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Sharp Optical Spectra of Impurities in Metals*

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We report sharp optical absorption spectra, lacking evidence of carrier-pair creation process, for both like and unlike rare-gas atom pairs in alkali metals. The excited molecular orbital is probably a virtual bound state. These pair spectra also provide insight into optical properties of solid rare gases.

Optical excitation spectra of local centers in metals usually have threshold edges with continuum absorption extending for many eV on the high-energy side.[1] The lack of sharp, symmetrical absorption lines has been attributed to the electron-hole pair-creation process occurring in the recoil of the Fermi liquid to its self-consistent excited configuration.[2] These are, for example, the characteristics of both host and impurity core excitations in metals when the hole is effectively localized on one lattice site. In this paper we report the first observation of sharp impurity spectra lacking free-carrier creation processes. The sharp lines are identified unambiguously as arising from pairs of rare-gas atoms in alkali metal hosts. In width and location they resemble the exciton lines observed in rare-gas solids. Their emergence in metallic hosts undoubtedly indicates that the excited diatomic molecular orbital exists as a virtual or bound level coupling weakly with the host electron gas.
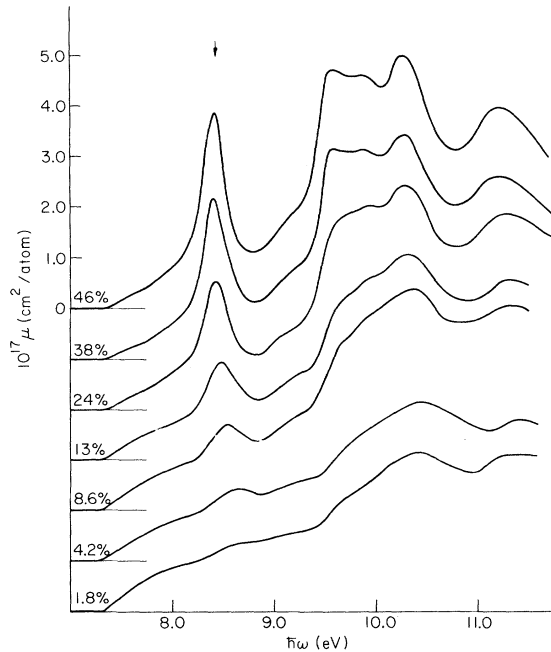
Figure 1(a) shows for various Xe concentrations c (at.%) the logarithm of the absorption *per impurity atom* by Xe impurities in K at 7°K. The experiments determined the loss of transmission, using methods described elsewhere.[3] Very similar results have been obtained for Xe and for Kr in all the alkali metals. In each case sharp lines emerge with increasing impurity concentration. The observed peaks are extraordinarily sharp (~ 200 meV full width) and symmetrical for metals. A different pattern of lines emerges in Fig.

1(b), which shows the impurity absorption when various concentrations of Ar are added to K containing ~ 2-at.% Xe.

The origins of the sharp structure are clarified by Figs. 2(a) and 2(b), which show the peak heights as functions of impurity concentrations c_{Xe} and c_{Ar}. In Fig. 2(a) the height of the peak in Fig. 1(a) is shown to depend linearly on c_{Xe}. As Fig. 1(a) depicts the absorption per Xe atom, Fig. 2(a) shows that the peak height rises in proportion to the probability with which sites neighboring each Xe are occupied by Xe atoms. In Fig. 2(b) the incremental heights of the absorption peaks for K containing both Xe and Ar [see, e.g., Fig. 1(b)] are shown to depend linearly on the product $c_{Xe}c_{Ar}$ of the impurity concentrations. For random distributions of species among sites in the alloys, the results of Fig. 2(a) establish unambiguously that the sharp peaks in Fig. 1(a) are associated with two Xe atoms occupying neighboring sites. Similarly, the results of Fig. 2(b) show that the peaks in Fig. 1(b) are associated with Xe-Ar pairs. The random nature of the alloys is established in the following paper[3] concerning the metal-insulator transition.

Figures 1 and 2 also indicate that nearest-neighboring rare-gas atoms in metals maintain two (or more) competing excitation channels that combine to keep the total oscillator strength approximately constant (as indicated by the areas under the curves in Fig. 1). This follows from the fact that a channel blurred by electron and hole creation processes is unlikely to produce

sharp structure. A detailed understanding of the channels must accommodate the observation that the sharp peaks grow linearly out to concentrations ~ 40 at.% (see Fig. 2) at which few if any impurities remain in isolated impurity pairs; most
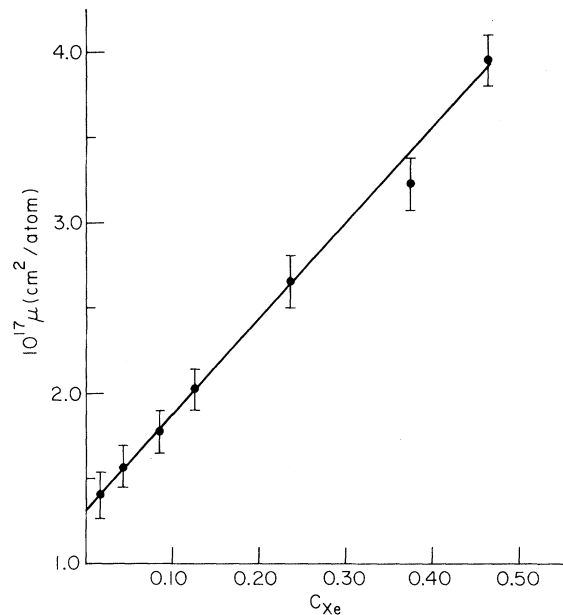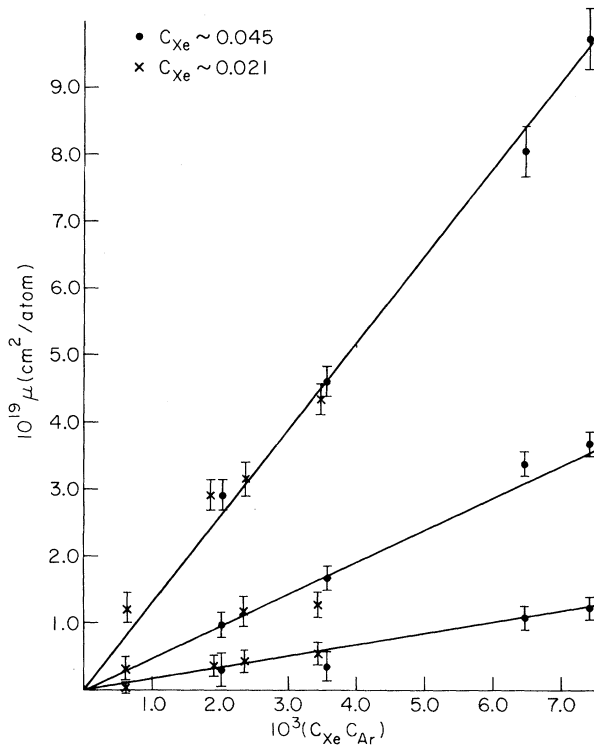

(a)
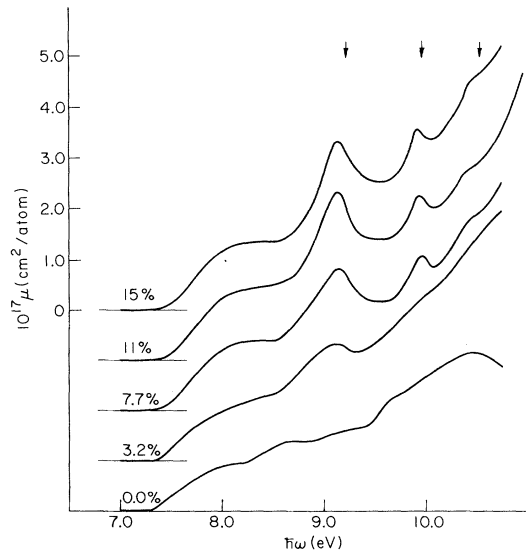
(b)

FIG. 1. (a) The optical absorption per atom of Xe in potassium for various Xe concentrations (at.%) at 7°K. (b) The absorption for 2% Xe in K containing the various Ar additions indicated (in at.%). Arrows mark the location of exciton peaks of solid Xe in (a) and of Xe in Ar in (b).

(a)

(b)

FIG. 2. (a) The peak height of the sharp line in Fig. 1(a) shown as a function of the Xe concentration c_{Xe} in K, and (b) the incremental height of the peaks in Fig. 1(b) shown as functions of $c_{Xe}c_{Ar}$. The linear variations with concentration identify the sharp peaks with excited states involving two rare-gas atoms.

Xe atoms must have several rare-gas neighbors in the concentrated alloys.

The sharp features therefore arise from pair *bonds* between rare-gas atoms regardless of other neighbors, rather than identifying only those rare-gas pairs that are isolated in the metal host. On the other hand, the threshold absorption, characteristic of Xe at dilution in K [see, e.g., the curve marked 1.8% in Fig. 1(a)], also persists at $c \sim 40$ at.% where essentially no isolated Xe atoms remain. In previous work[3,4] it has been shown that this latter process excites one Xe $5p$ electron into the electron gas and the channel is broadened by the creation of ~ 1 excited quasiparticle in the sensibly uniform excited conduction-electron distribution. These ground and excited states for isolated Xe impurities are shown in Figs. 3(a) and 3(b), and the analogous configuration for two neighboring impurities are shown in Figs. 3(c) and 3(d). The data indicate that the threshold and coupling to the electron gas are similar for excited configurations 3(b) and 3(d). Since it is not likely that these channels can contain sharp structure it follows that the sharp lines of Fig. 1 originate in an excited state other than that shown in Fig. 3(d). Therefore the pairs possess at least
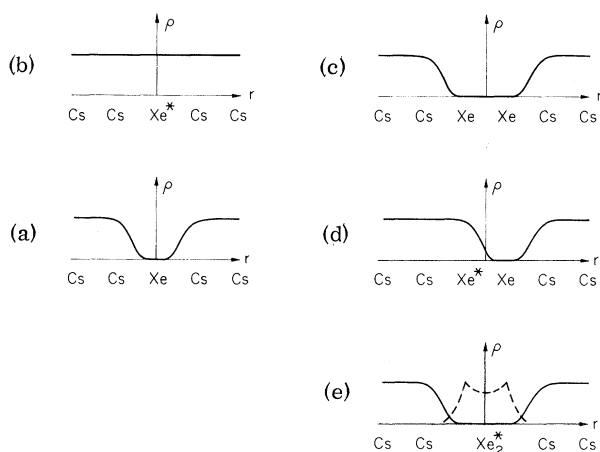

FIG. 3. Electronic density $\rho(r)$ near (a) the one-impurity ground state; (b) the one-impurity excited state; (c) the two-impurity ground state; (d) the two-impurity "metallic" excited state; and (e) the molecular excited state responsible for sharp-line absorption. A broken line indicates the excited molecular orbital. The figure is drawn for Xe in Cs, but the coarse screening structures must be insensitive to the particular alkali metal host and rare-gas impurity, and the electron densities indicated are therefore typical of the pertinent configurations for all alkali metal–rare-gas alloys.

two independent excitation channels.

An excited-state structure that explains the observed sharp excitation channel is shown in Fig. 3(e). It has a core hole shared between two Xe atoms and an excited electron occupying a diatomic molecular orbital that exists as a virtual bound state in the host electron gas. This structure explains the dependence of "pair-peak" oscillator strength on the number of bonds connecting rare-gas atoms, since each bond introduces a new excited orbital. It also explains the position of the sharp excitations in terms of the known excited levels of diatomic rare-gas molecules (close to the atomic resonance lines). Finally, the configuration 3(e) explains the sharpness of the "pair-peak" excitation lines as arising from an excited impurity structure that introduces only bound or virtual bound levels.[5]

It is shown elsewhere by Hartree-Fock methods that no carrier-pair creation accompanies any local excitation in a metal whose only effect is to to introduce a full virtual bound state into the ground-state structure.[6] Excitations of this type are therefore broadened only by lifetime effects. Space limitations preclude a full demonstration here but the main point is simple. A full virtual level introduces a phase shift of π at the Fermi level and therefore leaves the band orbitals near E_F unchanged (apart from central-cell effects negligible here). The excited-state determinant can then be obtained by a unitary transformation of a determinant constructed from the ground-state electron-gas orbitals together with a local orbital having the symmetry of the virtual level. As a consequence, the matrix elements coupling the ground configuration to locally excited configurations are zero whenever the excited states contain added electron-hole pairs. The spectrum is therefore a lifetime-broadened δ function near threshold, and this conclusion holds *a fortiori* for bound excited local orbitals. The sharp spectra of rare-gas pairs are thus explained in terms of an excited molecular orbital that presumably overlaps rather weakly with the surrounding electron gas. The possibility now emerges that many molecular impurities may, because of weak overlap, give sharp excitation spectra in metals, and this prospect holds equally for physisorbed and chemisorbed impurities.[6]

The arrows in Figs. 1(a) and 1(b), respectively, mark the locations of exciton resonances in pure solid Xe and in solid Ar containing ~ 1-at.% Xe impurities.[7,8] Clearly, the sharp spectra of pairs in metals bear a close relationship to the exciton

lines in rare gases. This tends to support sug-
gestions[9] that the exciton lines arise from pro-
cesses involving the pairwise association of rare-
gas atoms, rather than from processes more di-
rectly related to the band structure of rare-gas
solids. A similar insensitivity of the rare-gas
molecular spectrum to environment has been ob-
served in other condensed phases.[10] The diatom-
ic σ orbitals derived from Xe* $6s$ states probably
lie near the $6s$ one-electron energy of ~ -3.7
eV.[11] As this falls in the range of alkali metal
band energies, it seems likely that the excited
molecular orbital is virtual, rather than fully
bound, in alkali metal hosts.

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his active cooperation in this work.

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Metal-Insulator Transition in Metal—Rare-Gas Alloys*

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We present the results of electrical resistivity and optical absorption measurements
for compositions spanning the metal-insulator transition in RbKr and CsXe alloys. The
two transitions are similar and exhibit an apparently percolative character. No marked
emergence of excitons accompanies the disappearance of conductivity. Spectral features
associated with metallic conduction also persist through the transitions.

Much recent discussion has focused on the na-
ture and possible existence of Mott-type metal-
to-insulator transitions in which the electron gas
freezes into a nonconducting state.[1] Although no
physical systems actually undergoing Mott tran-
sitions have been clearly identified, it has been
suggested in several studies of rare-gas—metal
mixtures[2-4] that the metal-to-insulator transi-
tion that occurs with increasing rare-gas con-
centration in these materials is of the Mott type.
In this paper we present definitive results for
the RbKr and CsXe systems. These exhibit grad-
ual, rather than sharp, transitions to the insu-
lating phase that can be described quite well by
percolation theory. Opitcal absorption in these
materials undergoes no discontinuous or even

rapid variation in passing from insulating to me-
tallic samples. Indeed "metallic" features in an
energy range demonstrably associated with the
metal valence electrons persist in modified form
even in alloys containing 97 at.% rare gas. Sim-
ilarly, "excitonic" features naturally associated
with insulating hosts emerge in metallic hosts
containing only a few percent of rare-gas atoms.
The loss of conductivity observed at high rare-
gas concentrations therefore appears to have no
relationship to the phase transition visualized by
Mott.

Figure 1 shows as open circles the resistivi-
ties at 7°K of CsXe thin-film alloys 350 to 2000
Å thick, and shows as full circles similar re-
sults for RbKr alloys. The former data are