Spin-Orbit Effects in Non-Central-Force Systems: Host-Lattice Effects in F Centers

D. Y. Smith

Argonne National Laboratory, Argonne, Illinois 60439

and

A. H. Harker

Atomic Energy Research Establishment, Harwell, Oxfordshire OX11 0RA, United Kingdom

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Two new trends associated with spin-orbit effects in a non-central-force field are evident in recent data for F centers: (1) an inverse power-law dependence of spin-orbit splitting on the lattice parameter of the host crystal and (2) a direct dependence of the splitting on the size of the host-lattice ions. These features may be summarized by a simple semiempirical formula closely related to the Mollwo-Ivey relation for the absorption energy.

An electron trapped at an anion vacancy or vacancy complex in an ionic solid is an exemplar of spin-orbit effects in non-central-force fields. While the spin-orbit fine structure in such systems was first identified[1] and the inverted energy-level ordering explained[2,3] some years ago, only within the past two years have accurate measurements[4-6] become available to establish correlations between the fine structure of the F center —an electron trapped at a single anion vacancy— and the properties of the host crystal.

In the present note we call attention to the strong correlation of the F-center spin-orbit splitting with both the lattice parameter of the host crystal and the size of the host-lattice ions which is evident in these new data. We show that, despite the complications of a multicenter system, the splittings may be systematized in a surprisingly simple semiempirical formula which has a geometric interpretation and which is closely related to the Mollwo-Ivey law[7] for the F-band energy.

The observed spin-orbit splittings,[4-6,8-17] Δ_F, of the first excited Γ_4^u state of F centers in alkali halides with the rock-salt structure are given as a function of composition by the circles in Fig. 1. For a given alkali metal, the magnitude of the spin-orbit splitting increases monotonically with the atomic number of the halide. This trend is strongest for the light alkali metals and is weakest for the heavy alkali metals. In contrast, the variation of Δ_F with the atomic number of the alkali metal shows two qualitatively different patterns. For the fluorides, and perhaps the chlorides, Δ_F increases with alkali-metal atomic number, but in the bromides and

iodides, Δ_F first decreases and then increases with the atomic number of the alkali metal.

The first trend is intuitively reasonable. One expects larger values of Δ_F for hosts with high-atomic-number ions, since the only substantial contribution to the spin-orbit interaction arises near the nuclei of the neighboring host-lattice ions where the Coulomb field is large. However, the second trend runs counter to this argument.

The starting point for a theory of the effect is a wave function ϕ_i for the defect electron, which is accurate near the host-lattice ions. Thus, the usual theory[2] of spin-orbit effects for vacancy-trapped electrons starts from a vacancy-cen-
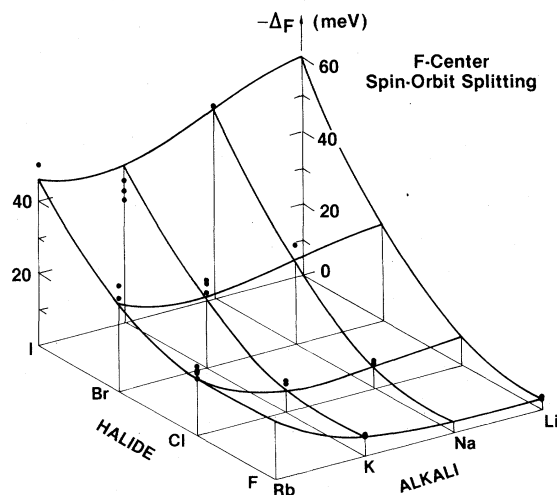

FIG. 1. The F-center spin-orbit splitting as a function of host-crystal composition. Experimental data are indicated by filled circles (Refs. 4–6 and 8–17), and theoretical results by the surface (Ref. 18).

tered model wave function, u_i, Schmidt orthogonalized to the ion-core states, φ_α:

$$\phi_i = (1 - \textstyle\sum_\alpha S_{\alpha,i}{}^2)^{-1/2}(u_i - \textstyle\sum_\beta S_{\beta,i}\,\varphi_\beta),$$

where $S_{\alpha,i}$ is the overlap integral $\langle \varphi_\alpha | u_i \rangle$ and the sums range over all occupied ion-core states of the host.

The expectation value of the spin-orbit interaction, $h_{s.o.}$, contains direct and cross terms in u_i and φ_α. Since the model wave function u_i is generally small relative to the ionic functions φ_α near the nuclei,[2] the only significant terms are bilinear in overlap. For the p-like excited states of the F center and for p-like core states, summation over the ions in the neighboring shells yields[3]

$$\langle \phi_i | h_{s.o.} | \phi_i \rangle$$

$$\simeq N_i{}^2 \sum_{\text{shells}} \tfrac{1}{3} n \sum_{\alpha,\beta} S_{p\pi,\alpha}(S_{p\pi,\beta} + 2S_{p\sigma,\beta})\lambda_{\alpha\beta}. \quad (1)$$

N_i is the normalization $(1 - \sum_\alpha S_{\alpha,i}{}^2)^{-1/2}$, n is the number of ions in a shell, and α and β are summed over the p-like core states of a single ion. $S_{p\pi}$ and $S_{p\sigma}$ are the π and σ integral for the overlap of the F center's excited p-state model wave function with the ion-core states. Multicenter terms have been neglected because $h_{s.o.}$ is highly localized near the nuclei, and $\lambda_{\alpha\beta}$ denotes $\langle \varphi_\alpha | h_{s.o.} | \varphi_\beta \rangle$.

A linear dependence of the F-center spin-orbit splitting on the ionic spin-orbit interactions is explicit in Eq. (1). There is, further, an implicit dependence on the F-center and ionic wave functions through the overlaps. The surface in Fig. 1 is the result of Harker's[18] evaluation of Eq. (1) using F-center wave functions calculated in the ion-size approximation.[19] The calculations predict the magnitude of Δ_F and the observed trends. Here we examine the source of these host-lattice dependences.

The principal experimental trend evident in Fig. 1 is that larger values of Δ_F are associated with host lattices having high-atomic-number ions. This follows from the increase of $\lambda_{\alpha\beta}$ with atomic number and is particularly apparent for the lithium halides and the alkali fluorides. An analysis[20] of these series confirms the linear dependence on the spin-orbit interaction and shows that the sum over matrix elements for core states may be approximated by a single linear dependence on the spin-orbit coupling constant,[21] λ_i, for the outermost p-like core state of the ith ionic species.

The second experimental trend, the initial decrease in Δ_F with increasing alkali-metal atomic number in the bromides and iodides, must be associated with a decrease in the overlap integrals. A consistent interpretation of these data is that, for the light alkali metals, Δ_F is dominated by the large bromide- or iodide-ion spin-orbit interaction. The light alkali-metal ions make a negligible contribution to Δ_F, but serve primarily as inert "spacers" between the F center and the near-neighbor halides. Larger "spacers" imply smaller overlaps and hence smaller splittings.

This suggests a correlation between the Δ_F and the nearest-neighbor distance, d, which is quantified in Fig. 2. The presentation suggests a power-law dependence $\Delta_F \sim d^{-n}$. An almost equally good fit is given by an exponential, $\Delta_F \sim \exp(-p'd)$. However, a nonlinear multiple-regression analysis slightly favors the power law.

In addition to the dependence of Δ_F on d, one anticipates that Δ_F depends on the ionic wave functions through the overlap integrals. This dependence can be isolated for the lithium halides (since lithium ions make no significant contribution to Δ_F) by forming the quantity $\Delta_F d^n / \lambda_{\text{halide}}$. This function is found to correlate strongly with the Goldschmidt or Pauling ionic radius of the
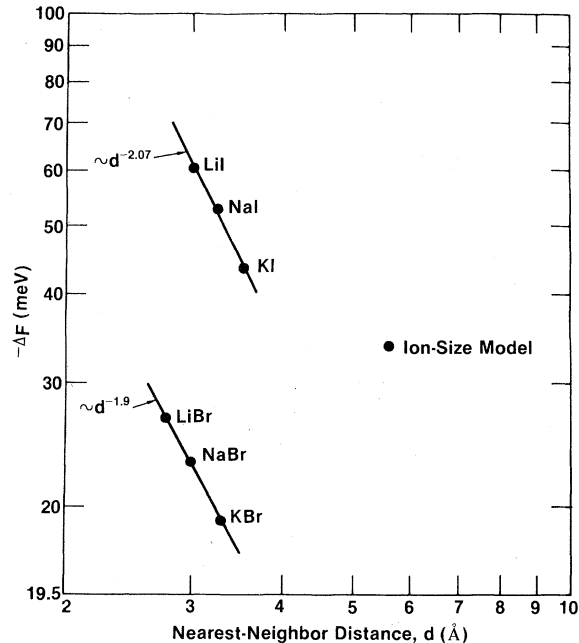

FIG. 2. The F-center spin-orbit splitting for the bromides and iodides of the light alkali metals vs nearest-neighbor distance.

halide ion, as shown at the lower right of Fig. 3. A similar plot may be constructed for the alkali-ion contribution, provided that the halide contribution to Δ_F is subtracted. This is shown for the alkali fluorides on the left of Fig. 3. In both cases a power-law dependence on ion size is apparent.

Combining the three correlations suggests that the contribution of the ith species to Δ_F may be described by $C r_i^m d^{-n} \lambda_i$, where C, m, and n are constants to be determined by fitting Δ_F. To determine the minimum number of parameters needed to characterize the theory, nonlinear multiple-regression fits were made to calculated values of Δ_F. It was found[20] that excellent fits (~5% rms error) could be obtained and that the standard estimate of error[22] was minimized with the three-parameter fit

$$\Delta_F = C_+ \left(\frac{r_+}{d}\right)^p \lambda_+ + C_- \left(\frac{r_-}{d}\right)^p \lambda_- , \qquad (2)$$
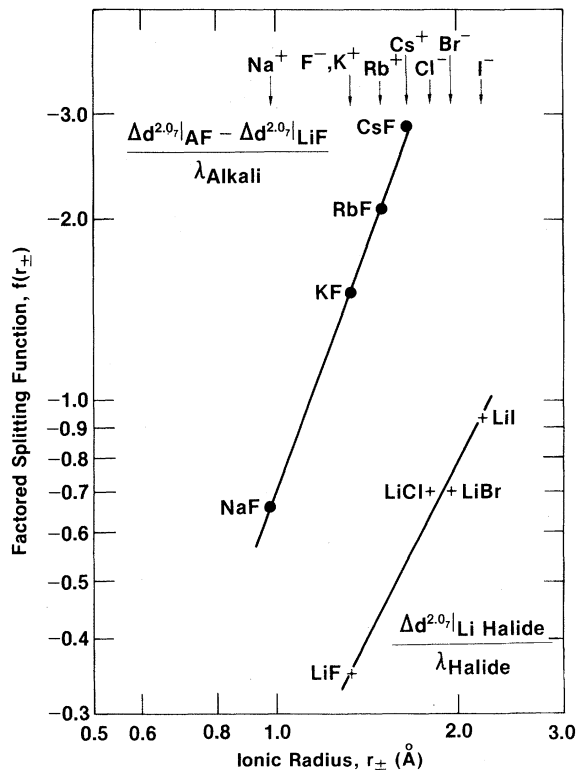
in which the spatial factors occur only as the dimensionless ratio r_i/d. This semiempirical formula was then fitted to the experimental data[4-6,8-17] with use of the Goldschmidt radii with the result

$$p = 2.74, \quad C_+ = -0.205, \quad C_- = -0.226 .$$

The rms relative error here was 15%, which is well within the uncertainty of the measurements; however, note that the lithium halides and the alkali fluorides are underrepresented in the experimental data.

The simplicity of this result, particularly that $p \approx 3$, suggests that the dependence on d and r_i may be largely geometric. The role of geometry is clearest for the F center since the size and depth of its potential well scale with lattice parameter. This scaling is explicit in the variational hydrogenic wave functions commonly used in approximate treatments[23] of the first excited state,

$$u_{2p}(\vec{r}) = (2/\sqrt{3})(\xi'/d)^{5/2} r \exp(-\xi' r/d)$$
$$\times Y_1^m(\theta, \varphi), \qquad (3)$$

where ξ' is a variational parameter and $Y_1^m(\theta, \varphi)$ are the spherical harmonics for p states. At a neighboring lattice point $r = \alpha d$ ($\alpha = 1, \sqrt{2}, \sqrt{3}, \ldots$), the amplitude is proportional to $\alpha d^{-3/2} \xi'^{5/2}$ $\times \exp(-\xi' \alpha)$. Since $\xi' \approx 2$ and is a slowly varying function of d,[23] the F-center wave function amplitude varies as $d^{-3/2}$ at the immediate neighbors.

The correlation with ion size is less well defined, because the concept of ionic radius is itself imprecise. However, the ionic radius is a rough measure of the spatial extent of the ionic core states, so that one expects the amplitude of the outer core wave functions to scale as $r_i^{-3/2}$. To estimate the spatial dependence of the overlap integrals, observe that the F-center excited state is diffuse and almost completely overlaps the more compact ion-core states (see Fig. 2 of Ref. 3). Hence the volume over which there is overlap between the F-center wave function and the core states is proportional to r_i^3. The overlap integrals in Eq. (1) thus scale as $d^{-3/2} \times r_i^{-3/2}$ $\times r_i^3 = (r/d)^{3/2}$. Then Δ_F, which is bilinear in overlap, should vary as $(r/d)^3$ in qualitative agreement with our fitting of the experimental data.

Appealing as this argument is, it cannot be pressed very far. The dependence of ξ' on d is not negligible beyond the first few neighbors since the term $\exp(-\xi' r/d)$ of Eq. (3) becomes

FIG. 3. Dependence of Δ_F on ion size. The function $(-\Delta_F d^n)_{\text{Li halide}}/\lambda_{\text{halide}}$ (right-hand curve) shows the variation of Δ_F in the lithium salts with the radius of the halide ion. A similar function may be constructed to show the dependence on alkali-ion size in a given halide sequence by subtracting the contribution of the halide ion, as illustrated for the fluorides by the left-hand curve.

important. The argument also glosses over specifics of the wave functions, neglects sums over deep core levels, etc.

As a final observation, note that an approximate d^{-3} dependence of Δ_F on nearest-neighbor distance is consistent with the Mollwo-Ivey law[7] (the F-band energy is approximately proportional to d^{-2}). The simplest model for the Mollwo-Ivey relation is an electron trapped in a spherical potential "box" of radius d. The average electron density for such a trapped electron scales as d^{-3}, just the dependence required of the F-center electron density at ions neighboring the vacancy to give $\Delta_F \sim d^{-3}$.

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