Decay of Zn Impurity Excitations in Simple Metals

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By tuning the $4p$ level of excited Zn* $3d^94s^24p$ impurities through the conduction-band bottom of alkali metals, we show that the rate at which the excited-impurity configuration decays into conduction-band excitations is insensitive to the extent of $4p$ admixture into the host conduction band. However, the optical matrix elements change markedly with the degree of valence mixing.

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The processes by which core holes in metals decay are not yet quantitatively understood. It is observed that fluorescence of the core-excited state is suppressed; this is consistent with the dominance of the competing Auger-like channels by which the locally excited state decays into conduction-band excitations of the metal.[1,2] A systematic documentation of these phenomena and of the solid-state effects that influence them nevertheless remains lacking. In this Letter we report experiments which identify the role of degenerate mixing between local levels and the states of the conduction band. Electronic screening in metals is completed in about the plasma period, typically $\sim 10^{-16}$ sec. A core hole whose lifetime exceeds this period must therefore be neutralized by valence states. This can be accomplished by a localized valence orbital which is bound below the conduction-band bottom, or by a local deformation of the conduction band itself. Our experiments employ the $3d^{10}4s^2 \to 3d^94s^24p$ excitation channel of an impurity, namely Zn, in alkali metals. By choice of alkali host the Zn* $4p$ level can either be bound below the band bottom as a localized state or made to mix fully into the conduction band. The effect of this level tuning on the excitation and on its decay characteristics are described in what follows.

The differential reflectance spectra in Fig. 1 for Zn at low coverage $\theta \sim 10^{14}$ cm^{-2} on each of the alkali metals were obtained by methods described elsewhere.[3,4] The spectra change with coverage to become Zn-like at $\theta \sim 10^{16}$ cm^{-2}. All samples were prepared *in situ* in ultrahigh vacuum on substrates held at liquid-He temperature. A thick reflecting layer of fresh Mg was first laid down, followed by ~100 Å of alkali metal; the Zn adsorbate layer was added after a background scan of the alkali surface, and the reflectivity change was then determined. We have previously established that for a Mg reflector in the present energy range these methods yield almost undistorted absorption spectra.[3] Results for Zn impurities alloyed into bulk alkali metals are quite similar to the results for the analogous adsorbate systems (see below).

Zn-adsorbate spectra have certain features in common for all the alkali substrates. In each host the Zn introduces an absorption continuum which is weakly dependent on Zn coverage and has the same magnitude within a factor of 2 for all alkali metals. It undoubtedly arises from optical excitations of electron-hole pairs in the con-

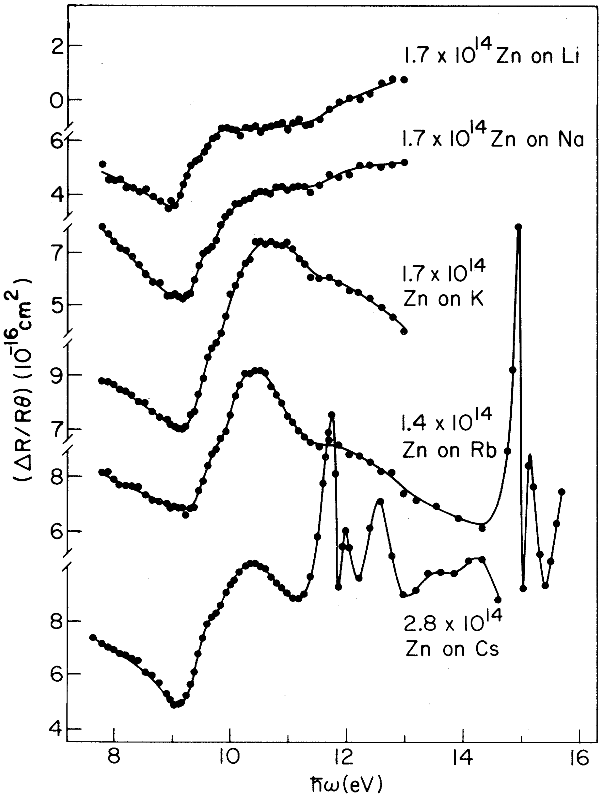

FIG. 1. Differential reflectance spectra for Zn at low coverage on alkali metals divided by θ (in 10^{14} cm^{-2}) to show the signal per atom.

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duction band. These impurity-induced processes must take place at impurity sites. A second major feature is the strong resonance visible in all cases near 9 eV. A dip in the continuum occurs there, followed at higher energy by increased positive absorption, and with clear evidence of doublet structure. Also, the normalized resonance amplitude increases with decreasing coverage as Zn near neighbors are eliminated. The resonance undoubtedly arises from the Zn $3d^{10}4s^2 \rightarrow 3d^9 4s^2 4p$ core excitation, red-shifted from its atomic position[5] near 11.17 eV, and with a core spin-orbit splitting of ~0.6 eV, similar to that observed by photoemission on pure Zn.[6] The impurity ground state, and the local Zn excitation and the excited continuum, are indicated in Figs. 2(a)–2(c).

It is clearly apparent from the experimental results that the excitation channel to the local configuration 2(b) interferes with that to the continuum state 2(c). This causes the absorption dip at the resonance threshold first explained by Fano and co-workers[7] for atoms. The effect in the metal is the analog of the autoionization which occurs in the excited Zn atom.[8] From the data one can determine the rate at which the local excitation decays into the continuum of host excitations, and the way the decay depends on the environment of the Zn atom. Fano profiles of core levels in metals have previously been recognized in absorption measurements[9] and in energy-loss[10] and photoemission data.[11] In the present case, the results permit a sensitive exploration of the influence of the Zn environment.

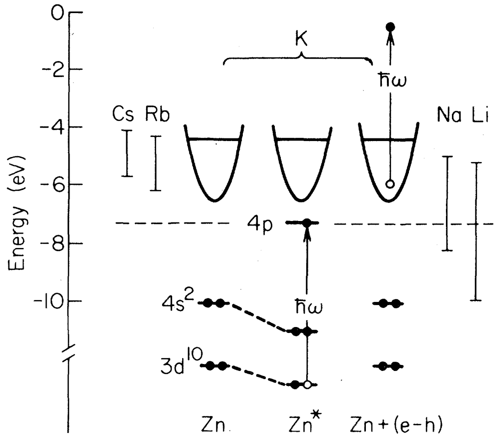

FIG. 2. The orbitals of Zn relative to the conduction band of K are shown in (a). Part (b) shows the locally excited configuration and (c) an electron-hole excitation into which (b) decays. The bands of the remaining alkali metals, indicated by bars, show that the Zn* $4p$ orbital mixes with the conduction bands of Na and Li but not Cs, Rb, and K.

Certain differences among the spectra in Fig. 1 also warrant immediate comment. Large, sharp features occur in the spectrum of Zn on Cs near 11.8 eV and Zn on Rb near 14.9 eV. These arise because the adsorbed Zn disturbs the O_{23} absorption edge of neighboring surface Cs atoms[12] or the N_{23} edge of the surface Rb atoms,[12] in the two cases; the effect is detected in the difference spectrum. Its occurrence in proportion to Zn coverage confirms that Zn does interact with the metal and is not clustered. A second observation, having fundamental significance, is that both the resonance and the continuum for Zn on the two lighter alkali metals differ from those for the remaining alkali metals. For the heavier alkali metals, the continuum appears to fall off rapidly above 10 eV. The resonance shows featureless absorption at high energy for Li and Na, but instead exhibits a sharp positive peak before tailing off for the heavy-alkali substrates K, Rb, and Cs. The same features have been observed in Zn–alkali-metal alloys. It is this distinction that makes the Zn resonance appear so different for the light- and heavy-alkali substrates.

Differences between the light- and heavy-alkali substrates may be quantified by fitting the observed spectra with a chosen background variation together with a Fano-Beutler interference profile[7]:

$$S(\hbar\omega) = A(q+\xi)^2/(1+\xi^2)\,, \qquad (1)$$

with

$$\xi = (\hbar\omega - E_0)/\Gamma, \quad \Gamma = \pi V^2, \qquad (2)$$

and

$$q^2 = |\langle l\rangle|^2/\pi V^2 |\langle c\rangle|^2. \qquad (3)$$

Here V is the Coulomb matrix element which causes the decay by coupling the local excitation l to the continuum states c, and q is the ratio of their optical matrix elements scaled as shown. Γ is the rate at which l decays into c, and E_0 is the line center when shifted by the interaction.

The fits to adsorbate and alloy Zn results shown in Fig. 3 for both light and heavy alkali metals employ a spin-orbit splitting near 0.6 eV and a ratio of 3:2 between the $D_{5/2}$ and $D_{3/2}$ hole amplitudes.[13] As indicated in Fig. 3 and Table I,

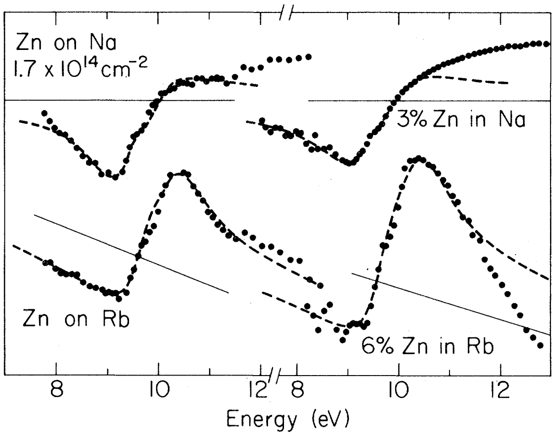

FIG. 3. Fits of Fano-Beutler profiles (solid lines) to the central parts of the resonances of Zn adsorbed on and desolved in Na and Rb (experimental points). The observed curves show more doublet structure at the line center than the synthesized curves, possibly because of $D_{5/2}, D_{3/2}$ $(J=1)$ interference. The main point of interest is the relatively constant width (see Table I).

a sloping continuum and $q \sim 1.5-2$ are required to fit the results for Rb, whereas the Na results can be accommodated by a flat continuum and $q \simeq 0.6$. Experience with the data has shown that the range of parameters giving acceptable fits over the line centers is rather limited. Therefore the results in Table I establish an unambiguous conclusion. The Zn* decay rate, Γ, does not vary by more than about 20% in passing from the surface to the bulk or from light- to heavy-alkali hosts. Instead, the striking observed change of line shape with host lattice arises almost entirely from a variation of the optical matrix elements $\langle l \rangle / \langle c \rangle$. Note that the doublet structure remains more prominent at the line center in the observed curves than in the fits. This may be a consequence of interference between the $D_{5/2}$ and $D_{3/2}$ $(J=1)$ processes, which occur in the atomic spectrum.[8]

To complete the interpretation we note here the critical fact that the Zn $4p$ level lies below the conduction-band bottoms of Cs, Rb, and K but mixes into the conduction bands of Na and Li. The range of band energies for each of the five alkali metals is displayed in Fig. 2, together with the Zn $4p$ energy. Note that these are not total energies needed to *extract electrons from the solid* (as in photoemission); they are orbital energies relevent to *exchange and mixing between* two states[14] so that surface effects (e.g., the work function) do not enter. In Table I, Γ varies very little among alkali hosts. We thus conclude that *the distinction between localized state and band screening has at most a small effect on configurational decay rates.* The contrary is true, however, of the optical matrix elements. Table I makes clear that the ratio $\langle l \rangle / \langle c \rangle$ is about 3 times larger for the bound excited $4p$ state in K, Rb, and Cs than for the admixed $4p$ state in Li and Na.

Although numerical values of q cannot be predicted at present, the qualitative behavior of the matrix elements has a simple significance in terms of the Zn* electronic structure. The closed-shell $3d^{10}4s^2$ Zn ground state is rare-gas-like and, being neutral, excludes conduction electrons from its atomic cell.[15] When the $4p$ level is bound, the $3d \rightarrow 4p$ transition is wholly corelike, and the conduction electrons are only weakly perturbed for K, Rb, and Cs. To the contrary, a transition to a $4p$ level which is admixed into the band causes a strong perturbation. As a result, the oscillator strength is spread to higher energies by the Anderson orthogonality catastrophe.[16] Thus $\langle l \rangle$ is reduced, and the profile is smeared over a range of energies above threshold, in qualitative accord with the observed profile and deduced q for the Li and Na substrates.

Our final, more speculative comments concern the rate at which local configurational decay takes place in metals. A recent view[17] holds that the Hartree-Fock description of optical properties

TABLE I. Parameters for fits of Fano-Beutler profiles to Zn resonances in Fig. 3. Note that the decay width Γ varies by only $\sim 20\%$.

Zn	q	Γ (eV)	A (10^{-15} cm^2)	E_0 (eV)	$\langle l \rangle / \langle c \rangle$	Spin-orbit (eV)	Ratio
On Na	0.50	0.47	1.08	9.3	0.61	0.60	3:2
On Rb	1.53	0.50	0.57	9.7	1.92	0.55	3:2
In Na	0.60	0.60	1.25	9.3	0.82	0.60	3:2
In Rb	1.70	0.55	0.95	9.75	2.23	0.50	3:2

breaks down because the electron and hole created in the optical event can attract each other to form a distinct excitation of the conduction-electron system. This happens even at low photon energy and in translationally invariant pure metals like Mg.[18] Also, the effect can be greatly enhanced by the added ability of an impurity field to trap the interacting electron and hole, and so form a locally deformed and excited configuration of the conduction-electron liquid. From the Hartree-Fock viewpoint one may have (i) both the electron and hole, (ii) just the hole, or (iii) neither the electron nor the hole occupying *bound* impurity orbitals. The relevance of the present work is the demonstration it provides that the transition from (i) to (ii) has little effect on the configuration lifetime, and the consequent indication that configurations of type (iii) also may be long lived. The $3s^2 \rightarrow 3s3p$ resonances of Mg at about 0.8 eV in pure Mg (bandwidth 6.5 eV)[18] and at about 2.8 eV in Li (bandwidth 4.5 eV)[17] are possible examples of long-lived localized resonances of two otherwise unbound carriers in a conduction-electron liquid. The excited $3p$ orbital of Mg* is much like the Zn* $4p$ orbital on which the present work is focused. It is therefore of some interest that the Mg* $3s3p$ width is similar to the decay rate Γ deduced here for the Zn* $3d^9 4s^2 4p$ configuration and that a type (iii) resonance may therefore have a lifetime comparable with those of type (i) and (ii) resonances.

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[1] H. W. B. Skinner, Philos. Trans. Roy. Soc., Ser. A 239, 95 (1946).

[2] A theoretical discussion is given by T. Kobayashi and A. Morita, J. Phys. Soc. Jpn. 28, 457 (1970). Several useful articles and references will be found in Jap. J. Appl. Phys. 17, Suppl. 17-2 (1978), Proceedings of the International Conference on X-Ray and XUV Spectroscopy, Sendai, 1978.

[3] J. E. Cunnginham, D. K. Greenlaw, and C. P. Flynn, Phys. Rev. B 22, 717 (1980).

[4] T. H. Chiu, Ph.D. thesis, University of Illinois, 1983 (unpublished).

[5] C. E. Moore, *Atomic Energy Levels* (National Bureau of Standards, Washington, D.C., 1971).

[6] A. D. McLachlan, J. G. Jenkins, J. Liesegang, and R. C. G. Leckey, J. Electron Spectrosc. Relat. Phenomena 3, 207 (1974).

[7] U. Fano, Phys. Rev. 124, 1866 (1961); U. Fano and J. W. Cooper, Rev. Mod. Phys 40, 441 (1968).

[8] See, e.g., A. W. Fliflet and H. P. Kelly, Phys. Rev. A 10, 508 (1974).

[9] R. Avci and C. P. Flynn, Phys. Rev. B 19, 5981 (1979).

[10] G. P. Williams, G. J. Lapeyre, J. Anderson, R. E. Dietz, and Y. Yafet, J. Vac. Sci. Tech. 16, 528 (1972).

[11] L. I. Johansson, J. W. Allen, I. Lindau, M. H. Hecht, and S. M. B. Hagstrom, Phys. Rev. B 21, 1408 (1980).

[12] See, e.g., T. Ishii, Y. Sakisaka, T. Hanyn, H. Ishii, and S. Yamaguchi, J. Phys. Soc. Jpn. 42, 876 (1977).

[13] This is the ratio for ideal spin-orbit components; other ratios may be observed in practice. See, e.g., R. A. Pollack, S. Kawalczyk, L. Ley, and D. A. Shirley, Phys. Rev. Lett. 29, 274 (1972).

[14] We treat the Zn$(3d^9 4s^2)^-$ and alkali metal $(np^6)^-$ cores as rigid. The atomic Zn ^4p and alkali metal $(n+1)s$ orbital energies are then the respective ionization energies. Both are lowered by cohesion into the metal, and the alkali-metal levels are further spread by E_F about this mean. These are the energies shown in Fig. 2. We employ the observed alkali-metal cohesion and bandwidth, and the "$Z+1$ model" for the impurity-level cohesion [see e.g., C. P. Flynn, J. Phys. F 10, L315 (1980)]. Similar ideas are employed to treat degenerate mixing in alkali-alkali alloys by T.-H. Chiu, D. L. Gibbs, J. E. Cunningham, and C. P. Flynn, J. Phys. F 13, L23 (1983).

[15] The $4s$ binding energy is 9.39 eV in vacuum. In the metal it must lie at or below the band bottom even for the Li host lattice (see Fig. 3).

[16] P. W. Anderson, Phys. Rev. Lett. 18, 1049 (1967).

[17] G. A. Denton, M. Bakshi, and C. P. Flynn, Phys. Rev. B 26, 3495 (1982). For a review of earlier ideas, see D. J. Sellmyer, *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1978), Vol. 33.

[18] M. Bakshi, G. A. Denton, A. B. Kunz, and C. P. Flynn, J. Phys. F 12, L235 (1982); A. B. Kunz and C. P. Flynn, Phys. Rev. Lett. 50, 1524 (1983).