thermal shift of the binding energies of the W $4f_{7/2}$ between 80 and 780 K. ΔE_c is the shift in the electrostatic potential, and ΔE_{rel} is the change in the relaxation energy. A 0.3% of expansion of the lattice is used (Ref. 1).

	ΔE_c (meV)	ΔE_{rel} (meV)	$\Delta_{s-\mathrm{band}}$ (meV)
W	13	22	35

$$W_d = W_0 \frac{1}{r^5}, \tag{4}$$

and

$$E_d = E_0\left(1 + \frac{5r_d^3}{\pi r^3}\right), \tag{5}$$

where E_0 and W_0 are characteristic atomic constants for each transition metal.[13] The factor 10 in n_d accounts for 10 d electrons per atom. In this model, the densities of states are parametrized as functions of the atomic sphere radius, which is proportional to the nearest-neighbor distance. Using these densities, the additive contributions to the thermal shift from the s band and the d band can be estimated separately. These are regrouped into three terms according to their origins: (i) $\Delta_{s-\mathrm{band}}$ (including both initial-state and final-state effects) originates from the s band, (ii) ΔE_F (a purely initial-state effect) is affected by both the s and the d bands, and (iii) $\Delta_{d-\mathrm{band}}$ (including both initial-state and final-state effects) is purely a d-band effect.

The methods for estimating the s-band contributions to the thermal shift have been discussed in detail by Riffe *et al.*,[1] in which the changes in the Fermi level, electrostatic potential, and relaxation energy are expressed in terms of atomic sphere radius, and the sum of these changes gives rise to the predicted thermal shift. In the present situation, the s-like states are approximated by a free-electron density with $r_s = 1.59$ (corresponding to tungsten) from Harrison's solid state table.[13] Using the formulas outlined in Riffe *et al.*,[1] the initial-state contribution due to electrostatic potential change and the final-state relaxation contribution from the s-like band can then be estimated from Eqs. (7) and (10) of Ref. 1 and are listed in Table I. The net effect of these two s-band contributions is to increase the binding energy as the lattice expands. For a 0.3% lattice expansion, a binding-energy shift, $\Delta_{s-\mathrm{band}}$, of 35 meV due to the s band is predicted (cf. Table I).

The Fermi level of a transition metal cannot be determined by the s-band alone. The d band should play a major role in determining the Fermi level since it has a higher density of states. By filling the s and d bands to the Fermi level, E_F, one should arrive at a value which is equal to the number of valence electrons, N_v. That is,

$$\int_0^{E_F} n_s\sqrt{E}\, dE + \int_{E_{d-(W_d/2)}}^{E_F} \frac{10}{W_d} dE = N_v. \tag{6}$$

Therefore, the Fermi level is related to the d-band width and the center of the d-band relative to the bottom of the conduction band in the following way. The total number of valence electrons is

$$\left(E_F - E_d + \frac{W_d}{2}\right)\frac{10}{W_d} + \frac{2}{3} n_s (E_F)^{3/2} = N_v. \tag{7}$$

Since E_d, W_d, and n_s depend on atomic sphere radius, r, the shift in the Fermi level due to lattice expansion can be obtained by taking the variation of Eq. (7), and is given as

$$\Delta E_F = \frac{1}{A_0}\left(-30\frac{\beta}{1+\beta}\frac{E_d^0}{W_d^0} - 50\frac{E_F^0 - E_d^0}{W_d^0}\right)\frac{\delta r}{r_0} - \frac{1}{A_0}\frac{2}{3} n_s^0 (E_F^0)^{3/2}\left(\frac{3}{2}\frac{3\beta}{1+\beta} + 3\right)\frac{\delta r}{r_0}, \tag{8}$$

where A_0 and β are

$$A_0 = \frac{10}{W_d^0} + n_s^0 (E_F^0)^{1/2}, \tag{9}$$

and

$$\beta = \frac{5r_d^3}{\pi r_0^3}. \tag{10}$$

The values of E_d^0, W_d^0, E_F^0, n_s^0, and r_0 are at equilibrium at zero temperature and are listed in Table II. Using Eq. (8), the shift in the Fermi level, ΔE_F, due to lattice expansion is -59 meV (cf. Table II), in which the d band makes two contributions. The first two terms in Eq. (8) are the result of the narrowing of the d band and the shift in the center of the d band relative to the bottom of the conduction band.[14]

There is an additional contribution from the d band, $\Delta_{d-\mathrm{band}}$, to the binding-energy shift as the lattice expands. This contribution, which is related to a change in the cohesive energy, can be obtained using a Born-Haber cycle. In our simplified Friedel model, the d-band contribution to the cohesive energy per atom ($\epsilon_{d-\mathrm{band}}^Z$) is

$$\epsilon_{d-\mathrm{band}}^Z = 5W_d\left[-\frac{Z_d}{10} + \left(\frac{Z_d}{10}\right)^2\right], \tag{11}$$

where Z_d is the number of d electrons. This parametrized cohesive energy can reproduce qualitatively the behavior of cohesive energy for transition-metal elements across the Pe-

TABLE II. The contributions from the d band to the thermal shift of the binding energies of W $4f_{7/2}$ between 80 and 780 K. ΔE_F is the shift in the Fermi level. The parameters Z_d, E_d^0 (eV), W_d^0 (eV), E_F^0 (eV), r_d (Å), and r_0 (Å) are from Harrison's solid state table (Ref. 13). A 0.3% expansion of lattice is used.

	Z_d	W_d^0	E_d^0	E_F^0	r_0	r_d	ΔE_F (meV)	$\Delta\epsilon_{d-\mathrm{band}}^Z$ (meV)	$\Delta_{d-\mathrm{band}}$ (meV)
W	5.04 [a]	11.44	9.45	10.35	1.56	1.27	-59	215	-16
Re	5.96 [a]	11.02			1.52			199	

[a] $Z_s + Z_d = 6$ for W (7 for Re) and Z_s is the number of s electrons.

riodic Table.[13] The bandwidth, W_d, depends inversely on the atomic sphere radius, r, to the fifth power[13,15] [cf. Eq. (4)], and the change in the d-band contribution to the cohesive energy due to lattice expansion is

$$\delta\epsilon^{Z}_{d-\mathrm{band}}=25W^{0}_{d}\left[\frac{Z_d}{10}-\left(\frac{Z_d}{10}\right)^{2}\right]\frac{\delta r}{r_0}. \qquad (12)$$

Thus, the d-band contribution to the cohesive energy due to lattice expansion can be considered as

$$\epsilon^{Z}_{d-\mathrm{band}}=\epsilon^{Z}_{d-\mathrm{band},0}-\delta\epsilon^{Z}_{d-\mathrm{band}}, \qquad (13)$$

where $\epsilon^{Z}_{d-\mathrm{band},0}$ is the equilibrium cohesive energy at 0 K evaluated with parameters in Harrison's solid state table.[13] Using a Born-Haber cycle where the core hole is assumed to be fully relaxed, it can be shown that the binding energy, E_B, of a core electron referenced to the Fermi level of a metal with atomic number Z is related to the cohesive energies of metal Z, ϵ^{Z}, and its next-nearest neighbor in the Periodic Table metal $Z+1$, ϵ^{Z+1}, as[16]

$$E_B=E^{A}+\epsilon^{Z}-\epsilon^{Z+1}-I^{Z+1}+E^{\mathrm{imp}}_{Z+1}(Z), \qquad (14)$$

where E^{A} is the binding energy of the free atom Z, I^{Z+1} is the ionization potential of free atom $Z+1$, and $E^{\mathrm{imp}}_{Z+1}(Z)$ is the dilute solution energy of metal Z in metal $Z+1$. It is suggested empirically that $E^{\mathrm{imp}}_{Z+1}(Z)$ is small, so it is neglected.[16] Since E_A and I^{Z+1} are atomic properties, the d-band contributions to the shift in the binding energy due to lattice expansion, $\Delta_{d-\mathrm{band}}=\delta E_B$, can be expressed as

$$\Delta_{d-\mathrm{band}}=\delta\epsilon^{Z+1}_{d-\mathrm{band}}-\delta\epsilon^{Z}_{d-\mathrm{band}}. \qquad (15)$$

Using the parameters from Ref. 13, the d-band contribution to the thermal shift is listed in Table II for W. For a 0.3% lattice expansion, a binding-energy shift, $\Delta_{d-\mathrm{band}}$ for W of -16 meV due to the d band is predicted using Eqs. (12) and (15) (cf. Table II). The simplified Friedel model indicates that the d-band contribution causes the binding energy of W $4f_{7/2}$ to shift to lower energy as the lattice expands.

If we combine the s- and d-band contributions, i.e., a sum of $\Delta_{s-\mathrm{band}}$, ΔE_F, and $\Delta_{d-\mathrm{band}}$, the simplified Friedel model predicts a thermal shift of -40 meV, which is close to the measured value within 13%. The good agreement based on such a simplified model may seem to be surprising. However, it should be remembered that this simplified model is derived using a variational principle, which can describe the energetics adequately even though the density of states is not accurate. Therefore, within the context of this Friedel model, it is concluded that the s and the d bands make substantial contributions to the thermal shift of the bulk W $4f_{7/2}$; the contributions from the s band cause an increase and the contributions from the d band cause a decrease in binding energies. However, the d-band contributions dominate the thermal shift of the bulk W $4f_{7/2}$; in particular, ΔE_F, a purely initial-state effect, is the main factor.

IV. CONCLUSION

In summary, we have shown that the thermal shift of bulk W $4f_{7/2}$ core level is opposite to that of the alkali metals reported by Riffe *et al.*[1] The difference can be understood as due to the contribution of the $5d$ electrons in the valence band of W which clearly dominate over the $6s$ valence electrons. Remarkably one can achieve a quantitative prediction of the thermal shift using a very simple model of the valence electron bands proposed by Friedel.[4] It would be interesting to see whether this simplified model can be applied to other $5d$ transition metals such as Ta, Re, etc.

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[*] Author to whom correspondence should be sent. Electronic address: madey@physics.rutgers.edu

[†] Present address: Physics Division, Army Research Office, Research Triangle Park, NC 27709-2211, and Physics Department, North Carolina State University, Raleigh, NC 27695.

[‡] G.K.W. has retired from Bell Laboratories.

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