Emission Spectra and Core-Hole Lifetimes from Anomalous X-Ray Edges in Alloys

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We report emission spectra and core-hole lifetimes for rare-gas and alkali-metal impurities in alkali-metal host lattices. The results lead to new proposed explanations for the anomalous core absorption edges reported in earlier work.

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Quasiparticles are created and scattered when a metal is suddenly perturbed in the locality of an atom, as when one core is excited. The resulting energy uptake may be determined on an energy scale of 10 meV to 10 eV by soft x-ray absorption (SXA) or emission (SXE), as well as electron spectroscopies such as photoemission.[1] In many instances the distinctive spectra near threshold agree fairly well with a ΔSCF (change of self-consistent field) treatment of the optical event known as Mahan-Nozières-de Dominicis (MND) theory.[1,2] An exception occurs when the core excitations of impurities are used a selective probes for the conduction-electron response in the simplest metals. Alkali-metal and rare-gas impurity centers in alkali metals have absorption spectra in qualitative disagreement with theory. For rare-gas impurities the edge anomaly expected from recent detailed theory[3] is completely suppressed,[4] while the alkali-metal edges exhibit major systematic changes of unknown cause.[5] These difficulties are significant because the systems are simple and the results should be straightforward. In this Letter we report the first SXE observations of the anomalous systems. By emission methods we have also made the first determinations of core-hole lifetimes of impurity centers in metals. The SXE spectra are consistent with the earlier anomalous SXA data. However, the combined results point to new interpretations of the measurements.

Our results were obtained with a high-brilliance emission apparatus in which core excitations are produced by a focused 2-keV electron beam. Samples were prepared *in situ* by dual-beam methods on a substrate maintained at temperatures down to about 12 K. This was necessary as the alloys of interest here are unstable and decompose above about 25 K. Earlier studies of emission from heavy alkali metals with this new system have been reported.[6] It can detect impurities at the 1% level with good signal-to-noise ratio. This is a difficult regime for electron spectroscopies (e.g., photoemission), where the shallow probe depth can lead to problems with signals from surface segregation for such dilute systems.

From alloys among the heavy alkali metals Cs, Rb, and K we observe core spectra that exhibit sharp, often cusped, threshold profiles, as in absorption.[5] This is generally consistent with the power-law edge profile of MND theory $\sim(\hbar\omega - E_t)^{-\alpha_0}$ with $\alpha_0 = 2\delta_0/\pi - 2\sum_l (2l+1)\delta_l^2/\pi^2$ positive. The δ_l are phase-shift changes for electrons at E_F. However, just as in SXA, qualitative changes of this threshold behavior are observed when these atoms are impurities in Li and Na. The SXE and SXA edge profiles for each impurity broaden, as shown in Fig. 1 for Cs, Rb, and K at dilution in Li. The important point is that in each case emission and absorption cross at about their half heights and do *not* begin abruptly at a common, electronically relaxed threshold energy. This establishes[7] that one or both spectra contains added

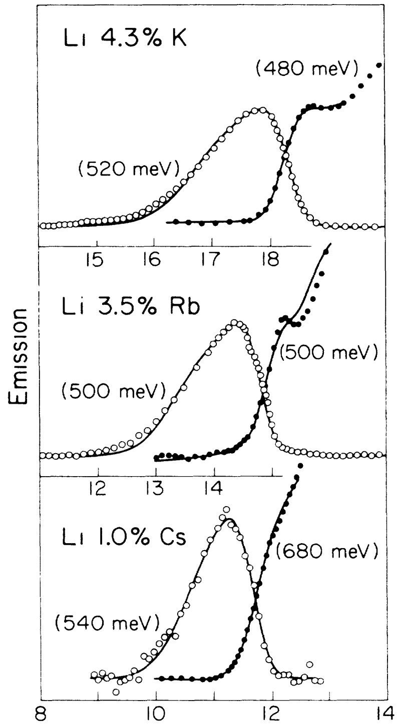

FIG. 1. Absorption (Ref. 5) and emission (present) data for K, Rb, and Cs impurities in Li for the concentrations noted. Solid lines are fits with pure metal spectra broadened by Gaussians of widths indicated.

broadening. In Fig. 1 the lines model the data by *pure* metal spectra,[6,8] each broadened by a single Gaussian of chosen width (see figure) that is similar in SXE and SXA. The associated host-induced energy shifts are quite small at ≃100 meV. While the fits are not perfect they suffice to establish that the main effect of the Li host (as for Na also) is to broaden the thresholds, with only small shifts.

Earlier discussions[5] of the SXA data presume that the extra width is largely electronic in origin. The new data show with certainty that this is not the case. In both SXE and SXA the threshold is broadened by some additional process. Candidate mechanisms are inhomogeneity, due to the different alloy environments samples by a species, and phonon creation caused by the differing relaxed positions of atoms in the ground and electronically relaxed excited states. Lifetime widths are eliminated as possible factors by results described below. Inhomogeneity cannot give widths that increase, as seen in both SXE and SXA, all the way to the dilute limit, because cores experience the most diverse environments near equiatomic mixtures, not when surrounded, e.g., by Li.[5] Defect structure caused by the large misfit of heavy alkali metals in Na or Li could possibly broaden the spectra at dilution; efforts to anneal such structure resulted in precipitate spectra, not narrower alloy spectra. Estimates of phonon widths from simple models[9] for alkali-metal impurities indicate Gaussian widths in excess of 0.5 eV for Cs in Li, and thus fall in the range of the observed effects. There remains a difficulty that the Stokes shift from so large a phonon coupling is normally >1 eV, and no such shift is observed.[5] Our results do not resolve these questions. They do show unambiguously that effects other than electronic recoil are present.

Shallow core holes in metals decay mainly by Auger processes[1]; at present few lifetimes are known. From the emission edges of Cs, Rb, and K,[6] by deconvolving temperature-dependent phonon and Fermi edge widths, we have determined the lifetime widths to be 50 ± 20 meV, 25 ± 10 meV, and 15 ± 10 meV, respectively.[10,11] With earlier estimates of 10 meV for Na (Ref. 7) and 15 ± 2 meV for K,[12] these allow the trend of width with mass through a column of the periodic table to be seen for the first time. No theory for this behavior is yet available. The Auger process short-circuits the photon emission and so determines the absolute emission intensity.[13] From the observed emission strengths, assuming that absorption and emission are not much changed, we have determined the lifetimes in alloys relative to the known values for the pure metals. We find that the relative lifetimes of K, Rb, and Cs obtained from the edge *widths* are correctly reproduced by their emission *strengths*, when scaled by optical matrix elements of the atom.[14] Figure 2 shows how the impurity lifetimes vary systematically with the bandwidth actually observed in emission for the particular alloy or pure metal. The smooth trend tends to support further the assumption that it originates largely in the Auger rate alone. These new techniques will be described in detail elsewhere. The large rate changes in Fig. 2 most probably occur in the Auger matrix elements, as the remaining factors in the Auger rate, as usually discussed,[1,13] concern only density-of-states terms that seem unlikely to produce such effects. If so, the role of the Coulomb interaction in the structure of these quite dilute electron liquids appears to be a determining factor.

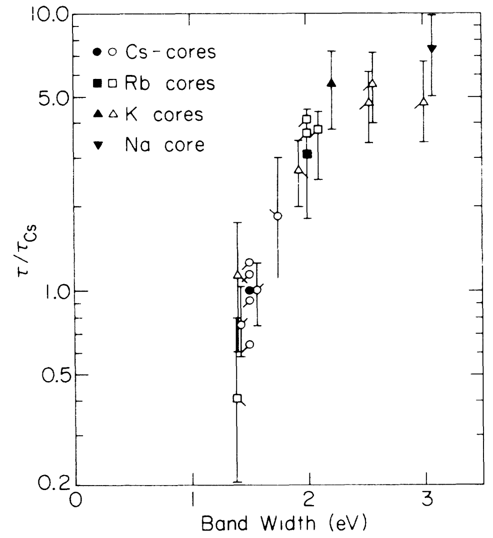

FIG. 2. Deduced core-hole lifetime vs bandwidth observed in emission. Solid points are results for pure metals from the profiles and open points are for alloys from the intensities. Alloy host lattices are coded by ticks as follows: lower right: Cs; upper left: Rb; upper right: K; lower left: Li.

In addition, we have successfully investigated the emission from rare-gas impurities in alkali-metal hosts. These are the first reports of the process. It is of special interest for the anomalous SXA profile[4] and because the $np^5(n+1)s$ excited rare gas resembles the $np^6(n+1)s$ alkali-metal ground state, so that recombination takes place from an electron liquid of almost uniform density.[4] SXE results for the dilute limit of Kr in Rb and Cs are shown in Fig. 3, together with the comparable SXA data.[4] To interpret the Kr emission we use recent detailed predictions (broken line) from Meltzer, Pinski, and Stocks[3] peaked by an MND exponent $\alpha_0 = 0.14$ and broadened by a 180-meV lifetime width to obtain the solid line through the data. This is a good fit except that the emission peak is too sharp (see inset) for the lifetime width needed to fit the emission edge. It is important that the absorption and unbroadened emission have the same threshold to within an uncertainty of ≃50 meV. A similar analysis of Xe data with use of the Kr calculation shifted and scaled yields the same overall result. We conclude that the rare-gas SXE and SXA *do* closely share a relaxed electronic threshold, which occurs at the

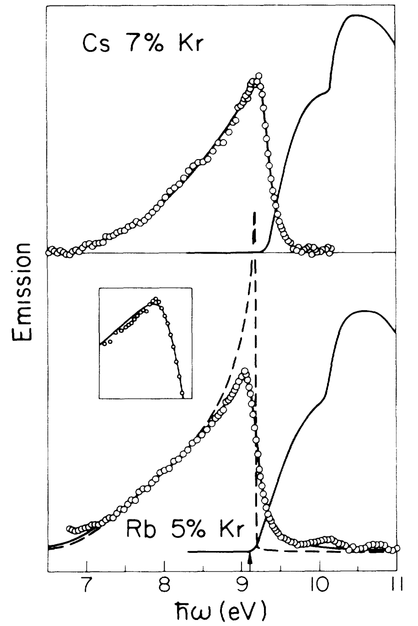

FIG. 3. Kr emission in Rb and Cs, for the concentration indicated, together with comparable absorption results (Ref. 4). The line through the emission for Kr in Rb is the theory shape (broken line) convolved with a lifetime width of 180 meV. Note the common threshold of absorption and unbroadened emission, close to the predicted position (arrow).

calculated position (arrow),[4] but show a striking lack of mirror symmetry. The results thus present a significant challenge.

From the emission intensity relative to the host alkali metal, we have also estimated the rare-gas impurity core-hole lifetimes, using theoretical[14] and experimental[15] oscillator strengths of the rare-gas and alkali-metal atoms to scale the relative excitation and emission rates for the two species in the metal. The apparent Auger lifetimes of Xe relative to K, Rb, and Cs are 1.1, 1.3, 6.7, and for Kr, 1.2, 1.3, 4.6, which give deduced widths of about 14 meV for Kr and Xe, without much host effect. These rare-gas effective lifetimes are comparable with, but less size dependent than, those of the alkali-metal atoms in the same metals. The Auger rate for the rare-gas *atom* is, of course, zero, but no sign of a corresponding increase of emission brightness is apparent in the alloy.

As the rare-gas edge behavior departs from standard models we offer the following discussion of its possible origin. The lowest excited level of the rare-gas *atom* has $J=2$ and is optically forbidden.[16] Core-valence exchange lowers $J=2$ some 100 meV below the $J=1$ $np^5(n+1)s$ optical process. We conjecture that these levels must remain, to a degree, distinct in the alkali-metal environment also. The absorption and emission are now explained as follows. Absorption takes place to the optical level, which then relaxes by spin flips to an appropriate admixture. Emission occurs in part from the optical level, whose fast spin-flip decay is measured by the broad emission edge, and in smaller part from the weakly emitting but longer lived relaxed level, which adds the sharpness of the emission peak. Excellent emission fits are achieved with the prediction of Meltzer, Pinski, and Stocks,[3] with 75% of the signal broadened by a 180-meV lifetime and 25% red shifted by 100 meV and having a 30-meV lifetime. In this language, the $J=1$ final state localizes a spin-down electron whereas the correctly screened excited level localizes a spin-up electron, with phase shifts at E_F of $\delta_\uparrow=\pi$ and $\delta_\downarrow=0$. It is thus of interest that with these phase shifts the MND theory gives a threshold exponent $\alpha_0=-1$, which is to be compared with the anomalous value $\alpha_0=-0.9\pm0.1$ actually observed for the rare-gas impurities.[4] In an alternative language, it is our conjecture that the optically forbidden level "eats a hole" (in the Fano[17] sense) into the threshold of the continuum of optically allowed transitions from the impurity core to the band, which modifies the profile. The reported connection[4] between the intensity of the core absorption and the density of host band states may occur through the Fano effect.

Existing studies of group VII (halogen), group VIII (rare gas), group I (alkali-metal) and group II (zinc) impurities in alkali metals place these ideas in context.[18] The $(n+1)s^2\,{}^1S_0$ excitations of the alkali-metal cores, which clearly lack valence degeneracy, also exhibit no Fano effect. However, group VII and group II centers display striking, if poorly understood, interferences of the core threshold with an underlying impurity-induced continuum. The same centers as adsorbates exhibit much the same behavior as the bulk impurities.[18] Fano-type processes at rare-gas thresholds may thus fit an established pattern of behavior. The way core-valence exchange affects core profiles of metals has been discussed widely[1] mostly for splittings small relative to E_F where the spin dependence of the δ_l is small. Here, in contrast, we propose that the configurations may have large spin polarizations consequent upon small interactions, $\simeq 100$ meV. Local configurational changes driven by small differences of *total* energy are indeed observed in metals, particularly in the alkali metals.[19] Thus these ideas remain as attractive possibilities to be explored further in future research.

In summary, we report emission profiles and lifetimes of outer core holes for alkali-metal and rare-gas impurities in alkali metals. The two cases differ in that the anomalous rare-gas profiles prove to have electronic origins, perhaps related to interference processes, while the alkali-metal width anomalies arise from other causes, most probably phonons. A new method for hole lifetime determinations appears to offer wide future applications.

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