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Giant Diamagnetism and Impurity Configurations in Alkali Metals*

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An unusually large diamagnetism ~−130 cgs/mole of certain positive-valence solutes in alkali metals is reported and explained in terms of a novel impurity configurational structure. Recent work on impurity-induced spin-flip scattering is also explained.

The observed large diamagnetism of positive-valence solutes in noble-metal solvents[1] has previously found no explanation in sign or order of magnitude. Kohn and Luming[2] and Graham and March[3] discuss impurity magnetism in metals. For a linearized impurity screen they find small paramagnetic susceptibilities rather than the observed large diamagnetism ~−100 cgs/mole. The discrepancy has tentatively been ascribed to band-structure effects.[2] In this Letter we present more structured results for the susceptibilities of impurities in alkali metals, and show how these results are related to a novel impurity structure. The observed[4,5] conduction-electron spin-flip rates induced by spin-orbit coupling in the impurity cell also find a natural explanation.

Figure 1 shows the measured susceptibilities of Au, Hg, Tl, Pb, Bi, Cd, In, Sn, Sb, and Te in liquid Na at 300°C. We have also obtained similar results for impurities in liquid K. An attempt was made to measure χ for I also but, unfortunately, NaI proved insoluble in liquid Na. Note, however, that the value $\chi = -52\times10^{-6}$ cgs/mole[6] for I^- in NaI fits smoothly into the present results for solutes in liquid Na. The peak diamagnetism for impurities of valence 5 and 6 is much larger than atomic susceptibilities.[7] Since core orbitals can hardly be affected, the valence diamagnetism is larger than that of free atoms by a factor up to 4. Band-structure effects can be discounted for this free-electron liquid solvent.

Also shown in Fig. 1 are the scattering cross sections deduced by Asik, Ball, and Slichter[4] and by Cornell and Slichter[5] for spin flips induced by spin-orbit coupling in the impurity cell. Clearly, these effects are also strongly valence dependent and giant diamagnetism emerges when the spin-flip scattering disappears. We believe that this happens because the two phenomena are sensitive to high densities of p-like impurity orbitals at the band bottom and at the Fermi surface, respectively.

The one-electron *atomic p* levels fall below the pure Na band bottom for higher valence solutes. This suggests that p-like impurity orbitals may emerge below the bottom of narrow conduction bands in a manner similar to the transition from virtual to bound $4f$ levels of rare-earth impurities recently reported by Blodgett and Flynn.[8]

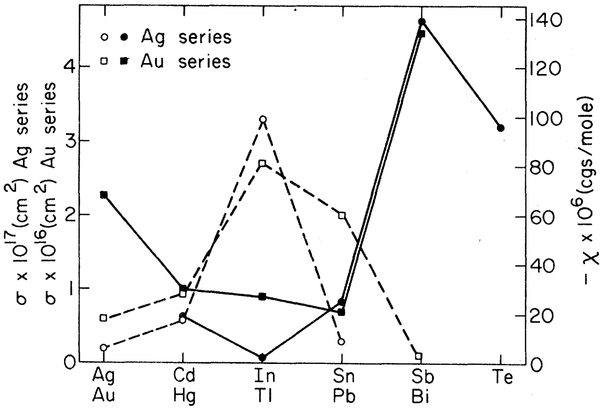

FIG. 1. The diamagnetic susceptibilities χ (closed points) and the spin-flip scattering cross sections σ (open points) for impurities in Na.

Bound states do not hybridize with the band, and tail off exponentially with distance from the impurity. The cases of f and p orbitals differ in that the observed effective moments of rare earths eliminate the possibility that a configurational transition accompanies the localization of the f levels, whereas it seems exceedingly likely that the giant diamagnetism reported in this Letter arises from a configurational change which transforms the impurity screen from one configuration to a second. In the present case the transition may involve the transfer of electrons between orbitals having differing symmetries. One must ask, for example, how an impurity such as Te could possibly bind four p states below the band bottom and not similarly accommodate electrons in the remaining two p orbitals. We propose that in the transition to bound states the p shells of Sb, Te, and Bi fill and that band electrons are then repelled in order to neutralize the impurity.

The configurational transition is brought into focus by the following discussion of a free Te atom at distance r from a plane metal surface. The chalcogens have a second affinity roughly equal to zero,[9] and so the common energy of the $5p$ orbitals of $\mathrm{Te}^{=}$ is approximately zero with respect to stationary electrons at infinity. All the $\mathrm{Te}^{=}$ levels are lowered by e^2/r by interaction with the image charge in the metal surface, and the six occupied p orbitals all lie *below* the Na band bottom (at ~−5 eV) when the ion comes in contact with the metal surface at $r \sim 2$ Å. When the ion is completely immersed, the image charge simply becomes repelled band states which ensure electrical neutrality in the bulk metal. The pattern of p-wave phase shifts consistent with this discussion and with the experimental facts is shown for impurities of various valence in Fig. 2(a). It is not to be supposed that this behavior is anomalous; a figure similar to that shown for Te is given by Mott and Massey[10] for a square well of radius a such that $k_F a \simeq 2$. The repulsion of band states becomes apparent when the formula

$$N_l(k) = (2/\pi)(2l+1)d\eta_l/dk \tag{1}$$

for the density of impurity l-wave states is applied to the p-wave phase shifts shown in Fig. 2(a). A decrease of η from the value π at $k=0$ for bound states is needed to satisfy the Friedel sum rule, and this decrease corresponds to a negative density of impurity states (i.e., repulsion of band electrons). The significance of this behavior in terms of configurational transitions has apparently not been understood previously.

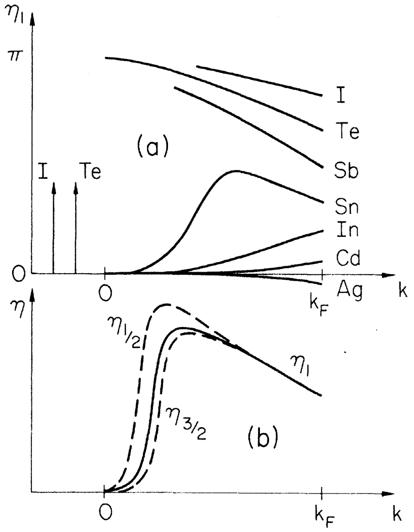

FIG. 2. (a) Hypothesized p-wave shifts for impurities in Na. Giant diamagnetism appears when p states occur near or below the band bottom and spin-flip scattering occurs when $d\eta/dk$ is large at k_F. The large diamagnetism of Au impurities may originate in similar effects for s levels. (b) The spin-orbit splitting of $\eta_{3/2}$ and $\eta_{1/2}$ depends on the time the electrons linger in the impurity, and therefore depends on $d\eta_1/dk$. The p-wave resonance shown may be appropriate to the case of Sn in Na.

The giant diamagnetism and the spin-flip results now find an immediate explanation. The former follows from the large values of $\langle r^2\rangle$ associated with the one-electron orbitals, which are weakly bound with respect to the band bottom. The hole left by the repelled electron gas contributes a potential which must help to localize the p orbitals. Note that an n-valent ion immersed in a monovalent electron gas cannot be screened in less than n cells of the host lattice and that the bound orbitals must tend to expand and occupy this volume. Furthermore, the spin-flip scattering cross section may be expressed (to the neglect of d-wave and higher order scattering) as[4,10]

$$\sigma = (16/9k_F^2)\sin^2(\eta_{3/2}-\eta_{1/2}), \tag{2}$$

in which $\eta_{3/2}$ and $\eta_{1/2}$ are the phase shifts at $k=k_F$ for $l=1$, $s=\frac{1}{2}$ and $l=1$, $s=-\frac{1}{2}$. Now since, for higher valence solutes, the band p states are repelled from the impurity ($d\eta/dk$ negative), the electrons at $k=k_F$ rarely experience the large impurity spin-orbit coupling and therefore $\eta_{3/2}$ and $\eta_{1/2}$ are nearly equal. The spin-orbit-split phase shifts consistent with the argument are shown schematically in Fig. 2(b) for the hypothetical case of an impurity giving rise to a p-wave resonance (this may apply to Sn in Na). It follows immediately from Eq. (2) that σ then becomes small whenever resonant (or bound) levels occur well below k_F. Thus, the appearance of giant diamagnetism automatically signals the disappearance of spin-flip scattering because phase shifts $\sim\pi$ near $k=0$ must decrease with k in order that the Friedel sum be satisfied at k_F.

In the case of noble-metal solvents, s and p levels must again emerge from the band bottom to cause a diamagnetism of high-valence impurities. It is possible that the one-electron levels are significantly broadened.[11] These phenomena will be discussed more fully in a future publication.

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Configuration Interaction in the X-Ray Photoelectron Spectra of Alkali Halides

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Satellites observed in the x-ray photoelectron spectra of the alkali halides are shown to arise from configuration interaction.

We have identified two-electron processes in the x-ray photoelectron spectra of alkali halides which are described by the final state of the excited atom and arise from configuration interaction. The observed effects are closely related to recently reported semi-Auger and radiative Auger satellites in soft-x-ray emission[1,2] and to some cases of electron "shake up."[3] The common feature of these experiments is the final state.

Satellites are produced whenever emission of either a photoelectron or an x ray is accompanied by the simultaneous excitation of another electron producing an atom with two inner-shell holes and one electron in an excited state. It is essential to distinguish between the intrinsic satellite structure resulting from this effect and the extrinsic structure due to energy loss suffered by the photoelectron as it leaves the crystal. Fortunately the electron energy-loss spectra of the alkali halides are well established.[4] Moreover, we have directly measured the energy-loss spectra for x-ray photoelectrons coming from our samples by exciting levels which should have no configuration-interaction satellites. The agreement between our observations and published data shows that the energy-loss spectra are very similar at 1.4 and 50 keV and help to avoid confusion between the two sources of satellite structure.[5]

Configuration-interaction satellites will be present in photoelectron spectra whenever there are other final states present with the same configuration (same total angular momentum and parity, or same total L and S in Russell-Saunders coupling) but somewhat greater binding energy than the single-hole final state. Perturbation theory further indicates that these other final states must have energies close to but greater than the single-hole final-state energy if the configuration-interaction satellites are to have reasonable intensities.[6] Final states with