Impurity excitation effects in metals

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Excitation spectra of Ag, Mg, Cu, and Fe impurities in alkali metals are reported. A detailed analysis identifies components derived from (i) single-particle scattering, (ii) perturbed plasmon processes, (iii) localized excitations, and (iv) the associated shakeoff effects.

It has been understood for some time that impurities introduce new optical excitation channels into metals in addition to the modification they cause in the basic host metal spectrum.[1] The new channels correspond to changes of *local* configuration. Host excitations are also modified, because impurities deform the *extended* states of the metal.[2] Two features of these effects have not previously been well recognized. First is the degree to which the impurity-induced channels can resemble atomic excitations of the free impurity atom. Second is the fact that these impurity-confined processes may exist as well-defined channels down to very low excitation energies. In this Communication we report optical transmission and ellipsometric determinations of the changes in excitation spectra induced by impurities in alkali-metal host lattices. In all cases the impurity concentration is in the dilute limit where each center is effectively isolated from the rest. We show how the observed effects may be attributed to four distinct, coexisting processes.

The atomic character of the spectra is a little elusive to document, but is fairly well illustrated by the case of Ag impurities in alkali metals. Figure 1 shows by way of example the extra absorption due to
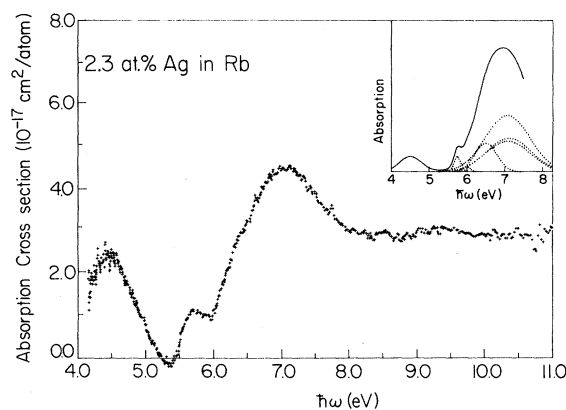

FIG. 1. Excess optical absorption caused by Ag impurities in Rb metal. Inset is a simulation derived from the spectral lines of *atomic* Ag.

Ag in Rb, normalized to unit impurity density. The data were obtained in the dilute impurity limit using methods described in detail elsewhere.[3] Also in Fig. 1, inset as a solid "theoretical" line, is a simulation derived from the spectrum of atomic Ag. Atomic lines may shift and broaden by interaction with a metallic environment. All lines in the simulation are red shifted by $1-1.5$ eV and then broadened to match the data. The parameters are listed in Table I. It happens that the required Ag oscillator strengths are lacking from the literature, so values for similar transitions of atomic Cu (Ref. 4) were employed instead. The synthesized curve bears a satisfactory qualitative resemblance to the observed absorption, given the simplicity of the procedure.

Figure 1 contains some unusual features. In the dilute alloy the Ag $4d^{10}5s \rightarrow 4d^{10}5p$ excitation lies below the 4.5-eV lower limit of transmission, near 2.1 eV, as we have verified by ellipsometric measurements mentioned below. The lowest peak in Fig. 1, near 4.5 eV, actually corresponds to the $4d^{10}5s \rightarrow 4d^{10}6p$ atomic oscillator strength. A sharp level associated with the $6p$ state is certainly unexpected. Above 7 eV are the $4d^{10}5s \rightarrow 4d^9 5s\,5p$ transitions. The simulation cannot be completed at higher energy because the oscillator strengths of higher lines have not been measured. The sharp shoulder near 6 eV arises in the synthesis from the oscillator strength of the quartet $^4P_{3/2}$ and $^4P_{1/2}$ levels of the $4d^9 5s\,5p$ configuration.[4] Evidently spin reversing transitions occur at the impurity much as in the atom. We have observed that these features also occur in the spectra of Ag in K and Cs. In Li, the d shoulder red shifts, and the greater opacity of the samples prevents the observation of lines at lower energy. The consistency of the experiments among different solvents affirms that the prominent features are impurity-specific excited configurations of the alloys. It appears to us unlikely that the similarity between experiment and atomic simulation is fortuitous. Rather, the data point to the existence of a richer spectrum of locally excited configurations of the Ag-metal complex than has previously been reported or predicted.

We have also investigated persistent impurity-

TABLE I. Parameters for Ag spectrum.

Excited configuration	Designation	Atomic level (eV)	Estimated f values	Assigned width (eV)	Assigned red shift (eV)
$4d^{10}5p$	$^2P_{1/2}$	3.79	0.215[a]	$\cdots$	$\cdots$
	$^2P_{3/2}$	3.82	0.43[a]	$\cdots$	$\cdots$
$4d^{10}6p$	$^2P_{3/2}$	6.01	0.018	0.6	1.5
$4d^95s5p$	$^4P_{3/2}$	7.25	0.005	0.18	1.5
	$^4P_{1/2}$	7.50	0.002	0.18	1.5
	$^4D_{1/2}$	8.0	0.003	0.6	1.5
Ag II limit					
	$^2P_{1/2}$	8.18	0.071	1.2	1.1
	$^2P_{3/2}$	8.18	0.13	1.2	1.1
	$^2D_{3/2}$	8.22	0.077	1.2	1.1

[a]Measured Ag f values.

specific effects at lower photon energies using ellipsometric methods by which the real and imaginary parts, ϵ_1 and ϵ_2, of the alloy dielectric function, $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, may be determined directly. A simple example is Mg, whose $2p^63s^2 \rightarrow 2p^63s3p$ excitations accounts for 90% of the entire $3s$ oscillator strength of the atom. In an alkali metal with $E_F \lesssim 4$ eV, the Mg $3s$-$3p$ splitting of 4.3 eV must cause the $3s$ level to lie at or below the band edge when the $3p$ level falls in the band (as it must for self-consistent screening). The question of whether or not a p-like local level persists in degeneracy with the s-like conduction band of other alkali cells can thus be investigated by observing the spectrum of Mg at dilution in alkali alloys.

Figure 2(a) shows $\omega\delta\epsilon_2(\omega)$, with $\delta\epsilon_2$ the impurity-induced changes of ϵ_2, as a function of photon energy for 1.25 at.% Mg in Li. The data were obtained by ellipsometry, using differential methods and polarization modulation techniques[5] on samples quench condensed at liquid-He temperatures, and are consistent with data obtained earlier by Mathewson and Myers for much more concentrated LiMg alloys.[6] The Mg $3s \rightarrow 3p$ excitation is clearly visible as a peak red shifted to about 2.8 eV from the atomic line at 4.3 eV, and with a leading edge broadened to a roughly Gaussian shape of full width ~ 1 eV. The additional increase of $\omega\delta\epsilon_2(\omega)$ as $\omega \rightarrow 0$ is a consequence of single-particle scattering by impurities. The Drude theory[7] leads to impurity-induced dielectric function changes:

$$\delta\epsilon_1 = -\frac{\omega_p^2}{\omega^2}\left\{\frac{\delta\omega_p^2}{\omega_p^2} - \frac{\gamma^2}{\omega^2}\left[\frac{2\delta\gamma}{\gamma} + \left(\frac{\delta\gamma}{\gamma}\right)^2\right]\right\}, \quad (1a)$$

$$\omega\delta\epsilon_2 = \frac{\gamma\omega_p^2}{\omega^2}\left[\frac{\delta\omega_p^2}{\omega_p^2} + \frac{\delta\gamma}{\gamma}\right], \quad (1b)$$
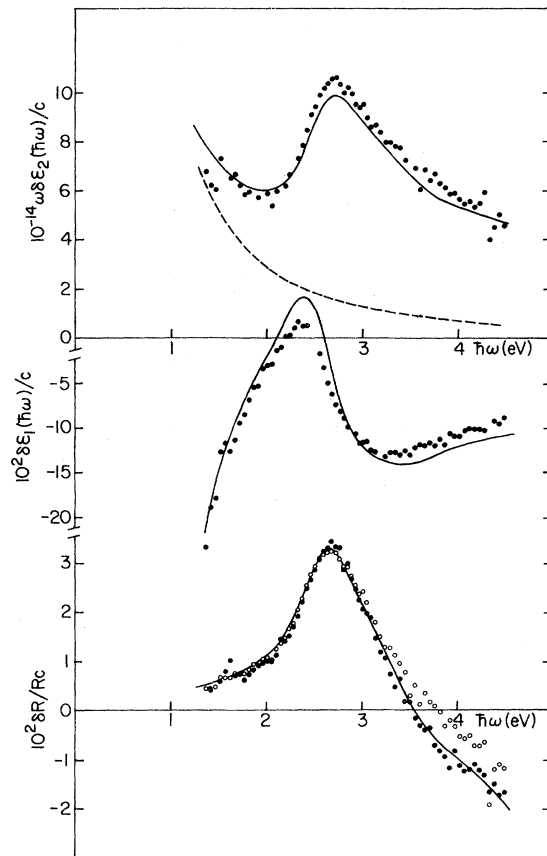

FIG. 2. Solid circles indicate measured values of the changes $\delta\epsilon_1$ and $\delta\epsilon_2$ caused by $3s^2 \rightarrow 3s3p$ excitations of Mg impurities at 1.25 at.% concentration in Li, and of the fractional reflectivity change. Open circles at the bottom indicate values of the reflectivity change calculated from ϵ_1 and ϵ_2. The solid lines represent a self-consistent fit of localized and delocalized contributions to all the data.

with $\delta\omega_p$ the change of plasmon frequency and $\delta\gamma$ the change of quasiparticle scattering rate. These equations must describe $\delta\epsilon(\omega)$ for $\omega \rightarrow 0$. In practice, the contribution of the $\delta\gamma$ term to Eq. (1) and of the $\delta\omega_p$ term to Eq. (2), is normally small. Figure 2(a) shows the *localized* spectrum $\delta\epsilon_2'(\omega)$ rising above a Drude scattering component corresponding to a specific residual resistance of Mg in Li. The resistance of ~ 3 $\mu\Omega$ cm required by the data of Fig. 2(a) compares adequately with the observed residual resistance[8] of 1.4 $\mu\Omega$ cm/at.% Mg in Li, given that the latter arises from quasiparticles near E_F while the optical value is for much higher energies. Note that the localized spectrum is not symmetrical. It is known that the shock of a local excitation can cause the production by shakeoff of quasiparticle pairs in the surrounding metal.[9] Additional energy uptake from pair creation broadens the line into the observed peaked shoulder. The shakeoff processes are the fourth component of the alloy spectrum.

The impurity-induced change in plasmon frequency follows by fitting Eq. 1(a) plus the Kramer-Kronig transform of $\delta\epsilon_2'(\omega)$ to the observed $\delta\epsilon_1(\omega)$. With $\delta\omega_p^1/\omega_p^2 = 0.0185$, there results the adequate fit to $\delta\epsilon_1$ shown in Fig. 2(b). Finally, in Fig. 2(c), the directly *observed* fractional change of reflectivity, $\delta R/Rc$, caused by impurity concentration, c, is compared with that calculated from the fitted values of $\omega\delta\epsilon_2'(\omega)$, γ, and $\delta\omega_p^2$. A second, independent, set of $\delta R/Rc$ values calculated from the *measured* values of $\delta\epsilon_1$ and $\delta\epsilon_2$, is also shown. The solid lines in the three parts of Fig. 2 indicate this self-consistent fit to all the data. The fact that the measured $\delta R/Rc$ agrees well with that calculated independently from $\delta\epsilon_1$ and $\delta\epsilon_2$ confirms the validity of the data (potential experimental errors caused by film inhomogeneity or roughness, for example, are clearly absent). Both sets of data agree well with the modeling in terms of the localized process together with the shakeoff it causes, with the addition of extended effects in the form of quasiparticle scattering and plasmon frequency changes. The local effects of Mg impurities are thus clearly separated from their delocalized effects, and the spectrum $\delta\epsilon'(\omega)$ of the $3s \rightarrow 3p$ excitation is determined.

Other impurities produce persistent spectra that are equally clearly characteristic of the ground state of the impurity-metal complex. We have found that the Ca spectrum in Li, for example, is quite similar to that of Mg, with extensive shakeoff, but with the peak near 2.0 eV. Cu and Fe in Li give spectra which are noticeably similar to each other and quite distinct from those of the divalent ions Mg and Ca. Figure 3 shows $\omega\delta\epsilon_2'(\omega)$ obtained for Cu and Fe in Li, using the values of the residual resistances cited in the figure. It seems quite clear that the $3d^6 4s^2$ divalent ground state of the free Fe atom has crossed over the monovalent $3d^7 4s$ configuration in the met-
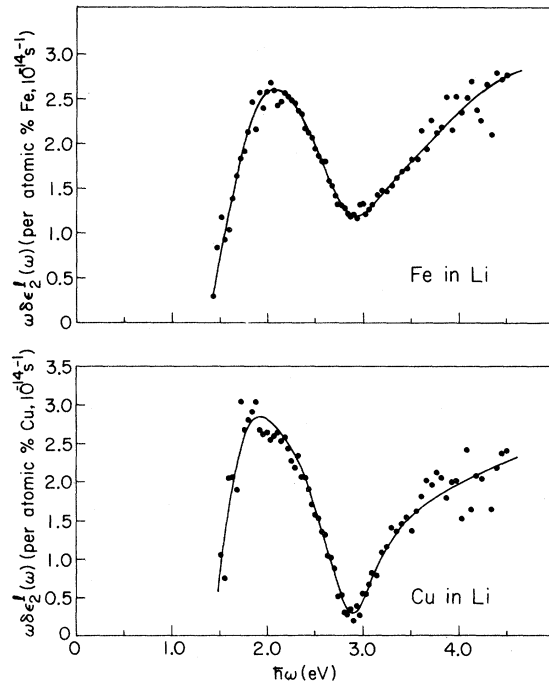

FIG. 3. Localized contributions of the excitation spectra of Fe and Cu in Li, obtained by subtraction of the Drude component.

al, through the interaction with the host atoms.[10] As expected from atomic spectra, the $3d$ threshold of Cu in Fig. 3 occurs at much lower energy than the Ag $4d$ threshold in Fig. 1.

Certain conceptual matters remain to be clarified in the conducting discussion. The reasons why rigid band, single-particle, descriptions of excitations in alloys[11] break down have never been accurately stated; nor have the conditions for the emergence of localized spectral features in alloys been specified. The key is that the local features arise from processes in which an electron and a hole of the single-particle picture resonate together at an impurity under the influence of their mutual attraction and of the impurity field. This effect depends on local interactions between quasiparticles and therefore explicitly involves multiparticle, rather than single-particle, processes. Metallic screening confines both carriers to an impurity cell which is approximately the size of the atom. Therefore the persistent features have atomiclike oscillator strengths and it follows that the spectrum can resemble that of the impurity atom to a noticeable degree. This configurational viewpoint makes contact with the virtual-bound-state (VBS) model of Caroli[12] and Kjollestrom[13] when the coupling of the configuration to the electron liquid is weakened, so that the impurity one-electron states become narrow virtual levels. With progressively weaker coupling[14] the spectrum must evolve into that

of the isolated impurity atom. The results for $\omega\epsilon_2'(\omega)$ of Mg in Li, shown in Fig. 2, are qualitatively very similar to the predictions of the VBS model,[13] even though it appears unlikely that the Mg $3p$ level can, in fact, be a sharp resonance in Li.

Our proposal that persistent impurity spectra be regarded as the result of two carriers resonating together at the impurity center leads to a suggestion about the conditions under which the impurity-specific effects become observable. Unless the excited center lives long enough to recombine radiatively, or can undergo multiphonon nonradiative decay, it must eventually release its stored energy in quasiparticle pair production. The rate w of this Auger-like channel measures the Coulomb coupling of the local configuration to the electron-hole pair continuum of the host metal. The larger the coupling the more the local state is spread into the host continuum and the less the local character remains apparent. Evidence for this coupling has been detected through Fano resonance behavior at threshold in certain persistent spectra.[15]

Counteracting these host lattice effects are the chemical couplings in the central cell, which determine the way that oscillator strength is distributed over energy in the atom. Suppose that a certain interaction, when screened by the metallic environment, causes a state i to remain split by an enery V_i from other states. Then these features can persist in the alloy only when $\hbar w_i \geq V_i$. For the structures observed in the Ag spectrum on an energy scale $|V|$ ~ 1 eV this criterion requires that the lifetime of the local particle-hole pair state be $\geq 10^{-15}$ s, which does appear quite reasonable.

[1]Examples of clearly identified impurity valence spectra are rare gases in alkalis [D. J. Phelps, R. A. Tilton, and C. P. Flynn, Phys. Rev. B <u>14</u>, 5754 (1976)] and halogens in alkalis [R. Avci and C. P. Flynn, Phys. Rev. B <u>19</u>, (1979)]. A variety of other data showing impurity-specific effects exists (Ref. 2), but has been interpreted in other ways. The basic ideas are discussed by J. J. Peters and C. P. Flynn, Phys. Rev. B <u>6</u>, 3343 (1972).

[2]A clear account of optical processes for extended states is given by D. J. Sellmeyer, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1978), Vol. 22.

[3]See, e.g., Avci and Flynn, Ref. 1.

[4]P. Hannaford and D. C. McDonald, J. Phys. B <u>11</u>, 1177 (1978).

[5]This general method is discussed by S. N. Jasperson and S. E. Schnatterly, Rev. Sci. Instrum. <u>40</u>, 761 (1969).

[6]A. B. Mathewson and H. P. Myers, J. Phys. F <u>3</u>, 629 (1973).

[7]For an elementary discussion see, e.g., F. C. Brown, *The Physics of Solids* (Benjamin, New York, 1967).

[8]T. E. Faber, Philos. Mag. <u>15</u>, 1 (1967). The value of resistance taken for pure quench-condensed Li was taken from R. Avci and C. P. Flynn, Phys. Rev. B <u>19</u>, 5967 (1979).

[9]This general problem is reviewed by G. D. Mahan, in *Solid State Phyiscs*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1974), Vol. 29.

[10]These type of effects are described by J. J. Peters and C. P. Flynn, Ref. 1. Recent NMR evidence suggests that Fe has crossed over to the monovalent state at the host electron density of Cu [D. Abbas, T. Aton, and C. P. Slichter, Phys. Rev. Lett. <u>41</u>, 719 (1978)]. Figure 3 suggests this change has already occurred at the lower electron density of Li.

[11]See, for example, Ref. 2 for a comprehensive discussion.

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[13]B. Kjollerstrom, Philos. Mag. <u>19</u>, 1207 (1969).

[14]C. P. Flynn, Phys. Rev. B <u>14</u>, 5294 (1976).

[15]Fano effects are reviewed by P. L. Altrick, in *Excited States in Quantum Chemistry*, edited by C. A. Nicholaides and D. R. Beck (Reidel, Dordrecht, Holland, 1979), p. 361. Experimental results on alloys are given by R. Avci and C. P. Flynn, Ref. 1.