Correlated Electron Effects in Low Energy Sr^+ Ion Scattering

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Resonant charge transfer during low energy ion scattering reveals correlated-electron behavior at high temperature. The valence electron of a singly charged alkaline-earth ion is a magnetic impurity that interacts with the continuum of many-body excitations in the metal, leading to Kondo and mixed valence resonances near the Fermi energy. The occupation of these resonances is acutely sensitive to the surface temperature, which results in a marked temperature dependence of the ion neutralization. We report such a dependence for low energy Sr^+ scattered from polycrystalline gold.

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A system of many electrons can display emergent phenomena that cannot be extrapolated from the behavior of independent electrons. Such correlated-electron effects lead to a variety of exotic phenomena and are a central focus of condensed matter physics research. A method for triggering correlated-electron behavior is to introduce a spin impurity into a metal, which then causes the free electrons to respond collectively as, for example, in the Kondo effect. This arrangement can be modeled at a fundamental level via low energy ion scattering experiments that employ a projectile with an unpaired valence electron [1–3], such as a singly charged alkaline-earth metal ion. Here, we report measurements of the neutralization of scattered strontium ions (Sr^+) from polycrystalline gold (Au) as a function of surface temperature, which provide the first clear experimental evidence that electron correlations can participate in atom-surface scattering.

Low energy ion scattering involves projectile kinetic energies in the range of 0.5–10 keV [4], where the ion-surface interaction is a mix of classical elastic collisions and quantum mechanical charge exchange. The elastic collisions are dominated by binary scattering events such that the energy spectrum of the scattered projectiles provides the mass distribution of surface species. Charge exchange can occur through a number of different mechanisms that depend on the specific electronic structures of the projectile and target. For the interaction of Sr^+ ions with a metal surface, resonant charge transfer (RCT) is expected to be the dominant process [5]. RCT occurs when there is sufficient overlap between the projectile's valence level and the surface conduction band so that electrons can transfer without gain or loss of energy.

Although RCT has been explored both theoretically and experimentally, the role of more complex correlated-electron processes in charge exchange has remained one of the challenging unsolved problems in the physics of atom-surface collisions [6]. Electron correlations induced by a single spin localized on the projectile could, in turn, affect the charge exchange during atom-surface scattering. Two independent theoretical investigations have supported this concept, and both predicted that an anomalous dependence of the charge transfer probability on the sample temperature would serve as the signature of correlated-electron behavior [1–3].

Figure 1 shows a schematic energy level diagram for Sr^+ interacting with a Au metal surface. The Sr 5*s* level and surface bands overlap, as the ionization energy of atomic Sr (5.7 eV) is slightly larger than the target's work function ($\phi = 5.1$ eV). As the projectile approaches the surface, the image charge causes the Sr 5*s* level to shift upwards towards the Fermi energy while overlap in the wave functions causes the level to broaden, as illustrated in the center of the figure. Since the scattering occurs on a very short time scale (on the order of femtoseconds), the charge state distribution is frozen in along the outgoing trajectory while the projectile is still close to the surface, typically within a few angstroms [5,7]. In the absence of multielectron effects, the measured neutral fraction (NF) depends on the alignment of the surface work function with the (broadened and shifted) projectile ionization level, as well as the

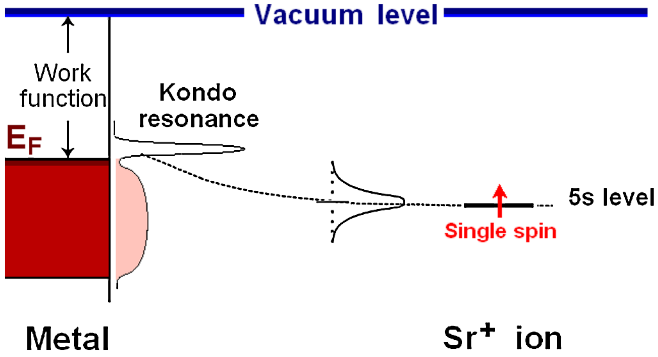

FIG. 1 (color online). Schematic energy level diagram for the half filled Sr 5*s* level (≈ 5.7 eV), interacting with a Au metal surface ($\phi \approx 5.1$ eV). The left side of the figure indicates the density of filled states in the metal and shows the position where a Kondo resonance would appear. The right side shows the Sr^+ ion with a single spin on its valence level. The center of the figure illustrates how the 5*s* level would broaden and shift as the projectile nears the surface.

velocity of the outgoing projectile. In general, the NF increases as ϕ is reduced, and vice versa.

When the projectile ion has a single unpaired electron or hole, correlated-electron behavior would induce either a Kondo resonance or mixed valence state at the Fermi energy, as first predicted by Shao, Nordlander, and Langreth [1] and illustrated in Fig. 1. The type of resonance formed would be a function of the projectile-surface distance, but the occupancy in either case would be a strong function of the surface temperature. Merino and Marston [2] used a different theoretical approach and concluded that, under certain conditions, the Kondo resonance would cause a negative temperature dependence of the neutralization probability in alkaline-earth ion scattering. Thus, it is expected that electron correlations would manifest through a dramatic temperature dependence of the neutralization probability.

We measured the temperature dependence of the neutralization of 2.0 keV $^{88}\mathrm{Sr}^+$ ions scattered from a polycrystalline Au surface. For comparison, the same set of experiments was performed with 2.0 keV gallium (Ga^+) ions. Ga^+ has a pair of valence electrons with no net spin and is therefore not expected to induce correlated-electron behavior.

The experiments were performed in an ultrahigh vacuum chamber described previously [8]. A polycrystalline Au foil was cleaned *in situ* by cycles of 0.5–1 keV Ar^+ sputtering for 60 min and heating to 650 °C for ~5 min to remove the embedded Ar. The purity of the surface was confirmed with Auger electron spectroscopy using low energy electron diffraction optics as a retarding field analyzer. In addition, we monitored the emission of recoiled impurities induced by Ar^+ bombardment as a sensitive measure of surface cleanliness [4]. The surface work function was monitored by the position of the secondary electron cutoff measured with the retarding field analyzer [9].

Time-of-flight (TOF) spectroscopy was used to collect spectra of the scattered projectiles. 2.0 keV Sr^+ and Ga^+ ions were produced and accelerated in a Colutron ion source chamber by heating Sr metal and gallium iodide, respectively, in an Ar^+ plasma. The desired isotope was selected with a velocity filter and deflected across an aperture to produce ~100 ns ion pulses at 25 kHz. The beam was electrostatically bent by 5° before entering the main chamber to prevent primary neutrals from reaching the sample. After the primary ions have impacted the Au surface, the particles scattered at 135° were collected by a microchannel plate detector positioned at the end of a TOF leg containing a pair of deflection plates. The deflection plates were held at ground potential to collect the total scattered yield, while a voltage was placed between them to remove the ion signal and collect spectra of the scattered neutrals.

Figures 2(a) and 2(b) show typical TOF spectra of the total yield and neutrals for 2.0 keV Sr^+ ions scattered from clean Au foil at surface temperatures of 300 and 573 K, respectively. The spectra each display a pronounced single-scattering peak (SSP) that results from projectiles that have undergone a single binary elastic collision with a surface atom [4]. The SSP rides on a broad structure that results from multiple scattering. The NF is calculated by dividing the area of the neutral SSP by that of the total yield SSP after first subtracting a background [10], as indicated by shaded regions in Fig. 2. It can be seen from the raw data, for example, that the NF is enhanced by about a factor of 2 when the surface temperature increases from 300 to 573 K.

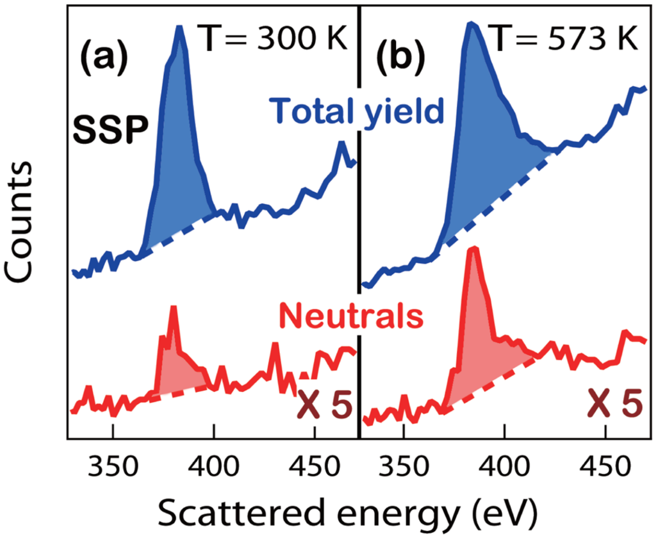

FIG. 2 (color online). TOF spectra of the total yield and neutrals (enhanced by a factor of 5), collected at a 135° scattering angle for 2.0 keV Sr^+ ions scattered in the surface normal direction from clean polycrystalline Au at (a) 300 and (b) 573 K. The shaded regions indicate how the areas of the SSP were determined.

Figures 3(a) and 3(b) show the temperature dependence of the NF for 2.0 keV Sr^+ and Ga^+ ions, respectively, scattering from clean polycrystalline Au. While the Ga data show a monotonic rise in NF with temperature, the NF of Sr rises with temperature until it reaches a maximum at around 600 K, above which it drops.

Although polycrystalline Au is not expected to undergo structural or compositional changes with temperature, we are able to exclude this possibility with the following considerations. First, the sample was reprepared often to assure reproducibility. Second, the curves in Fig. 3 are reproducible whether subsequent spectra were collected by increasing or by decreasing the temperature. If there were temperature-dependent changes to the composition or structure, they would likely occur while the sample temperature was high and would be irreversible. Finally, the work function of the sample was monitored as its temperature was adjusted, and the variations in going from 300 to 873 K were found to be negligible, which is a strong indication that the surface structure does not change with temperature.

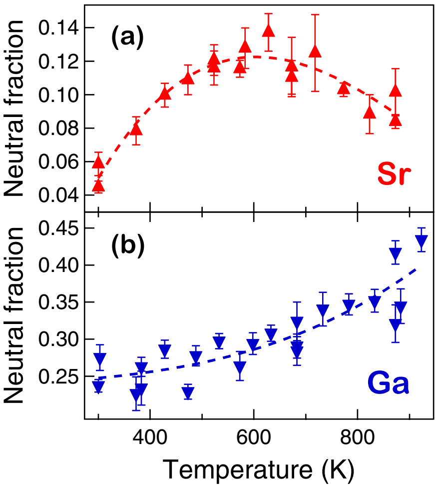

FIG. 3 (color online). Neutral fraction vs surface temperature for 2.0 keV (a) Sr^+ and (b) Ga^+ scattered at 135° from clean polycrystalline Au along the surface normal direction. The dashed lines are drawn to guide the eye.

A rise in surface temperature increases the electron occupancy above the Fermi energy, which could then lead to an increase in the measured neutralization within the RCT model [11–14]. This has sometimes been shown to have a negligible effect on measured neutralization rates, however, as the magnitude of the additional occupancy is usually small compared to the typical energy scale in ion scattering. Thus, a positive or negligible temperature dependence of the neutralization rate would be expected based on single electron physics, and this could explain the initial rise in the NF with temperature for Sr and the rise for Ga.

The original RCT model cannot, however, explain the negative temperature dependence for Sr^+ neutralization above 600 K. The decrease in the NF above 600 K can result from the formation of collective many-body states due to the spin impurity. The unpaired valence electron induces the formation of a Kondo resonance near the Fermi energy [2], as illustrated in Fig. 1. As the affinity level bends up and crosses the Fermi level, the slow fluctuations between the projectile's broadened electronic spectral function and the Kondo resonance peak produce a sharp mixed valence state. The measured charge distribution of the scattered ions is directly related to the occupancy of this sharp state, which has a very pronounced dependence on the surface temperature. Merino and Marston predicted a negative temperature dependence of neutralization probability by including the Kondo effect in their calculation of the NF for alkaline-earth ion scattering with Ca^+ [2]. Although the calculations in Ref. [1] were for negative ion formation, extrapolation of their results to positive ion formation would also result in an inverse dependence of the neutralization on temperature.

The Kondo effect is applicable to our experiments as, based on the calculations of Ref. [2], the projectile's perpendicular exit velocity (~ 0.0134 a.u.) is sufficiently small for a well-developed resonance to form. Such correlated-electron effects can be observed well above room temperature in this experiment because the projectile's ionization level shifts and crosses the Fermi energy as it approaches the surface where the interaction between the localized and conduction electrons is very strong. Merino and Marston predicted a Kondo temperature around 0.1 eV (~ 1000 K) [2], which is close to the position of the maximum shown in Fig. 3(a).

The calculations in Refs. [1,2], however, predict a monotonic decrease in NF with temperature rather than a maximum. The maximum in the temperature dependence for Sr^+ scattered from Au could possibly result from a transition from thermal effects based on independent electron physics to the correlated-electron behavior, if it is assumed that the empty resonance level lies primarily above the Fermi energy. When the surface temperature is below 600 K, the electron distribution has not yet reached this sharp peak. As a result, the increased population of states leads to the normally expected increase in NF. As the surface temperature increases further, however, electrons are eventually promoted to the resonance state where the correlated-electron effects lead to a negative temperature dependence of the NF. This is one manner in which the complexity of the electronic states for Sr^+ scattering from Au could lead to a nonmonotonic dependence.

To verify that the negative temperature dependence occurs only in the presence of a single unpaired electron, it is useful to compare to experiments using ions that have either no valence electrons or a pair of electrons that have no net spin. Experiments in the literature for the scattering of hyperthermal Na^+ from metal surfaces [15,16] show that, in the absence of valence electrons, only a positive temperature dependence is observed. In these experiments, increases in the neutralization probability of about a factor of 2–3 were found when the sample temperature was raised from room temperature to 900 K. Figure 3(a) shows a similar factor of 2–3 increase in the NF of scattered Sr^+ when the surface temperature goes from 300 to 600 K. Figure 3(b) shows that when a group III ion with a pair of valence electrons, Ga^+, is employed, there is also a monotonic increase of the NF with temperature. By inserting the Ga velocity from the present measurements (~ 0.0186 a.u.) into the results given in Ref. [16], a similar increase would also be predicted. Thus, the magnitudes of the NF enhancements as the temperature is raised up to 600 K are all consistent with the single electron physics, while the decrease in the Sr^+ NF above 600 K is not.

In comparing the Sr and Ga results, two things can be noted. First, 2.0 keV ^{88}Sr has a velocity of 0.0134 a.u. after scattering from Au, which is slower than the velocity of scattered Ga. Thus, the temperature increase due to traditional RCT should be more dramatic for Sr than for Ga. In going from room temperature to 600 K, the Sr NF increases by almost a factor of 3, while the Ga NF increases only slightly, thus confirming this expectation. Second, the Sr ionization potential is smaller than that of Ga (6.0 eV), which explains why the Sr NF is always less than for Ga scattering.

In summary, we have demonstrated the role of correlated-electron effects in the scattering of low energy ions from a solid surface. A negative temperature dependence is seen with alkaline-earth ions that have an unpaired valence electron that acts as a spin impurity (Sr^+) and is absent when the ion has no net spin (Na^+ and Ga^+). Neutralization in ion-surface scattering is a novel approach for investigating the electronic structure of complex materials, which could lead to a better understanding of collective phenomena in general. Further experiments will involve well-characterized single crystal surfaces to enable detailed studies of the relationships between the formation of correlated-electron states and the atomic structure of the solid. We also expect this result to trigger a renewed theoretical interest in the problem of correlated-electron contributions to atom-surface scattering.

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