Physical Basis of the Mollwo-Ivey Relation between Lattice Constant and Optical Absorption of Defects in Ionic Crystals

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We derive the Mollwo-Ivey power-law relation between optical absorption energy and lattice constant for defects in ionic solids from the spatial scaling of the defect's electronic charge distribution. Our starting point is the Vinti sum rule, which relates the rms size of the electronic ground state to the absorption spectrum. We treat F centers and impurity ions in alkali halides in detail, but the general theory should be widely applicable.

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The principal optical absorption energy E_d of many defects in ionic solids exhibits a remarkable power-law dependence on lattice parameter. Mollwo [1] first observed this in 1931 for the F center, an electron trapped at an anion vacancy in alkali halides. From limited data, he inferred an inverse-square dependence. Subsequently, Ivey [2] found that many classes of defects obeyed the generalization

$$E_d = Ca^{-n}, \tag{1}$$

where a is the nearest-neighbor separation.

For F centers a fit to data for all NaCl-structure alkali halides yields [3] $C = 17.3 \pm 2.8$ eV and $n = 1.81 \pm 0.10$. Similar rules hold for many other defects, including F-aggregate centers [2], substitutional anions [4,5], and possibly defects in oxides [6]. However, the Ivey exponent is often far from Mollwo's value of 2, ranging from less than 0.6 for Au^- in rubidium halides [4] to 3.6 for defects in the alkaline-earth fluorides [7].

Theoretical understanding of the Mollwo-Ivey relation has remained incomplete, especially with regard to the exponent. Fröhlich [8] gave the first theoretical treatment for F centers shortly after Mollwo's paper. He assumed an embedded alkali-atom model and viewed the F band as the transition of the atom's outer electron from one conduction band to another. Since nearly-free-electron band-structure energies scale quadratically with Brillouin zone dimensions (which are proportional to a^{-1}), the resulting F-band energy had strict inverse-square dependence on lattice constant. (This atomic model is distinct from another early F-center model which involved Landau's [9] idea of an electron "self-trapped" by its polarization of the lattice.) Arguing that the F center is highly localized, de Boer and de Groot [10] showed the Fröhlich treatment was inapplicable. Stöckmann [11] then treated the F-center electron as confined to a rigid box with dimensions of the lattice constant and reproduced the Mollwo relation in this highly localized model. Although Stöckmann's result is widely quoted [12], the ground and excited states have very different spatial extent [13] so the notion of rigid confinement is an oversimplification.

More realistic F-center calculations [12], based on semicontinuum, point-ion, LCAO, and pseudopotential models of the F center, all predict a Mollwo-Ivey relation with exponent somewhat less than 2 in the alkali halides. In addition, pseudopotential calculations explain small, ion-dependent deviations from the Mollwo-Ivey law as a result of the finite size of ions neighboring the defect [14]. Wood [15] showed that, at least for the F center, the transition energy can be expressed as a power series in the lattice constant with the principal term varying as a^{-2}. His argument was based on observations of Gourary and Adrian [16], and of Wood and co-workers [17] that the ionic crystal field largely determines the extent of the trapped electron's wave function, which scales directly with a. The kinetic energy then scales as a^{-2}, while the Madelung energy and other potential energy terms scale as a^{-1}. When combined, these yield a net energy dependence only slightly less rapid than a^{-2}.

However, the wide applicability of the Mollwo-Ivey law and the large range of n require a more general explanation. To explore this, we have used the Vinti sum rule [18,19], which relates the mean square radius of the ground state of a quantum system, $\langle 0|r^2|0\rangle$, to moments of its optical absorption,

$$\langle 0|r^2|0\rangle = \frac{3\hbar}{2m_e}\frac{\mu_{-1}}{\mu_0}. \tag{2}$$

Here m_e is the free-electron mass. The nth moment of the absorption spectrum is

$$\mu_n = \int_0^\infty \omega^n K(\omega)\,d\omega, \tag{3}$$

where $K(\omega)$ is the absorption coefficient.

The Vinti sum rule holds generally for dipole transitions in nonrelativistic systems with velocity-independent interactions [18]. It is used extensively in atomic physics [20], but for application to defects, it is common [21] to separate the defect absorption from that of the host crystal. This leads to approximate defect sum rules modified for interactions with the host. These modifications include [21] replacement of m_e by m^*, an effective electron mass, and introduction of a frequency-dependent local radiation field. The effective-field correction appears in both moment integrals in Eq. (2), but with different weightings. However, the fields are nearly constant over the absorption spectrum of the defects considered, so effective-field effects tend to cancel. The effective-mass correction is important for shallow-donor-like impurities with diffuse electronic states [22]. For highly localized ground states, the free-electron mass is more appropriate.

The spectra of many defects consist of one or two prominent absorption bands followed by a few weak absorptions at higher energies. While broad, the bands are often sufficiently symmetric to be approximated by δ functions of oscillator strength f_i and energy E_i. Then the Vinti sum rule becomes

$$\langle 0|r^2|0\rangle \approx \frac{3\hbar^2}{2m^*}\frac{\sum_i f_i E_i^{-1}}{\sum_i f_i}. \tag{4}$$

The result of applying Eq. (4) to alkali-halide F-center spectra is shown in Fig. 1. Line a is based on measurements of the F, K, and L bands in potassium and rubidium halides by Lüty [23]. Line b was derived from Dawson and Pooley's [3] measurements of the F band alone. In both instances, the free-electron mass was used [24]. Comparison of the two data sets shows that the weak K and L absorptions contribute less than 5% to $\langle 0|r^2|0\rangle^{1/2}$. We will neglect these weak bands in the following.

The striking feature of this analysis is the linear relation between $\langle 0|r^2|0\rangle^{1/2}$ and nearest-neighbor distance. The scatter of data points about the linear regression is small and likely arises from ion-size effects [14]. Moreover, $\langle 0|r^2|0\rangle^{1/2}$ is less than the nearest-neighbor distance by 0.4 to 1 Å, indicating [25] that the bulk of the F-center ground-state charge is contained within the anion vacancy. (This observation justifies the above use of the free-electron mass.) We therefore conclude that to an excellent approximation, the rms size of the F-center ground state scales linearly with host crystal nearest-neighbor separation,

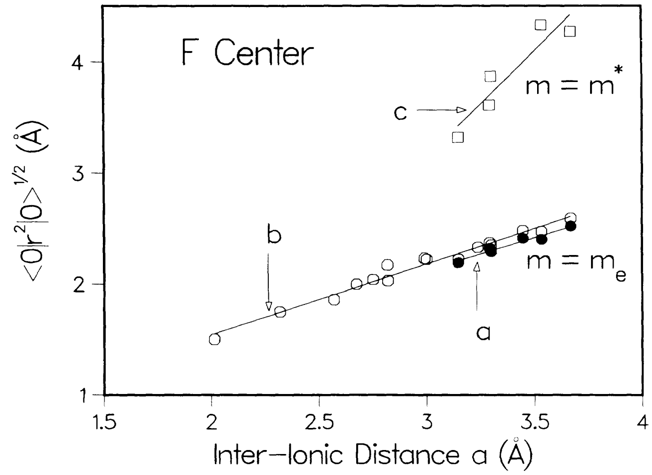

FIG. 1. The rms radius of the F center vs nearest-neighbor separation in the NaCl-structure alkali halides as determined from optical spectra (see Refs. [3], [23], and [31]) via the Vinti sum rule. Curve a: F, K, and L bands included; curve b: F band alone; curve c: F band alone, but assuming the cyclotron effective mass (Ref. [24]).

$$\langle 0|r^2|0\rangle^{1/2} = \xi a + \eta. \tag{5}$$

This generalizes the pure linear scaling with $\eta = 0$ assumed by Gourary and Adrian [16], and Wood [15].

The analysis further suggests an extension to other defects: Physically, it is reasonable to assume that the spatial extent of a defect wave function is a continuous function of lattice constant for localized defects in ionic systems in which ion-size and ion-dependent polarization [26] effects are small relative to crystal-field effects. Over the small range of lattice constants found in nature, a Taylor expansion of this function may be expected to be dominated by the term linear in a. The Mollwo-Ivey relation then follows via the Vinti sum rule, Eq. (4), which can be written for a single dominant defect absorption at energy E_d as

$$E_d \approx \frac{3\hbar^2}{2m^*\langle 0|r^2|0\rangle}. \tag{6}$$

The right-hand side of Eq. (6) may be treated by rewriting Eq. (5) in terms of an arbitrary lattice parameter a_0 near the center of the range of a,

$$\langle 0|r^2|0\rangle^{1/2} = r_0 + \xi(a - a_0), \tag{7}$$

where r_0 is the rms radius, $\xi a_0 + \eta$, of a defect with $a = a_0$. On substituting Eq. (7) into Eq. (6), one finds that the denominator on the right-hand side of Eq. (6) consists of a polynomial which may be identified with the first few terms of an expansion of a^n about a_0. Now, E_d on the left-hand side may be written in the Mollwo-Ivey form, C/a^n, and a^n expanded in powers of $(a - a_0)/a_0$, provided $(a - a_0)/a_0 < 1$. [In the alkali halides $|(a - a_0)/a_0| \le 0.3$.] Equating coefficients of the zeroth and first powers of $(a - a_0)/a_0$ in the two expansions yields

$$C \approx \frac{3\hbar^2}{2m^*}\frac{a_0^n}{r_0^2}, \tag{8}$$

and

$$n \approx 2\xi\frac{a_0}{r_0} = 2\frac{a_0}{r_0}\frac{d\langle 0|r^2|0\rangle^{1/2}}{da}. \tag{9a}$$

Thus, the Mollwo-Ivey exponent is twice the slope of $\langle 0|r^2|0\rangle^{1/2}/r_0$ vs a/a_0. In terms of ξ, η, and a_0,

$$n \approx \frac{2}{1 + \eta/\xi a_0}. \tag{9b}$$

(Note that the coefficients of terms quadratic in $[(a - a_0)/a_0]$ in the two expansions are identical for $n = 2$ and do not differ significantly for $0.5 < n < 4$, the experimental range of the Ivey exponent.)

In Fig. 2 we compare the observed F-band energy with two fittings based on values of ξ and η determined from a

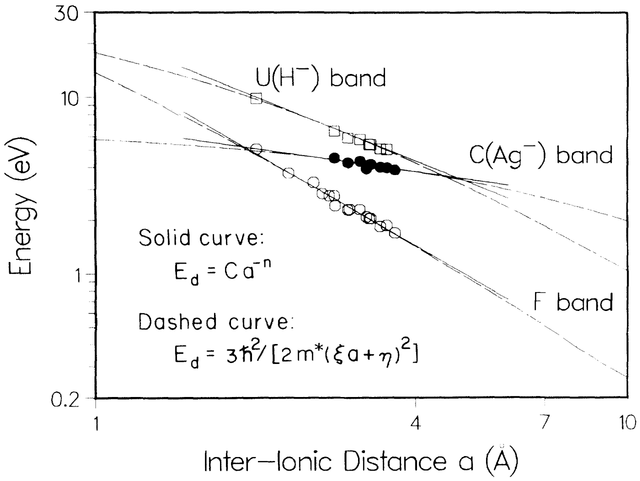

FIG. 2. A comparison of the experimental F, $U(\mathrm{H}^-)$, and $C(\mathrm{Ag}^-)$ band energies with best-fit Mollwo-Ivey relations (solid lines) and the Vinti sum-rule predictions assuming a linear relation between rms radius and nearest-neighbor separation (dashed curve). Values of ξ and η were taken from least-squares linear fits to $\langle 0|r^2|0\rangle^{1/2}$ and are listed in Table I.

TABLE I. Mollwo-Ivey exponents and linear-fitting parameters, ξ and η, for common ionic-crystal defects. The exponent n_E was derived from power-law fits to the absorption-band energy vs nearest-neighbor separation; n_r was calculated via Eq. (9) from ξ, η, and a_0, the average nearest-neighbor separation in the host crystals for which the defect spectra were measured. The parameters ξ and η are defined by Eq. (5). They were found by least-squares fits to $\langle 0|r^2|0\rangle^{1/2}$, which, in turn, was determined from measured optical spectra via the Vinti sum rule; the data used were taken from the sources shown for n_E.

Band	Host crystal	n_E	ξ	η (Å)	a_0 (Å)	n_r
	Alkali halides					
F	NaCl structure	1.77[a]	0.64	0.27	2.84	1.74
F	CsCl structure	2.50[b]	0.74	−0.32	3.76	2.26
	Alkaline earth					
$F+$	Sulfides	2.59[c]	0.97	−0.66	3.01	2.58
$F+$	Oxides	3.13[d]	1.25	−1.16	2.46	3.21
$F^{(+?)}$	Fluorides	3.60–3.85[e]	1.72	−2.15	2.52	3.97
	Alkali halides					
$U(\mathrm{H}^-)$	NaCl structure	1.10[f]	0.28	0.52	2.84	1.21
$U(\mathrm{H}^-)$	CsCl structure	1.54[g]	0.33	0.28	3.76	1.63
	Alkali halides—NaCl structure					
(OH^-)	Na halides	0.85[h]	0.35	1.26	2.70	0.86
(OH^-)	K halides	1.03[h]	0.39	1.34	3.32	0.98
	Alkali halides—NaCl structure					
$C(\mathrm{Ag}^-)$	Na halides	1.03[i]	0.28	0.81	3.01	1.02
$C(\mathrm{Ag}^-)$	K halides	0.75[i]	0.19	1.03	3.32	0.76
$C(\mathrm{Ag}^-)$	Rb halides	0.64[i]	0.13	1.24	3.45	0.53
$C(\mathrm{Au}^-)$	K halides	0.63[i]	0.13	1.05	3.32	0.58
$C(\mathrm{Au}^-)$	Rb halides	0.57[i]	0.13	1.07	3.45	0.59
$C(\mathrm{Cu}^-)$	K halides	0.65[i]	0.15	1.20	3.32	0.59
	Alkali halide—CsCl structure					
$C(\mathrm{Ag}^-)$	Cs halides	0.97[i]	0.21	0.92	3.76	0.92

[a] Reference [3], updated with new LiI F-band data from Ref. [31].
[b] Reference [28].
[c] Reference [29].
[d] Reference [30].
[e] Reference [7].
[f] References [2] and [32].
[g] Reference [27].
[h] Reference [5].
[i] Reference [4], average values, Table 8.

Vinti moment analysis of the absorption spectra (see Table I). The solid curve is a traditional Mollwo-Ivey power-law approximation, *but* with C and n calculated via Eqs. (8) and (9). The dashed curve is the single-absorption Vinti expression Eq. (6), with $\langle 0|r^2|0\rangle$ evaluated using Eq. (5). Over the crystallographic range of a, the two calculated values are indistinguishable to within the scatter of F-center energies attributable to ion-size effects.

Our result for the Ivey exponent [Eq. 9(b)] also explains the success of very different F-center theories in correctly predicting the observed power-law behavior: Any theory, right or wrong, which gives defect wave functions scaling principally as ξa (i.e., for $\eta/\xi a_0 \ll 1$) predicts $n \simeq 2$. Thus, Stöckmann's particle-in-a-box model and Frölich's free-electron model both predict $n \equiv 2$, since the crystal potentials for both models scale with the lattice constant. In more realistic F-center models, the principal part of the defect potential remains the Madelung energy, which scales with a^{-1}. Minor modifications such as cutoffs, polarization corrections, ion-size effects, etc., destroy this exact scaling with a, but do not alter its dominance.

Figure 3 extends these ideas to other Mollwo-Ivey centers. With the possible exception of the oxides, the rms radii of the electronic ground states all scale linearly with a. The expansion parameters ξ and η for a number of defects are listed in Table I together with the Ivey exponent n_E found directly from a Mollwo-Ivey plot of $\ln E_d$ vs $\ln a$, and the exponent n_r calculated indirectly from fits of a linear regression to $\langle 0|r^2|0\rangle^{1/2}$ via Eq. (9). The agreement is good. In Fig. 2 we also compare observed energies of U and $C(\mathrm{Ag}^-)$ bands with the transition energies as calculated from ξ and η. As with the F center, the energies predicted assuming a generalized linear spatial scaling of the wave function are indistinguishable from the Mollwo-Ivey fits over the natural range of crystal lattice constants.

A fuller discussion of the parameters ξ and η will be given in a subsequent publication. Here we simply observe that the linear term ξa should dominate the rms radii of defects such as F and F-aggregate centers, which involve vacancies and, consequently, have potential wells dominated by the crystal fields. Moreover, if the defect electron(s) are trapped primarily within the vacancy, ξ should be roughly unity. (For highly localized defects such as F^+ centers, η may be negative to offset the rela-

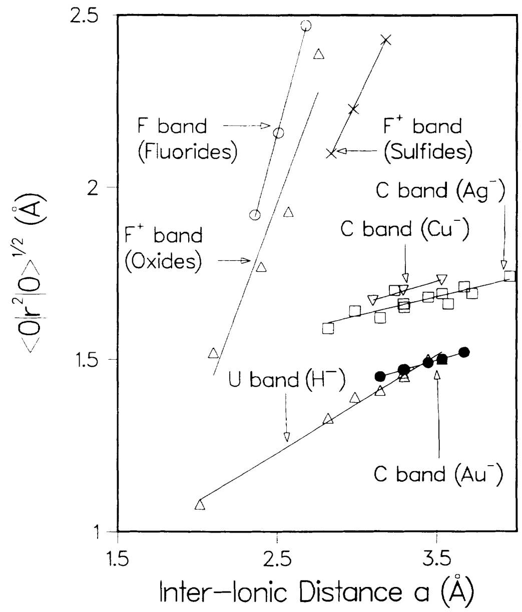

FIG. 3. The rms radii of various defects in ionic solids as determined from optical spectra via the Vinti sum rule assuming the free-electron mass. The data were taken from the sources referenced in Table I.

tively large value of ξa.) In contrast, the wave functions of ionic impurities are largely determined by the ion's own potential so that the constant term η dominates $\langle 0|r^2|0\rangle^{1/2}$. Then η is positive and of the order of an atomic radius. Table I shows that these expectations are borne out experimentally.

In summary, the Vinti sum rule may be used to derive the Mollwo-Ivey relation from a generalized linear scaling of defect charge distribution with lattice parameter for electron-excess centers in ionic solids. The wide range of Ivey exponents reflect the importance of the crystal field relative to the impurity ion's field in determining the defect's extent.

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