Breakdown of spatial inversion symmetry in core-level photoemission of Pt(001)

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We have measured the spin polarization of the 4*d* and 4*f* core-level photoelectrons from Pt(001) by using unpolarized laboratory x-ray sources under a highly bulk sensitive condition. The 4*d* and 4*f* photoelectrons are highly spin polarized perpendicular to the reaction plane as defined by the incident photons and the outgoing electrons. The measured spin polarization and a close look at the core-level photoemission process demonstrate that the bulk core-level photoemission with unpolarized light contributes to the measured spin polarization. This result is in contrast to the valence band photoemission from nonmagnetic solids, wherein the bulk cannot contribute to the measured spin polarization due to the existence of spatial inversion symmetry. Thus, the argument based on spatial inversion symmetry does not apply to the core-level photoemission. The measured spin polarization is in good agreement with an atomic model.

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In atoms, the existence of spin polarized photoelectrons from unpolarized atoms by circularly polarized light was theoretically predicted by Fano[1] and experimentally verified.[2] In principle, for circularly polarized light, which is compatible with parity conservation, all three spin polarization components are nonzero. However, due to axial symmetry, the average polarization over all directions of emission has a component only along the direction of the light propagation. Not long after the discovery of the so-called Fano effect, it was discovered that not only circularly polarized light but also linearly polarized light and even unpolarized light can produce spin polarized photoelectrons from unpolarized atoms.[3–7] For linearly polarized and unpolarized light, the electron spin polarization from unpolarized atoms has only a component perpendicular to the reaction plane defined by the incoming photons and the outgoing electrons and disappears if it is averaged over the directions of emission due to axial symmetry.[8] In fact, after integration over the electron emission angles, the degree of spin polarization becomes equal to zero when linearly polarized light or unpolarized light is absorbed and remains nonzero for absorption of circularly polarized light.

In nonmagnetic solids, the Fano effect obtained by using circularly polarized light was first confirmed by using polycrystalline Cs.[9] After that, spin resolved valence band photoemission using circularly polarized lights has been successfully applied to study the relativistic electronic structures of nonmagnetic solids.[10–13] In contrast to the atomic case, it was believed for a long time that linearly polarized and unpolarized light cannot produce spin polarized photoelectrons in valence band photoemission of nonmagnetic crystals because of the spatial inversion symmetry, which does not exist in atoms but does exist inside crystals.[14,15] The existence of spatial inversion symmetry requires the use of circularly polarized light to produce a non-zero-spin polarization in photoemission from the valence bands of nonmagnetic crystals. Therefore, it is interesting to investigate the effect of removing the spatial inversion symmetry by modifying the arrangement of the atoms in a crystal by varying external parameters such as temperature or pressure. An easy way is to look at a surface where the spatial inversion symmetry is broken. Indeed, non-zero-spin polarizations from surface effects were theoretically predicted[16–19] for excitation with linearly and even unpolarized light in photoemission from nonmagnetic Pt surfaces, and, in fact, have been experimentally observed.[20–25] Especially in the case of a W(110)-(1×1) H surface, where the surface and bulk contributions can be completely separated in the photoemission spectrum, the surface states give rise to 100% spin polarization, while the bulk states produce zero-spin polarization.[26]

Now, consider the case of core-level photoelectrons from the bulk. Here, an open question is; Does the spatial inversion symmetry govern the bulk core-level photoemission of nonmagnetic crystals so that linearly polarized and unpolarized light cannot produce spin polarized photoelectrons? There are experimental results that the core levels of Cu 2*p*, 3*p*, and of W 4*f* are spin polarized perpendicular to the reaction plane with linearly polarized light.[27,28] But, unfortunately, the kinetic energies of the measured core-level photoelectrons were around ~100 eV, which is very surface sensitive. Therefore, these results cannot be used to answer the question given above. Instead, we have performed a very bulk sensitive experiment by measuring the spin polarization of the core levels 4*d* and 4*f* from nonmagnetic Pt using unpolarized photons of $h\nu=1253.6$ eV (Mg $K\alpha$) and $h\nu=1486.6$ eV (Al $K\alpha$). The kinetic energies of the 4*d* and 4*f* photoelectrons are in a range of 920 and 1410 eV. The results are very surprising: in contrast to the valence band photoemission from the bulk, the core levels 4*d* and 4*f* from the bulk are highly spin polarized perpendicular to the reaction plane. Therefore, the aim of this Brief Report is to report on the experimental verification that the spatial inversion symmetry argument requiring circularly polarized light does not apply to the core-level photoemission from the bulk. Furthermore, a non-zero-spin polarization in a core-level photoemission from the bulk with linearly polarized and unpolarized light are allowed.

The experimental setup is shown in Fig. 1. Unpolarized Mg $K\alpha$ light ($h\nu=1\,253.6$ eV) and Al $K\alpha$ light ($h\nu=1\,486.6$ eV) from an x-ray tube located in the *Y*-*Z* plane at an angle of 45° with respect to the surface normal hits a Pt(001) surface. The energies of the photoelectrons normally emitted are analyzed by the hemispherical electron energy analyzer followed by the Mott detector where the two trans-

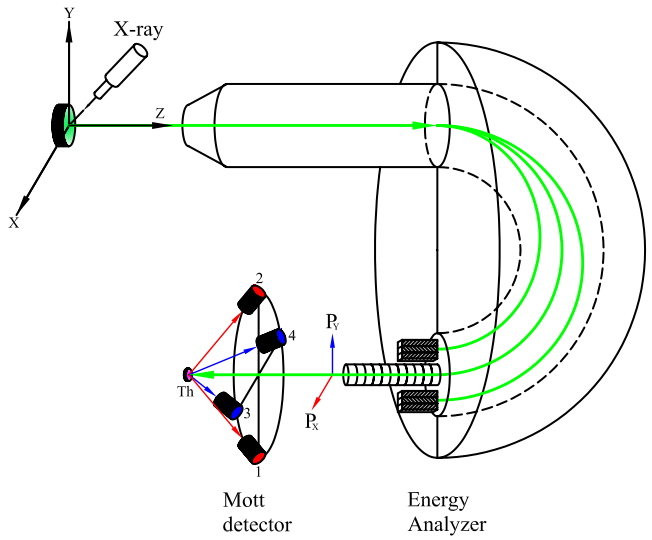

FIG. 1. (Color online) Sketch for the spin resolved photoemission setup recently installed at Lawrence Livermore National Laboratory. Unpolarized x rays hit the sample at an angle of 45° with respect to the surface normal. The x-ray tube is located on the *Y*-*Z* plane, which is the reaction plane. The energies and the spins of the normally emitted photoelectrons are analyzed by a hemispherical electron energy analyzer and the Mott detector, which has a thorium target operated at 25 keV and a Sherman function of 0.16 ± 0.04, respectively. Two transversal spin components P_X and P_Y can be simultaneously measured in the Mott detector.

versal spin components P_X and P_Y are simultaneously determined (SPECS PHOIBOS 150 system combined with spin detection). The different counting rate between counters one and two (counters three and four) gives rise to P_X (P_Y). It turned out that the P_Y component is always unpolarized in the all of the measurements for the 4*d* and 4*f*. The Sherman function *S* of the Mott detector is 0.16 ± 0.04 for a thorium target voltage of 25 keV. The 3 eV resolution at full width at half maximum (FWHM) for 4*f* (6 eV at FWHM for 4*d*) has been chosen to allow a reasonable signal in the Mott detector since the efficiency of the Mott detector ($S^2 I/I_0$) is on order of 10^{-5}. The Pt(001) surface is cleaned by using the standard cleaning process by sputtering with Ar ions and heating in oxygen, and the surface was characterized by low energy electron diffraction and x-ray photoelectron spectroscopy.

Spin resolved 4*d* core-level spectra with unpolarized x rays of an energy of 1253.6 eV have been displayed in Fig. 2. The spin integrated total intensity *I* is separated into the partial intensities for spin parallel I_+ and antiparallel I_- to *X* direction for P_X (to *Y* direction for P_Y), by means of $I_\pm = (I/2)(1 \pm P)$. From the left panel of Fig. 2, it is clear that the spin-orbit split $4d_{3/2}$ and $4d_{5/2}$ states are approximately −6% and 4%, respectively, spin polarized along the *X* direction, which is perpendicular to the reaction plane. From the right panel of Fig. 2, the P_Y component, which is parallel to the reaction plane, is unpolarized. There is always a superimposed background in the photoelectron spectrum from a crystal due to the inevitable energy lost from the photoelectron scattering during emission process; free atoms, in contrast, should in principle contain no background. Since we intend to compare the core-level spectra from the crystal to

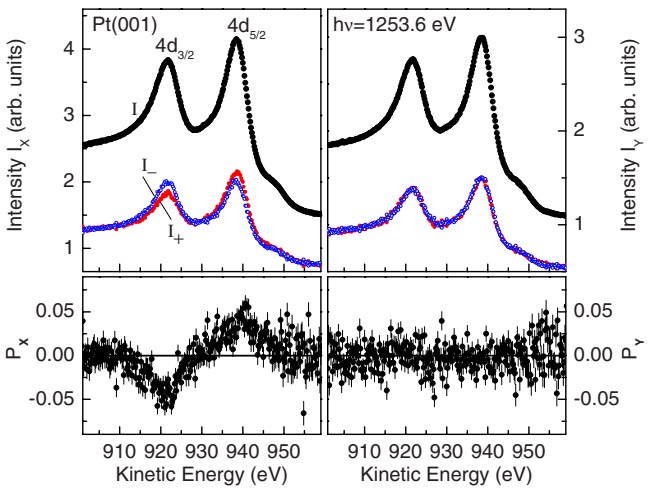

FIG. 2. (Color online) Spin resolved 4*d* core-level spectra from Pt(001) with unpolarized x rays of $h\nu = 1\,253.6$ eV. The left (right) panel presents the *X*(*Y*) component. The partial intensities $I_\pm$ are derived from the spin integrated total intensity *I* and the polarization *P* by $I_\pm = (I/2)(1 \pm P)$. The error bars give the statistical uncertainties.

an atomic case, the assumed backgrounds are subtracted from the $4d_{3/2}$ and $4d_{5/2}$ spectra measured along the *X* direction, as shown in Fig. 3. When the linear background is subtracted from the spectrum, the spin polarization approximately reaches −16% for $4d_{3/2}$ and approximately 9% for $4d_{5/2}$. The spin resolved 4*f* spectra are analyzed in an identical way. After the background subtractions, the final spin polarizations of the core levels 4*d* and 4*f* for the two photon energies (1253.6 and 1486.6 eV) are presented in Fig. 4 with the theoretical spin polarizations calculated by using the pure atomic model[3,4] and the tabulated radial dipole matrix elements and phase shifts.[29] It is evident from Fig. 4 that the spin polarizations measured from the core levels 4*d* and 4*f* under a highly bulk sensitive condition are quantitatively in good agreement with the theoretical values calculated with the pure atomic model.

These spin resolved core-level spectra clearly demonstrate that the photoemission from the 4*d* and 4*f* core levels are highly spin polarized with unpolarized light even under highly bulk sensitive experimental conditions, i.e., with the high kinetic energy photoelectrons (920–1410 eV). However, if the spatial inverse symmetry governs the spin polarization in the bulk core-level photoemission, as it does for the bulk valence band photoemission,[26] a non-zero-spin polarization cannot be expected with unpolarized light. In the following, therefore, we address the hypothesis that the argument based on spatial inversion symmetry does not apply for the determination of the spin polarization in core-level photoemission excited by linearly polarized and unpolarized light, and that the spin polarization can be determined by the atomic model.

The argument for spatial inversion symmetry developed for the spin polarization of photoelectrons emitted from the valence band of nonmagnetic crystals is based on the model of direct (**k** conserving) transitions, which is suitably valid for the valence band photoemission with lower photon energies, such as UV, and it requires zero-spin polarization in

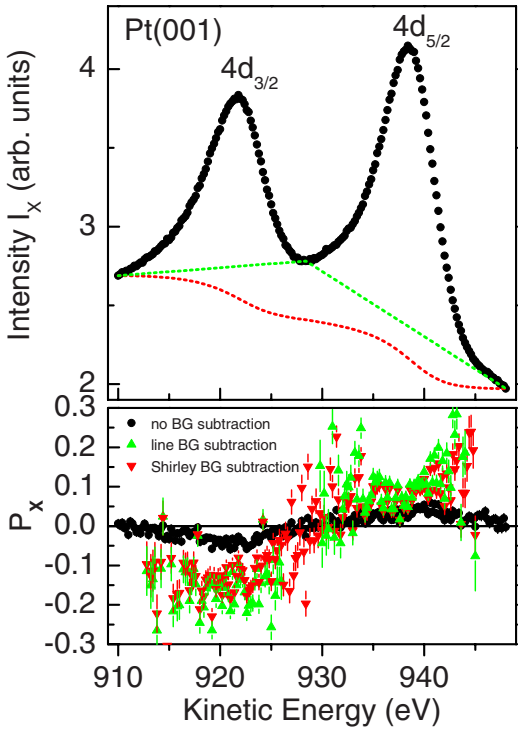

FIG. 3. (Color online) Subtraction of background (BG) from the 4*d* core-level photoemission spectrum from Pt(001) with unpolarized x rays of $h\nu=1$ 253.6 eV for the *X* component. Two different backgrounds are assumed as a straight line and a Shirley type, as shown in the upper panel. After background subtractions, the corrected polarizations are plotted in the lower panel as up triangles for the straight line subtraction and as down triangles for the Shirley type subtraction. The circles are the polarizations without background subtraction.

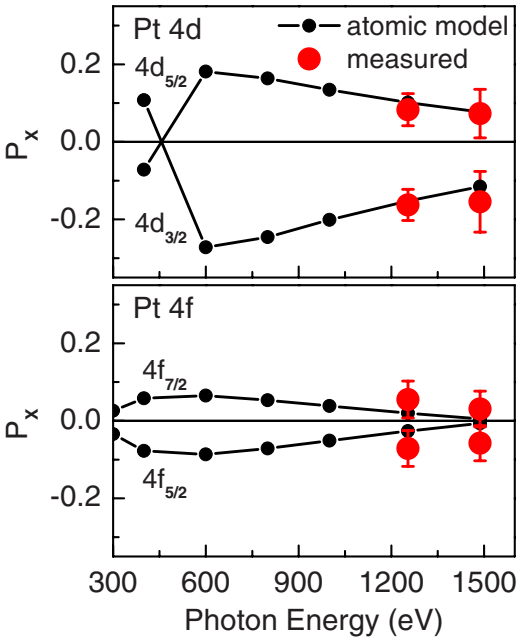

FIG. 4. (Color online) Comparison between the experimental spin polarizations measured from the 4*d* and 4*f* core levels of Pt(001) with unpolarized x rays of 1253.6 and 1486.6 eV and the theoretical values calculated by using the atomic model. Equation (1) with the tabulated radial matrix elements, the phase shifts, and the β^j from Ref. 29 is used for the theoretical spin polarization. The experimental spin polarizations are plotted after background subtractions. The upper panel is for 4*d* and the lower panel is for 4*f*.

photoemission with linearly polarized and unpolarized light.[14,15] However, a closer look at the photoemission process reveals that the argument is not transferable from the valence band to the core level. First, in a core-level photoemission with higher photon energies such as x rays, the wave vector $\mathbf{k}$ is not conserved ($\mathbf{k}_i \neq \mathbf{k}_f$). Clearly, the photoemission process from the core level corresponds to the nondirect transition.[30] The vanishing of the spin polarization in the photoemission of the bulk valence band from nonmagnetic crystals with linearly polarized and unpolarized light is correlated with $\mathbf{k}$ conservation during the excitation process and the condition of the $\mathbf{k}$ conservation is relaxed in the process of the core-level photoemission. Therefore, the argument does not apply to the core-level photoemission. Furthermore, for the core-level photoemission, the initial state is highly localized while the final state involves a delocalized free electron state with a localized core hole state left behind.[30] Clearly, the photoemission process from the core level is much more analogous to the photoemission process in atoms, wherein the initial state is necessarily localized in an atom, whereas the final state involves a delocalized continuum state describing the outgoing photoelectron and a localized state of the single ionized atom left behind. The experimental observation of spin polarization in the P_X channel and its absence in the P_Y channel are completely consistent with the atomic picture.

Consider the pure atomic case. If $\mathbf{k}_p$ and $\mathbf{k}_e$ represent the unit vectors in the directions of incoming unpolarized photons and outgoing electrons, forming an angle θ, the spin polarization of the photoelectrons perpendicular to the reaction plane may be written as[3,4]

$$\mathbf{P}_j^{un}(\theta) = \frac{\xi^j \sin\theta\cos\theta}{1-\frac{1}{2}\beta^j\left(\frac{3}{2}\cos^2\theta-\frac{1}{2}\right)}\mathbf{k}_p\times\mathbf{k}_e, \qquad (1)$$

where $\xi^j=(-1)^{j-\ell-1/2}/2j+13\sqrt{\ell(\ell+1)}d_{\ell+1}d_{\ell-1}\sin(\delta_{\ell+1}-\delta_{\ell-1})/d_{\ell-1}^2+d_{\ell+1}^2$ and β^j denotes the angular distribution of the photoelectrons. As a consequence of its quantum mechanical nature, the spin parameter ξ^j is very sensitive to the radial dipole matrix elements $d_{\ell\pm1}$ and the corresponding phase difference $(\delta_{\ell+1}-\delta_{\ell-1})$ of the continuum wave functions induced by the Coulomb force. This phase difference is the origin of the polarization. For example, if a *d* electron is ejected, the electron can reach *P* and *F* states by the dipole selection rule of $\Delta\ell=\pm1$. Consequently, we have the phase difference $(\delta_F-\delta_P)$, which is the physical origin of the measured spin polarization. This phase difference is caused by the Coulomb force, which is much stronger than the weak spin-orbit interaction in the continuum.

In any case, it should be mentioned that linearly polarized and unpolarized light cannot produce the spin component P_Z along the photon propagation direction, which can be produced by circularly polarized light only, but linearly polarized and unpolarized light can produce a P_X component in the core-level photoemission from both the bulk and the sur-

face atoms. In order to legitimize our conclusions, however, it is important to properly justify that the contribution to the spin polarization predominantly comes from the bulk atoms. At the low kinetic energy of ~100 eV (surface sensitive), the core-level $4f_{7/2}$ spectra from the noble metals (W, Pt, and Au) contain almost equal contributions from the bulk and the surface.[31–33] The lower coordination of the surface atoms leads to a different core-level binding energy compared to the bulk and introduces a clear separation of the surface peak from the bulk one. However, at high kinetic energy the contribution from the surface is significantly reduced and it is almost unnoticeable; in the case of Au $4f_{7/2}$ spectrum with Al $K\alpha$ light, a quantitative analysis shows that the $4f_{7/2}$ spectrum is composed by mainly the bulk contribution (90%) and by a small surface contribution (10%) at the lower binding energy side.[32] Therefore, it is not unreasonable to assume that the contribution to the spin polarization predominantly comes from the bulk.

In conclusion, we have presented spin resolved spectra of the $4d$ and $4f$ core-level photoelectrons from Pt(001) with unpolarized x rays under highly bulk sensitive conditions. The core-level photoelectrons are highly spin polarized along the perpendicular to the reaction plane. Based on the measured spin polarization and the atomic theory, it is demonstrated that, in contrast to the bulk valence band photoemission, the spatial inversion symmetry does not dictate zero-spin polarization for bulk core-level photoemission, and that the core-level spin polarization can be described by the atomic model.

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