Double electron excitation in He ions interacting with an aluminum surface

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Observation of Auger electron emission from Al under the impact of He ions, at energies below the excitation threshold of Al-Al collisions, gives evidence for charge transfer in He-Al collisions. Excitation of $2p$-shell electrons in Al is produced by vacancy transfer, following double excitation of He by promotion of its $1s$ level. Studies of ion scattering from surfaces currently neglect the double excitation of He. We discuss implications on the debate about electronic excitations and energy deposition, which is relevant to many fields, since helium ions are applied in the characterization and imaging of materials.

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I. INTRODUCTION

The energy lost by atomic particles moving through solid materials governs important effects, such as scattering, sputtering, electron emission, and damage, that are of importance in many areas of research and technology, including astrophysics, plasma physics, materials science, and biomedical research [1–3]. Energy losses involve both nuclear and electronic stopping, meaning that the projectile kinetic energy is transferred to both the electronic subsystem of the solid, producing excitation and ionization [kinetic electron excitation (KEE)], and the nuclei, via the elastic scattering of the projectiles with target atoms. At low projectile velocity, both the nuclear and the electronic processes are sizeable. Moreover, elastic collisions generate recoils that, in turn, suffer from electronic and nuclear stopping, thus making the separation of the total energy loss into nuclear and electronic components a complex problem.

The basic known mechanisms of KEE, in the interaction of slow ions with metal targets, are excitation of valence electrons (mostly treated as an idealized Fermi gas) in binary projectile-electron collisions [4] and electron promotion in close atomic collisions [5]. Electron promotion occurs when atomic collisions transiently create quasimolecular systems in which some electronic levels are promoted to higher orbital energies. These processes are characterized by well-defined energy thresholds, which depend on the particular combination of collision partners and which can be experimentally determined and theoretically estimated from molecular-orbital (MO) correlation diagrams [5]. Promotion occurs either in binary collisions between the projectile and a target atom (asymmetric P-T collisions) and between recoiling target atoms (symmetric T-T collisions) in the atomic collision cascade initiated by incident projectiles. Excitations are accompanied by electron capture and loss processes in nonlocal interactions with the surface, before and after the close atomic encounter. These processes determine the charge, excitation states, and energy loss of scattered projectiles and of recoiling target atoms.

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Electron emission experiments have shown that electron promotion and charge-exchange processes play a major role in KEE induced by heavy ion impact on aluminum targets [6–8]. The Auger decay of Al $2p$ excitations produced in symmetric T-T collisions is the dominant primary KEE mechanism [7,8]. At impact energies lower than the threshold for excitation in T-T collisions, measurements performed using sodium projectiles showed that a significant contribution to the total electron emission yield comes also from a vacancy transfer process that produce Al $2p$ excitation in asymmetric P-T collisions between target atoms and incoming ions that have survived neutralization at the surface [8].

For light He ions, electron promotion effects do not produce a significant contribution to the kinetic electron emission yields that results proportional to the projectile velocity [4,9]. This observation is consistent with the expected linear behavior of the electronic stopping power (i.e., the energy lost to the electrons per unit length traveled by the projectile) for a light ion moving with a velocity lower than the Fermi velocity in a free-electron gas and measured in earlier experiments using the transmission technique [10,11]. On the other hand, measurements of the electronic stopping power of He ions backscattered from nanometer-thick polycrystalline Al films grown on Ta substrates revealed a surprising deviation from linearity at impact energies below 10 keV [12]. The nonlinear trend was attributed to charge-exchange processes induced by the repeated promotion of the $1s$ level of He close to the Al cores, in addition to valence electron excitations. At low impact velocity, the nonlinear electronic stopping power reported in Ref. [12] is lower than that reported in earlier measurements [10] and in very recent time-dependent density-functional-theory calculations [13,14], which do not consider electron promotion effects. This indicates an underestimation of the electronic stopping power in the backscattering experiments, likely due to the difficulty of disentangling the nuclear stopping contribution [9].

The interpretation of the nonlinearity in the electronic stopping power requires an energy loss of about 20 eV, determined by promotion of one electron at energies below the vacuum level, so that electron emission experiments do not

reveal the process. In this article we discuss the observation of the *LMM* Auger electron emission from Al excited by slow He ions, at impact energies below the threshold for excitation in symmetric T-T collisions. The $2p$ excitation in Al occurs in P-T collisions and is ascribed to a vacancy transfer process, similar to those observed for neon and sodium projectiles [8,15]. The process requires that promotion of the He $1s$ level produces a double vacancy in the projectiles, which is not considered in the commonly accepted view of helium ion scattering from surfaces [12]. Therefore, electron emission spectra provide unambiguous evidence for the occurrence of electron promotion and charge-exchange effects in He-Al collisions. Differently from heavier projectiles, promotion processes leading to Al $2p$ excitation do not produce significant effects on the total electron emission yields [4,9]. This indicates that KEE in the interaction of slow He ions with Al is dominated by valence electron excitation.

II. EXPERIMENTS

Electron energy spectra have been measured in an ultrahigh-vacuum system used in previous electron emission studies [9]. Electrons ejected from the Al sample were energy analyzed with a double-pass cylindrical mirror spectrometer operated inside a magnetic shield at constant pass energy of 50 eV and a resolution of 0.2 eV. The surface of the sample was normal to the axis of the spectrometer and at 12° and 45° with respect to the directions of the noble gases and Na beams, respectively. Sodium ions were produced in a thermal ionization source and noble-gas ions were produced in an electron-impact source, operated with 30-eV electrons to prevent contamination of the ion beam with doubly charged ions. The high-purity polycrystalline Al surfaces were sputter cleaned by 4-keV Ar^+ ions at 12° glancing incidence. The sputtering was continued beyond that required to remove any detectable level of contamination by Auger spectroscopy, and until the structure in the electron energy spectra became constant.

III. RESULTS

Figure 1 shows the peak, due to Auger decay of $2p$ excitation in aluminum, observed at ~63eV in the energy spectra excited by the impact of He^+ and Na^+ ions on Al, at impact energies E_0 of 1.5 and 0.55 keV, respectively. The spectra are shown arbitrarily normalized and displaced on the vertical scale for an easier visual comparison. $2p$ promotion in Al cannot occur in asymmetric P-T collisions with lighter atoms, as the promoted molecular orbital is the $4f\sigma$ one correlated with the $2p$ level of the lighter collision partner [5]. Moreover, at the impact energies of Fig. 1, $2p$ promotion in Al in symmetric T-T collisions between recoiling Al atoms is also excluded. The maximum energy that can be transferred in a collision between a projectile of mass m_1 and energy E_0 and an Al target atom of mass m_2 is $E_t = \gamma E_0$, where $\gamma = \frac{4m_1m_2}{(m_1+m_2)^2}$. With a helium ion energy E_0 of 1.5 keV, E_t takes a value of 675 eV, which is lower than the threshold energy $E_{\rm th} \sim 900$ eV required for the promotion of Al $2p$ electrons in binary T-T symmetric collisions between two recoiling target atoms. This is confirmed by the scatter plot in

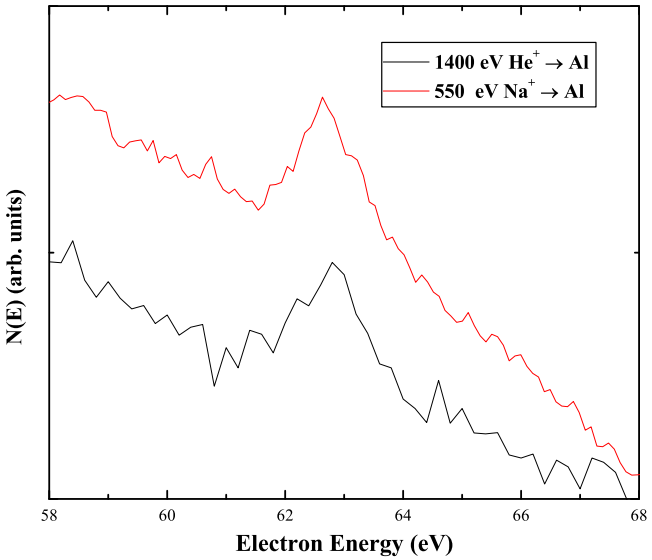

FIG. 1. Auger spectra of Al under the impact of Na^+ and He^+ ions at impact energies close to the observation threshold. The incidence angles of the Na^+ and He^+ ions are 45° and 78°, respectively, with respect to the surface normal.

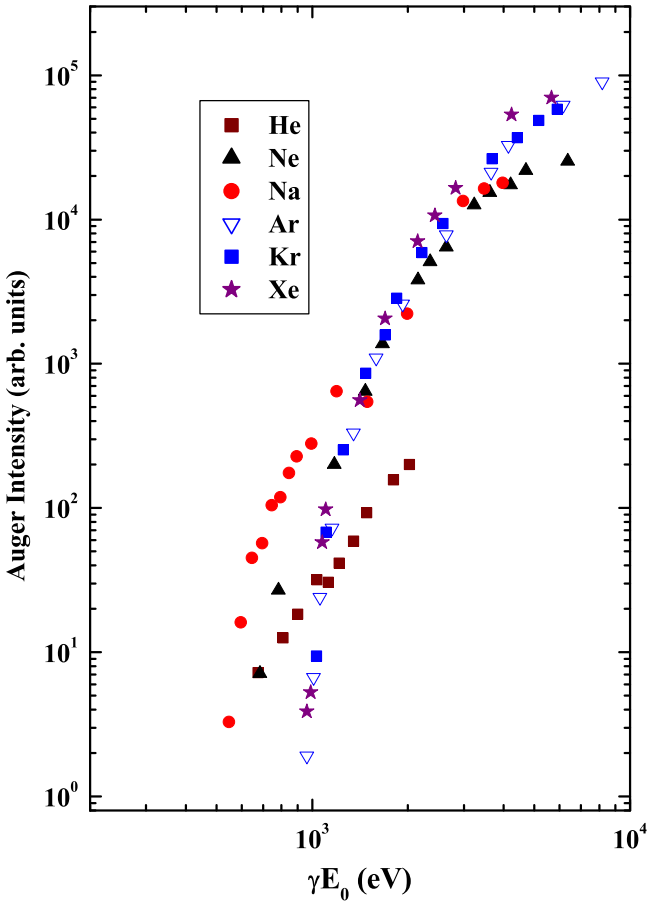

FIG. 2. Al Auger emission intensities for several projectiles vs γE_0, the maximum energy transfer in a projectile-Al collision. Data for noble-gas ions are taken from Ref. [18] and are shown after proper rescaling.

Fig. 2, reporting the intensities of Al *LMM* Auger electron emission in the interaction of several projectiles with Al, versus γE_0. Intensity of Auger electron emission from Al under ion impact has been studied extensively in the past [7,8,15–19]. In Fig. 2, the data for noble-gas ions have been taken from Ref. [18]. When Al L-shell excitation is dominantly produced in T-T collisions, near the threshold the Auger yields show the same behavior versus γE_0, independent of the projectiles [18,19]. The divergence of the yield curves at high γE_0 has been discussed in Ref. [19], and reflects the divergence of the cross section for P-T collisions, the precursor of the T-T collisions. Figures 1 and 2 show that lighter projectiles, such as He and Ne, as well as Na, produce Al Auger signals at impact energies below the threshold for T-T collisions. Therefore, these observations indicate that the L-shell vacancy in the target Al atoms can also be created in asymmetric collisions with lighter projectiles, where the promotion occurs in molecular levels correlated to atomic states of the projectiles. Therefore, we ascribe excitation of the $2p$ level of Al to a vacancy transfer process during the separation of the two atoms.

IV. DISCUSSION

A. Charge-exchange processes

For the He-Al collision systems, the promoted molecular orbital is the $3d\sigma$, correlated to the He $1s$ level [12,20]. This is also shown in the schematic energy diagram of Fig. 3, derived from adiabatic molecular-orbital correlation diagrams calculated in Ref. [20]. In a fast collision, the electronic system cannot evolve adiabatically, and electronic transitions can occur at the expense of the kinetic energy of incoming particles at the adiabatically forbidden crossings between molecular orbitals. The energy diagram indicates the diabatic promotion path of the $3d\sigma$ MO correlated to the projectile's $1s$ level in the separate atom limit. After He $1s$ promotion, excitation of the $2p$ level of aluminum is produced by a vacancy transfer process, during the separation of the two colliding partners. The important point here is that the initial state of the vacancy transfer process that produces the $2p$-shell vacancy in Al requires two holes in the $1s$ level of helium. Indeed, any transition in projectiles with only one hole would not release enough energy to excite a $2p$ electron in Al (whose binding energy is ~80.5 eV). It is likely that the vacancy transfer occurs during the separation of the two atoms via a two-electron transition similar to those observed for the Ne^+-Al and Na^+-Al systems, as well as for some other projectile-target combinations [8,15]. In this process, indicated by the arrows in Fig. 3, one of the two holes in the He projectiles is filled by an outer electron and the excess energy is simultaneously used to transfer a $2p$ Al electron into the other hole. Calculated MO correlation diagrams for the He-Al system [20] indicate that the process is energetically possible in the receding path over an extended range of internuclear distances.

The double projectile excitation and vacancy transfer in He-Al collisions implies a correlation between excitations in the projectile and in the target atom. This is reflected in electron emission experiments on the He-Al system [21]. These experiments showed that the Al Auger emission and

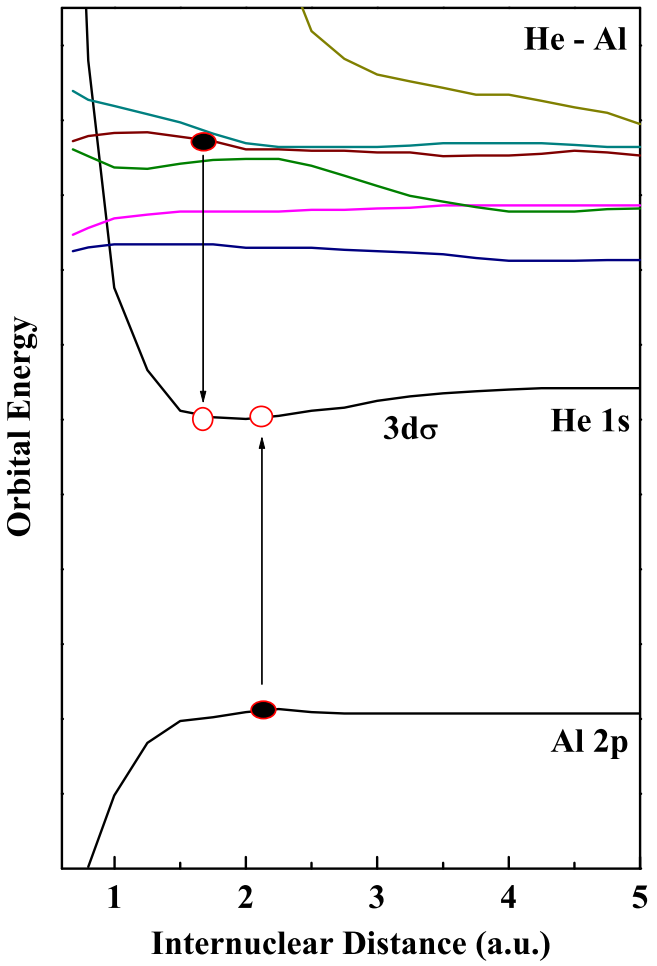

FIG. 3. Schematic energy levels for the He-Al quasimolecule, indicating the diabatic promotion path for the $3d\sigma$ molecular orbital correlated to the He $1s$ level in the separated atom limits. The arrows indicate the two-electron transition that produces a hole in the $2p$ level of Al.

the spectrum in the 15–40 eV electron energy range, due to the decay of collisionally excited states of projectiles, have the same dependence on impact energy as observed by a factor analysis of reported experimental spectra. An important implication of the double excitation in helium projectiles is the population of autoionizing states [22,23] that produce electron emission in the 30–40 eV energy range of the electron energy spectra. Judging from electron emission spectra in He-Al interactions [21], autoionization emission can produce a contribution, which calls for further experimental investigation and which should be considered in calculations.

B. Electron promotion and energy deposition

Electron promotion and Auger decay of the $2p$ excitation in Al is the primary electron excitation mechanism in the case of slow, heavy projectiles such as Ne, Na, Ar, and Kr [7,8,16,17]. This is particularly evident in the case of slow sodium projectiles, for which potential electron emission is also excluded, revealing a sharp increase of the total electron emission yields at the threshold for Al $2p$ excitation via

vacancy transfer [8]. Our findings show that processes leading to Al Auger decay are also active in the case of slow He ion impact on Al, but, in contrast, they are not even revealed in measurements of total electron emission yields [4,9], showing that the energy deposited into the electronic subsystem by promotion processes in He and Al atoms is far less than that deposited by direct excitation of valence electrons.

Moreover, the interpretation of the recently reported nonlinearity of the electronic stopping power of He in Al relies on energy losses of about 20 eV, so that electrons are excited below the vacuum level and not revealed in electron emission experiments [9,12]. This interpretation is based on the single-electron promotion and reionization process first proposed by Souda *et al.* [20]. The observation of Al Auger electrons demonstrates that electron promotion and charge-exchange processes can result in electron excitation well above the vacuum level and projectile energy losses larger than those considered in the single-electron promotion mechanism [12,20]. This implies an important change in the current view of electron promotion, electronic energy losses, and excitation in He scattering from surfaces, as the double He excitation is the only promotion and charge-exchange process that is demonstrated, whereas the reionization mechanism [9,12,20] is not conclusively established. This calls for an extensive investigation, whose need is further stressed by the observation that two-electron promotion is the dominant excitation channel in neutralized Ne projectiles scattered off Al surfaces, whereas energy losses associated with single-electron promotion have not been revealed (see Refs. [24,25], and references therein). Therefore, measurements of autoionization electron emission and of the inelastic losses for different charge states of scattered projectiles are in order to clarify the interplay and competition between processes involved in scattering and electronic excitation of He ions at the surfaces.

V. CONCLUSIONS

The Auger decay of the Al $2p$ shell, excited in binary asymmetric collisions with incoming helium projectiles at impact energies below the threshold for excitation in symmetric collisions between recoiling Al atoms, signals the production of a double excitation of the projectiles in asymmetric collisions. This provides unambiguous evidence of electron promotion and charge transfer in the He-Al system, showing that these processes play a minor role in kinetic electron excitation that, for the He-Al system, is dominated by direct valence electron excitations. The notion of the double excitation needs to be considered for a detailed description of excitations and charge-exchange processes produced by He ions. This provides direction for further extensive investigations to improve the knowledge of the scattering and energy loss of He ions at surfaces, which is relevant to many fields of research, in view of the important applications of helium ions in scattering spectroscopy and in microscopy.

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