XPS measurements for detection of collapsed-core atoms

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A considerable heat capacity anomaly of metals with unfilled d states at high temperature is explained using the Core Collapse Model (CCM). The XPS measurement of Pt atoms embedded in Cu matrix has been performed at different concentrations. The analogous measurement of Au atoms has been used as a reference. A difference in Pt levels' behavior and their dramatic narrowing with diluting have been interpreted in favor of the CCM.

I. INTRODUCTION

Many metals[1,2] (in particular transition metals but actually also lantanoides, actinoides, Cs, Ba — the definition will be given further on) exhibit an anomalous thermodynamic behavior in their high-temperature region. The heat capacity of these metals considerably deviates from the linear behavior common for ''regular'' metals as Cu, Ag, Au, Al, etc., and two–three times exceeds the usual ''Dulong-Petit'' law[3] value. Figure 1 presents the typical ''anomalous'' heat capacity behavior for a few metals in comparison with ''regular'' Cu (or Au) behavior. The excess heat capacity fits rather well to the well-known Shottky-type point-defect contribution:[4]

$$\Delta C(T) = A \left(\frac{\Delta E}{k_B T} \right)^2 \exp \left(\frac{-\Delta E}{k_B T} \right), \qquad (1)$$

where A is a material constant and ΔE is an activation energy, T is a temperature.

The similarity of the Eq. (1) with the vacancy contribution tempted some authors[5] to interpret the heat capacity excess in terms of vacancies. But the high values of concentration of these hypothetic defects in many metals has made this interpretation difficult to accept. The defects' concentrations are, for instance, 7.5% and 12% at the melting point of molybdenum and tungsten,[1] respectively. Simultaneously the quenching experiments on molybdenum and tungsten[6] have indicated a vacancy concentration in the range 0.01 to 0.1% at their melting point.

It seems more fruitful to use a hypothesis of Friedel[7] who assumed for explanation of uranium anomalous heat capacity behavior at high temperature an $7s \rightarrow 6d$ transition in a part of atoms resulting from thermal fluctuations. Figure 1 shows that this behavior is not a particular property of U (and Th)[7] but is typical for any atom with unfilled d level, which is distinctive enough from the energetically nearest s state. Such a transition, indeed, had been observed in Cs and Ba for $6s \rightarrow 5d$ levels under high pressure.[8] From these experiments we knew that the Cs and Ba atoms may shrink considerably ($\sim$15% of their volume) changing their quantum state with absorbing the energy ΔE (so-named isostructural phase transition).[9] Then the Core Collapse Model (CCM) (Ref. 10) was generalized also for thermodynamic behavior of Ce and Ce-Th alloy.[11,12] (Although in the case of Ce the

matter is complicated by involving the $4f$ level). The CCM gives a plausible way to explain peculiar diagrams of states of Cs, Ce and many others.[13] It might be a cause of a shortening of La-Al bonds' length observed in La-Al metallic glass[14] and two humps in its heat capacity temperature dependence.[15]

However, the difficulty of this consideration is a lack of a direct way to independently estimate the number of the collapsed atoms. One cannot detect straightforwardly the excited d states among the number of atoms in their s state. The x-ray photoelectron spectroscopy (XPS) may provide a valuable possibility to estimate the presence of this effect.
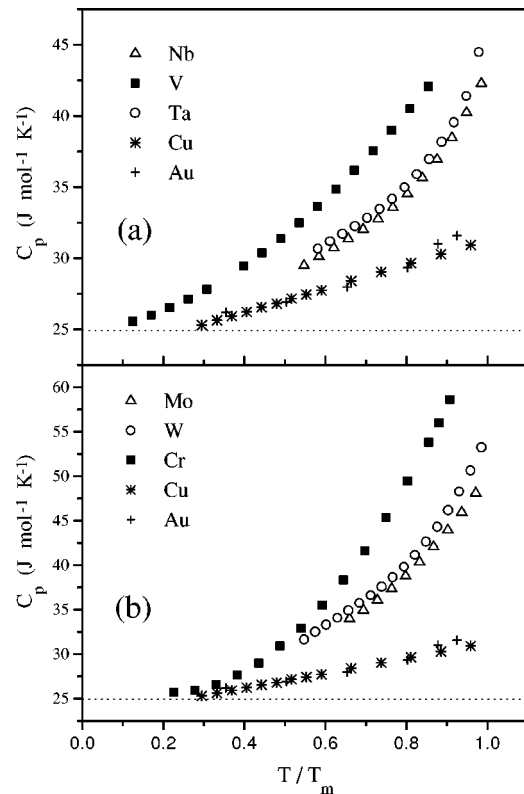

FIG. 1. (a) Heat capacity of V, Nb, and Ta vs reduced temperature T/T_m, T_m is a melting temperature. (b) Heat capacity of Cr, Mo, and W vs reduced temperature T/T_m. Cu and Au curves are added for comparison. Dashed lines show the Dulong-Petit value of heat capacity. Data are taken from Refs. 1 and 2.

TABLE I. Our experimental XPS data on binding energy of Au in pure Au and in a dilute $Au_{0.06}Cu_{0.94}$ alloy.

Level of Au	E (eV) for pure Au	E (eV) for $Au_{0.06}Cu_{0.94}$ alloy	Energy shift (eV)
$4f_{7/2}$	83.42 ± 0.01	83.90 ± 0.01	0.48 ± 0.01
$4f_{5/2}$	87.08 ± 0.01	87.56 ± 0.01	0.48 ± 0.01
$4d_{5/2}$	334.64 ± 0.02	335.11 ± 0.02	0.47 ± 0.03
$4d_{3/2}$	352.71 ± 0.02	353.16 ± 0.03	0.45 ± 0.04

TABLE II. Our experimental XPS data on binding energy of Pt in pure Pt and in a dilute $Pt_{0.07}Cu_{0.93}$ alloy.

Level of Pt	E (eV) for pure Pt	E (eV) for $Pt_{0.07}Cu_{0.93}$ alloy	Energy shift (eV)
$4f_{7/2}$	70.46 ± 0.01	71.21 ± 0.01	0.74 ± 0.02
$4f_{5/2}$	73.85 ± 0.01	74.55 ± 0.01	0.71 ± 0.02
$4d_{5/2}$	314.10 ± 0.03	314.49 ± 0.03	0.39 ± 0.04
$4d_{3/2}$	331.08 ± 0.04	331.25 ± 0.05	0.17 ± 0.06

II. X-RAY PHOTOELECTRON SPECTROSCOPY MEASUREMENT

The high resolution XPS measurement gives an interesting opportunity to detect the atom, which underwent the core-collapse transition. To make this problem concrete let us consider a behavior of Pt atoms embedded into a copper lattice in comparison with the analogous Au atoms' behavior. The electronic configuration of Pt is $[Kr]4d^{10}5s^25p^64f^{14}5d^96s^1$, where $[Kr]$ is the Kr-structured core. It is important here that the $5d$ level of Pt is not saturated and $6s \rightarrow 5d$ transition is possible. The distinction between the $5d$ and $6s$ levels has a trend to be preserved for many transition metals within the crystalline lattice.[16] Moreover it is known from Refs. 8,11 amd 12 that such a transition may be induced by implementing pressure or by alloying. Since the size of the collapsed atom is smaller (the $5d$-wave function has the smaller radius than the $6s$ one) this transition reduces the inner pressure in the alloy.

The Au atom follows immediately after Pt in the Periodic Table and its electronic structure can be distinguished from the Pt one only by a presence of one additional electron making its $5d$ level fully saturated. As it was mentioned above the Au heat capacity behavior is ''regular.'' The size of both Pt and Au atoms (2.78 Å for Pt and 2.88 Å for Au) considerably exceeds the interatomic space within the Cu matrix (2.56 Å). Therefore, both atoms should be compressed within the Cu surrounding. The atomic size of Au is even greater than the Pt diameter, thus the effect of compression is expected to be even more pronounced. This effect has to be higher for the lower concentrations since in a dilute limit the greater atom is surrounded by the smaller ones only.

Our XPS measurement gives the positions of the Pt and Au $4d_{3/2}$, $4d_{5/2}$, $4f_{5/2}$ and $4f_{7/2}$ levels versus the Fermi energy. The levels' positions of both atoms are expected to be shifted since they are implanted into the Cu matrix. Table I gives the characteristics of the Au levels for $Au_{0.06}Cu_{0.94}$ alloy in comparison with the pure gold. Table I exhibits a homogeneous shift of all the checked energy levels as a result of the compression within the Cu lattice. In contrast to Au Table II exhibits a sharply different picture for Pt atoms: the shifts are drastically different for different levels. Figure 2 illustrates this difference between the Au (''regular'') and Pt (''anomalous'') metal behavior.

It is important to note that these experimental data are consistent with the CCM. Really, for the implanted Au atom (without collapse) one may expect the constant shift originated from the smooth redistribution of the electron density in the alloy. This redistribution is approximately constant on the scale of the radius of the wave functions of the deep inner levels. However, in the case of $6s \rightarrow 5d$ transition the shift may be different for different levels since the core collapse changes the conditions for deeper electronic states in a different way. Indeed, the $5d$-wave function has both a smaller radius[8,9,11] and a different symmetry (angular dependence and spin) than the $6s$ one. Thus one may expect that the effective potential for each deeper level changes in a different way.

To check our hypothesis of the core collapse presence the widths of both Pt and Au $4d_{3/2}$, $4d_{5/2}$, $4f_{5/2}$, and $4f_{7/2}$ levels in Pt_xCu_{1-x} and Au_xCu_{1-x} alloys as functions of concentration have been measured. The result is presented in Fig. 3. The widths of the Au levels become a little bit wider in the dilute limit (because of a strong dependence of the compression on the local surrounding). However, the widths of the Pt levels are unexpectedly narrowing for the smaller concentrations. It might be understood if one assumes that Pt in the alloy is a mixture of two states (regular and collapsed one). Therefore, the measured XPS spectra is a superposition of two signals from these states. The closer we are to the
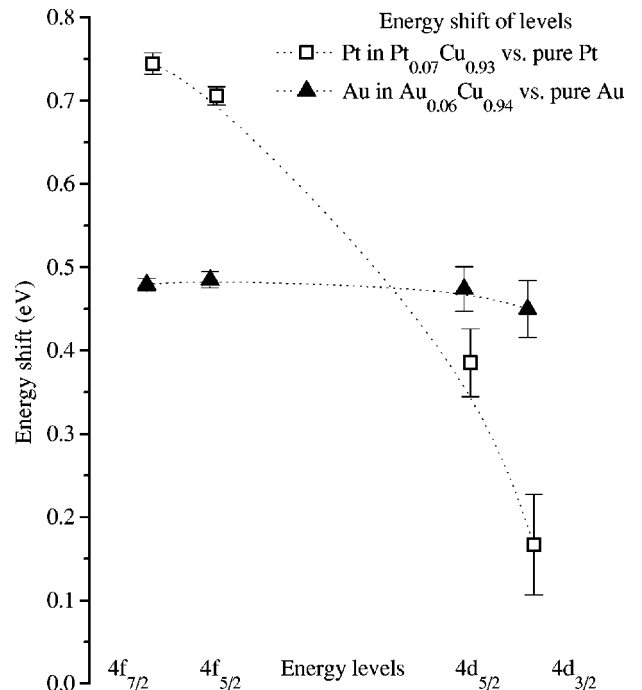

FIG. 2. Energy shift of Pt levels in $Pt_{0.07}Cu_{0.93}$ alloy from the values for pure Pt (squares) and Au levels in $Au_{0.06}Cu_{0.94}$ alloy from the values for pure Au (triangles). Dashed curves are added to lead the eye.
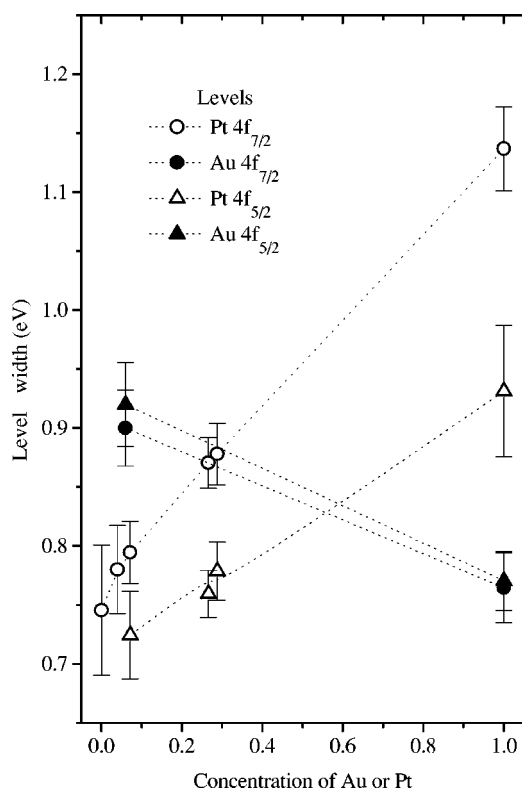
FIG. 3. The widths of Pt and Au $4f_{7/2}$ and $4f_{5/2}$ levels in Cu matrix vs concentration. Dashed curves are added to lead the eye.

dilute limit the higher part of implanted Pt atoms is transformed into the collapsed state. As a result the observed peak width becomes narrower.

III. X-RAY ABSORPTION FINE STRUCTURE

In Ref. 14 the La-Al bond shortening has been noticed at the $Al_{0.91}La_{0.09}$ metallic glass. The La atoms have unfilled both $5d$ and $4f$ states. While to notice the analogous effect (originated from the core collapse) in pure Pt is probably too difficult a task at high temperature, a mean-square deviation (MSD) of bond length σ^2 may be a more sensitive parameter. One can expect that the σ^2 has to exhibit a strong nonlinear behavior (analogous to the heat capacity anomaly) in

the high-temperature region because of an additional disorder, which is produced by the size mismatch between the shrunk and normal atoms: $\sigma^2 = \sigma_0^2(T) + B\Delta R^2 \exp(-\Delta E/k_B T)$, where $\sigma_0^2(T)$ is a usual dynamical MSD. For $T > \Theta_{eins}$ the first term is a linear function of temperature, Θ_{eins} is an Einstein temperature, ΔR is a difference in the radii of the shrunk and the normal atom, B is a material dependent constant. The second term in the equation for σ^2 has to produce a nonlinear contribution, which becomes important at high temperature.

It has been shown earlier[17] that the thermodynamic parameters of ''regular'' metals can be reliably obtained from XAFS spectra. One may expect that a comparison of the XAFS experiment for Pt at high temperature with direct measurements of the heat capacity may confirm the nonlattice (electronic) character of its anomalous behavior.

IV. CONCLUSIONS

(1) It has been shown that a considerable heat capacity anomaly at high temperature is typical for metals with unfilled d states. This behavior of the metals is ascribed to the $6s \to 5d$ (or $7s \to 6d$) transition leading to the core collapse.

(2) To initiate the core collapse the Pt atoms (with unfilled d-state) have been implanted into the Cu matrix. The Au atoms (with filled d-state) similarly implanted into the Cu matrix have been used as a reference. The XPS of the deeper ($4f$ and $4d$) levels of both Pt and Au have been measured as a function of concentration.

(3) The different behavior of the Pt and Au levels' positions have been observed. This difference is consistent with the core-collapse hypothesis.

(4) The dramatic narrowing of the $4d$ and $4f$ Pt levels in the dilute alloys has been observed in the contrast to the widening of the $4d$ and $4f$ Au levels. This result is interpreted in favor of the core-collapse hypothesis.

(5) The possibility of the XAFS detection of the core collapse of the Pt atoms is suggested.

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