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Sum rules for F centers in alkali halides*

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The purpose of the present paper is the application of sum rules to the study of the unperturbed F-center ground state in three alkali halides (KBr, KCl, and RbCl). The comparison between theoretical expressions for the moments of the absorption spectrum and their numerical values computed from the experimental spectra, gives the mean radius, the mean kinetic energy, and the mean charge density seen by the electron. These parameters allow a determination of the shape of the electron charge density, which is found to be in good agreement with electron-nuclear-double-resonance measurements.

I. INTRODUCTION

F centers have been the subject of numerous papers for many decades. De Boer's model of the F center is now universally accepted. However, the F-center wave function is not yet well known, and even the size of the center is still a subject of controversy. Good reviews discussing the present status of this question are given in the papers by Stoneham,[1] Petrashen *et al.*,[2] Gourary and Adrian,[3] and in Chap. IX of the paper by Markham.[4] A bibliography can also be found in the recent paper by Schmid.[5]

On the other hand, it is well known in atomic physics that oscillator-strength sum rules introduced by Vinti[6] give direct information on the physical properties of the electron which undergoes the optical transition. A review of the applications of the sum rules in atomic physics is given in Chap. X of the book by Hirschfelder *et al.*[7]

Among other results, these sum rules show that the first few moments of the absorption spectrum are directly related to the mean radius of the electron orbit, the mean kinetic energy of the electron, and the mean charge density seen by the electron in its motion.

The sum rules are not by any means unknown in F-center theory. In 1952, Lax[8] used moments of the absorption spectrum to discuss the validity of a semiclassical approximation. However, most of the work based on the calculation of moments deals with the modifications of the F band due to external perturbations such as a change in applied magnetic or electric fields,[9,10] temperature,[11] etc. Osborne and Stephens[12] used a moment analysis of the absorption bands and magnetic circular dichroism to calculate the spin-orbit splitting and orbital g value for the F-center excited state. A review can be found in the paper by Henry and Slichter.[13]

The purpose of the present paper is the application of these sum rules to the study of the properties of the F-center ground state in the absence of external perturbations. The procedure used is the following: the moments of the absorption coefficient are numerically computed from the experimental F absorption band. Then a comparison with the theoretical expressions of these moments directly gives the values of characteristic parameters of the F center, which are of great physical interest. Finally, the values of these parameters are used to roughly evaluate the shape of the electron charge distribution, which is found to be in good agreement with electron-nuclear double-resonance (ENDOR) measurements.[14]

The main reason for our interest in the sum rules is that they are "exact" relations, i.e., they can be deduced from the Hamiltonian of the system in a rigorous way. In solid-state physics, however, the number of interacting particles is so large that sum rules based on the Hamiltonian of the actual system seem difficult to obtain. Moreover, they would probably be useless because of their complicated expressions. Therefore it seems preferable to start from a simple model leading to simple results for the sum rules. The model used throughout the present paper is based on the following assumptions.

Following the suggestion by Mott and Gurney[15] (used, e.g., by Smith and Spinolo[16]), it is supposed that the F and K bands are due to transitions of a single electron initially in the F-center ground state. Chiarotti and Grassano[17] have given strong experimental evidence for the Mott-Gurney suggestion. They have also shown that the L bands are due to transitions from the same F-center ground state to higher excited states. However, the intensity of these L bands is very low. For example, in the case of KCl, Lüty[18] gives values ranging from 0.005 to 0.02 for the oscillator strengths of the L bands, compared to 0.85 and 0.11 for those of the F and K bands, respectively. Thus the contribution of these L bands can be neglected and our evaluation of the moments with the measured F and K bands seems to include all significant absorptions. On the other hand, many-body effects involving transitions of more than a single electron are neglected. The usual dipole approximation is used to describe the interaction with the electromagnetic radiation.

Three alkali halides (KBr, KCl, and RbCl) are studied in the present paper. In these compounds, the F-center transition frequency is far larger than the ion oscillation frequency. As a consequence, an adiabatic approximation can be used to describe the displacements of the ions.

The interaction of the electron in the F center with the periodic rigid lattice is described by the band-mass approximation: the mass of the electron is replaced by an effective mass known from cyclotron resonance measurements, for instance. Although used by many authors in F-center theory, this approximation is questionable. It is probably valid when the electron is far from the center of the defect, but becomes criticizable when the electron is at distances shorter than the nearest-neighbor distance.

As far as its polarization is concerned (ionic as well as electronic), the lattice is assumed to behave as a continuous medium. As the size of the center is at least of the order of the shortest distance between ions, this is probably not too bad an approximation.

II. CALCULATION OF MOMENTS

The absorption coefficient is defined as the ratio of the absorbed power per unit volume to the incident light intensity I. Let ω be the frequency of the photon absorbed during the transition $E_0 \rightarrow E_f$ of the F center. The absorption coefficient $K(\omega)$ is related to the transition probability per unit time $W(\omega)$ by

$$K(\omega) = NI^{-1}\hbar\omega W(\omega), \tag{2.1}$$

where N is the concentration in absorbing centers. The transition probability $W(\omega)$ is given by Fermi's golden rule

$$W(\omega) = 2\pi\hbar^{-1}\sum_f |\langle f|e\mathcal{E}z|0\rangle|^2 \times\delta(E_f - E_0 - \hbar\omega). \tag{2.2}$$

As we are interested here in spectra taken at relatively low temperature, the initial state is the ground state $|0\rangle$ with energy E_0. The index f denotes all the possible final states with energy E_f, e is the electron charge, and $\mathcal{E}$ is the electric field.

However, the value of the field to be used here requires a discussion. Indeed, the problem of the interaction between the electron and the incident radiation is more complicated in a crystal than in a vacuum: the electron in its motion around the vacancy does not feel the vacuum electric field of the electromagnetic wave, but a local field varying from point to point in the lattice. As a consequence the electric field in the dipolar interaction term must be replaced by an effective value which is an average taken over the electron orbital. This effective value $\mathcal{E}(t)$ is proportional to the strength of the electric field in vacuum, and its time dependence is given by

$$\mathcal{E}(t) = \mathcal{E}(e^{i\omega t} + e^{-i\omega t}). \tag{2.2$'$}$$

Relation (2.2′) gives a precise definition of the symbol $\mathcal{E}$ used here. The direction of polarization of the incident light is taken as the z axis. Thus, in Eq. (2.2), z denotes the z component of the electron position measured with respect to the position of the vacancy.

The moments of the absorption coefficient are defined,

$$\mu_n = \int_0^\infty K(\omega)\omega^n\, d\omega \quad (n \text{ integer}). \tag{2.3}$$

They are related to the transition probability by

$$\mu_n = NI^{-1}\hbar\int_0^\infty W(\omega)\omega^{n+1}\, d\omega. \tag{2.4}$$

Using expression (2.2) for $W(\omega)$, these moments can be written

$$\mu_n = 2\pi NI^{-1}e^2\mathcal{E}^2\int_0^\infty \sum_f \langle 0|z|f\rangle\langle f|z|0\rangle \times\delta(E_f - E_0 - \hbar\omega)\omega^{n+1}\, d\omega. \tag{2.5}$$

Parity arguments immediately show that the expectation value of z in the ground state is zero; so that this ground state can be included in the summation over the final states f. Then these final states constitute a complete set of wave functions. This leads to

$$\mu_n = \kappa\hbar^{-n}\langle 0|z(H - E_0)^{n+1}z|0\rangle, \tag{2.6}$$

with

$$\kappa = 2\pi\hbar^{-2}NI^{-1}e^2\mathcal{E}^2. \tag{2.7}$$

In this expression, H is the Hamiltonian of the F center.

Here one is interested in the expressions of the moments corresponding to $n = -1$, 0, 1, and 2. The value of higher-order moments is very sensitive to the high-energy tail of the experimental spectra. Since it seems difficult to determine experimentally the behavior of the F-center absorption spectrum at high energies accurately, it is not possible to evaluate these high-order moments with sufficient precision to warrant consideration if $n > 2$.

For $n = -1$, one has

$$\mu_{-1} = \kappa\hbar \langle 0|z^2|0\rangle . \tag{2.8}$$

For cubic symmetry, this relation becomes

$$\mu_{-1} = \tfrac{1}{3}\kappa\hbar\langle 0|r^2|0\rangle . \tag{2.9}$$

For $n = 0$, the expression (2.6) gives

$$\mu_0 = \kappa\langle 0|z(H - E_0)z|0\rangle . \tag{2.10}$$

Using the fact that $|0\rangle$ is an eigenstate of the F-center Hamiltonian with eigenvalue E_0, one can transform this expression into

$$\mu_0 = \kappa\langle 0|[z,H]z|0\rangle$$

or

$$\mu_0 = \kappa\langle 0|z[H,z]|0\rangle .$$

Taking the half-sum of the last expressions, one ends up with

$$\mu_0 = \tfrac{1}{2}\kappa\langle 0|[z,[H,z]]|0\rangle . \tag{2.11}$$

If the F center can be described in terms of one-electron states, as it is assumed in this work, with a velocity-independent potential V, the only term in the Hamiltonian which does not commute with z is the kinetic energy

$$H_K = p^2/2m ,$$

where m is the electron band mass and p the electron momentum. This leads to

$$\mu_0 = \tfrac{1}{2}\kappa\hbar^2 m^{-1} , \tag{2.12}$$

which is essentially the Thomas-Reiche-Kuhn sum rule for F centers. The applicability of this sum rule and its connection with Smakula's equation is discussed in detail by Smith and Dexter.[19]

For $n = 1$, one obtains in the same way

$$\begin{aligned}\mu_1 &= \kappa\hbar^{-1}\langle 0|[z,H][H,z]|0\rangle \\ &= \tfrac{2}{3}\kappa\hbar m^{-1}\langle 0|(p^2/2m)|0\rangle .\end{aligned} \tag{2.13}$$

For $n = 2$, one has

$$\begin{aligned}\mu_2 &= \kappa\hbar^{-2}\langle 0|[z,H][H,[H,z]]|0\rangle \\ &= \kappa\hbar^{-2}\langle 0|[[z,H],H][H,z]|0\rangle\end{aligned} \tag{2.14}$$

and, taking the half-sum,

$$\begin{aligned}\mu_2 &= \tfrac{1}{2}\kappa\hbar^{-2}\langle 0|[[H,[H,z]],[H,z]]|0\rangle \\ &= \tfrac{1}{2}\kappa m^{-2}\langle 0|[[p_z,H],p_z]|0\rangle .\end{aligned} \tag{2.15}$$

Since p_z commutes with the kinetic energy, this last expression can be written

$$\begin{aligned}\mu_2 &= \tfrac{1}{2}\kappa m^{-2}\langle 0|[[p_z,V],p_z]|0\rangle \\ &= \tfrac{1}{2}\kappa\hbar^2 m^{-2}\left\langle 0\left|\frac{\partial^2 V}{\partial z^2}\right|0\right\rangle \\ &= \tfrac{1}{6}\kappa\hbar^2 m^{-2}\langle 0|\nabla^2 V|0\rangle\end{aligned} \tag{2.16}$$

for reasons of symmetry. If the interaction of the electron with the host lattice is due to Coulomb forces, the Poisson equation gives

$$\mu_2 = -\tfrac{2}{3}\pi e\kappa\hbar^2 m^{-2}\epsilon_\infty^{-1}\langle 0|\rho(\vec{r})|0\rangle , \tag{2.17}$$

where ϵ_∞ is the dielectric constant at high frequency, which is related to the electronic polarization. The charge distribution $\rho(\vec{r})$ is the positive charge of the vacancy plus the bound charge, which is the source of the electric field produced by the ionic polarization. Hopfield[20] has given a sum rule for the imaginary part of the dielectric function that is closely related to Eq. (2.17).

These expressions (2.12), (2.13), and (2.17) of the moments depend upon the parameter κ, which is generally not known. To eliminate this factor, let us consider the ratio of the different moments to μ_0

$$\mu_{-1}/\mu_0 = \tfrac{2}{3}\hbar^{-1}m\langle r^2\rangle , \tag{2.18a}$$

$$\mu_1/\mu_0 = \tfrac{4}{3}\hbar^{-1}\langle p^2/2m\rangle , \tag{2.18b}$$

$$\mu_2/\mu_0 = \tfrac{1}{3}m^{-1}\langle\nabla^2 V\rangle , \tag{2.18c}$$

where the angular brackets denote the expectation value of operators for the ground state. With Eq. (2.17), the last of these relations becomes

$$\mu_2/\mu_0 = -\tfrac{4}{3}\pi e m^{-1}\epsilon_\infty^{-1}\langle\rho(\vec{r})\rangle . \tag{2.19}$$

Therefore, the first two ratios are, respectively, proportional to the mean-square radius and mean kinetic energy of the F center in its ground state; the third ratio is proportional to the mean charge density seen by the electron in its motion, including the bound charge, which describes the ionic polarization induced by the F center.

Only two approximations have been used in the derivation of relations (2.18) and (2.19): the band-mass approximation to take the band structure into account and the dielectric-constant approximation to describe the effects of the electronic polarization.

On the other hand, these ratios can be easily computed by numerical integration. For this purpose, we have used the experimental spectra given by Dutton and Maurer[21] for KBr, and by Lüty[22] for KCl and RbCl. These spectra have been taken at sufficiently low temperature for the F centers to be initially in their ground state.

From these results, it is straightforward to deduce the values of the mean-square radius, mean kinetic energy of the electron, and mean charge

TABLE I. Static dielectric constant ϵ_0, high-frequency dielectric constant ϵ_∞, and ratio of the electron band mass m to the free-electron mass m_e, for the compounds studied here, as compiled in Ref. 23.

	KBr	KCl	RbCl
ϵ_0	4.52	4.49	4.58
ϵ_∞	2.39	2.20	2.20
m/m_e	0.369	0.434	0.432

density seen by it. In this latter calculation, we used the values of the band-mass compiled by one of us[23] (EK) and reproduced in Table I. The results are collected in Table II. It is interesting to note that, for the alkali halides studied here, the mean radius of the F-center ground state is comparable to the nearest-neighbor distance.

III. CHARGE DISTRIBUTION IN F CENTERS

In Sec. II, it has been shown that ratios of moments of the absorption spectrum are related to the mean radius of the F center, the mean kinetic energy and the mean charge density seen by the electron during its motion around the vacancy. The numerical computation of these moments for KBr, KCl, and RbCl has led to the numerical knowledge of these constants.

The purpose of this section is to use these results to determine the charge distribution in F centers. For the alkali halides considered here, the excitation energy of the F center is far larger than the phonon energy and an adiabatic approximation is valid; the ions do not follow the motion of the electron and adapt themselves to the mean electronic charge density.

The F-center mean radius and the charge seen by the electron do not depend much upon the dynamics of the electron in the center, but rather upon the charge distribution. On the contrary, the kinetic energy is far more sensitive to the dynamics of the system. For this reason, use will be made of the ratios μ_{-1}/μ_0 and μ_2/μ_0 in the determination of the charge distribution.

Obviously, with these two pieces of information, it is not possible to obtain the detailed structure of the charge density related to the discrete structure of the lattice, but rather the envelope of this charge distribution.

For our purpose, a better understanding of what we called the mean charge $\langle\rho(\vec{r})\rangle$ seen by the electron is required. As pointed out in Sec. II, it consists of two parts: (a) the first contribution is the positive charge due to the vacancy $|e|\delta(\vec{r})$; and (b) the second contribution is the bound charge $\rho_b(\vec{r})$ describing the ionic polarization induced by the positive vacancy and by the mean electron charge density, which can be considered as a static charge distribution. Therefore, the expectation value of the charge density encountered by the electron is

$$\langle\rho(\vec{r})\rangle = \int |\Psi(\vec{r})|^2[\,|e|\,\delta(\vec{r}) + \rho_b(\vec{r})]\, d^3r, \tag{3.1}$$

where $\Psi(\vec{r})$ is the F-center ground-state wave function.

To calculate this bound charge, let us consider Poisson's equation, which can be written in two different ways.

In the first way, the total charge distribution

$$\rho_t(\vec{r}) = \rho_p(\vec{r}) + \rho_b(\vec{r}), \tag{3.2}$$

where $\rho_p(\vec{r})$ is the physical charge density [the positive charge of the vacancy $|e|\delta(\vec{r})$ and the electron charge distribution $\rho_e(\vec{r})$], is explicitly considered as the source of the electrical potential. However, as the electronic polarization follows perfectly the motion of the electron, the Coulomb interaction is screened by the high-frequency dielectric constant ϵ_∞, so that Poisson's equation is

$$\nabla^2\phi(\vec{r}) = -(4\pi/\epsilon_\infty)\rho_t(\vec{r}). \tag{3.3}$$

In this relation, $\phi(\vec{r})$ is the electric potential related to the electron potential energy by

$$V(\vec{r}) = e\phi(\vec{r}). \tag{3.4}$$

TABLE II. Results obtained for the mean-square radius $\langle r^2\rangle^{1/2}$, the mean kinetic energy $\langle p^2/2m\rangle$, and the mean charge density $\langle\rho\rangle$ seen by the electron. The values given in parenthesis are obtained by replacing the band mass with the free-electron mass. Fourth line: nearest-neighbor distance (Ref. 24).

	KBr	KCl	RbCl
$\langle r^2\rangle^{1/2}$ (Å)	3.88 (2.36)	3.36 (2.22)	3.56 (2.34)
$\langle p^2/2m\rangle$ (eV)	1.54	1.74	1.56
$\langle\rho\rangle/\lvert e\rvert$ (Å^{-3})	0.0082 (0.0223)	0.0114 (0.0262)	0.0090 (0.0209)
d (Å)	3.29	3.14	3.27

In the second way, the physical density of charge $\rho_p(\vec{r})$ alone is considered as the source of the field. In that case, the dielectric constant to be used in Poisson's equation is the static dielectric constant ϵ_0, so that

$$\nabla^2\phi(\vec{r}) = -(4\pi/\epsilon_0)\rho_p(\vec{r}). \tag{3.5}$$

Comparing Eqs. (3.3) and (3.5) gives

$$(\rho_p+\rho_b)/\epsilon_\infty = \rho_p/\epsilon_0 \tag{3.6}$$

or

$$\begin{aligned}\rho_b &= (\epsilon_\infty/\epsilon_0 - 1)\rho_p\\ &= \epsilon_\infty(1/\epsilon_0 - 1/\epsilon_\infty)[\,|e|\,\delta(\vec{r}) + \rho_e(\vec{r})].\end{aligned} \tag{3.7}$$

Let us now turn to the evaluation of the electron charge density $\rho_e(\vec{r})$. The F-center mean-square radius is

$$\langle r^2\rangle = \int |\Psi(\vec{r})|^2 r^2\, d^3r. \tag{3.8}$$

On the other hand, relations (3.1) and (3.7) immediately give

$$\langle\rho(\vec{r})\rangle = \int |\Psi(\vec{r})|^2[(\epsilon_\infty/\epsilon_0)\,|e|\,\delta(\vec{r}) + \epsilon_\infty(1/\epsilon_0 - 1/\epsilon_\infty)\rho_e(\vec{r})]\, d^3r. \tag{3.9}$$

Obviously the square of the modulus of the wave function is the electron charge distribution divided by e so that

$$\langle r^2\rangle = \frac{1}{e}\int \rho_e(\vec{r}) r^2\, d^3r, \tag{3.10}$$

$$\langle\rho(\vec{r})\rangle = -\frac{\epsilon_\infty}{\epsilon_0}\rho_e(0) + \frac{\epsilon_\infty}{e}\left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon_\infty}\right)\int \rho_e^2(\vec{r})\, d^3r. \tag{3.11}$$

As the charge density probably falls off exponentially at large distances, it is natural to expand it in Laguerre functions. This expansion is restricted to two terms, since only two relations are available [Eqs. (3.10) and (3.11)] to determine the coefficients of the expansion. This leads us to write

$$\rho_e(\vec{r}) = eA(1+ar)e^{-\chi r} \quad (a, \chi > 0), \tag{3.12}$$

where A is a normalization constant, such that

$$A\int(1+ar)e^{-\chi r}\, d^3r = 1, \tag{3.12$'$}$$

which gives

$$4\pi A[2\chi^{-3} + a(3!)\chi^{-4}] = 1. \tag{3.13}$$

TABLE III. Values obtained for the parameters a, χ, and A defined in the charge distribution [Eq. (3.12)]. The values given in parenthesis are obtained by replacing the band mass with the free-electron mass.

	KBr	KCl	RbCl
a (Å^{-1})	1.095 (4.32)	1.41 (4.52)	1.44 (4.64)
χ (Å^{-1})	1.093 (1.85)	1.27 (1.96)	1.20 (1.86)
A (Å^{-3})	0.013 (0.0314)	0.0186 (0.0383)	0.0149 (0.0304)

With this form [Eq. (3.12)] of the charge distribution, Eqs. (3.10) and (3.11) become

$$\langle r^2\rangle = A\int(1+ar)e^{-\chi r} r^2\, d^3r,$$

$$\frac{\langle\rho(\vec{r})\rangle}{e\epsilon_\infty} = -\frac{A}{\epsilon_0} + \left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon_\infty}\right)A^2\int(1+ar)^2 e^{-2\chi r}\, d^3r,$$

or, after integration,

$$\langle r^2\rangle = 4\pi A[(4!)\chi^{-5} + a(5!)\chi^{-6}], \tag{3.14}$$

$$\langle\rho(\vec{r})\rangle/e\epsilon_\infty = -A/\epsilon_0 + (1/\epsilon_0 - 1/\epsilon_\infty)4\pi A^2 \times[2(2\chi)^{-3} + 2a(3!)(2\chi)^{-4} + a^2(4!)(2\chi)^{-5}]. \tag{3.15}$$

The relations (3.13), (3.14), and (3.15) constitute a system of three equations which is solved numerically.

The results are reported in Table III and the electron charge density $\rho_e(\vec{r})$ versus the distance from the vacancy r is represented in Fig. 1, where it is compared, in the case of KCl, with the experimental data obtained by Kersten[14] using electron nuclear double-resonance (ENDOR) measurements. In first approximation, these experimental data have a decreasing exponential behavior versus the distance r. The mean-square fitting using an exponential law $e^{-\chi r}$ for this experimental charge distribution gives $\chi = 1.10$ Å^{-1}. The same fitting of the charge distribution obtained in the present work gives $\chi = 1.18$ Å^{-1}, in good agreement with the experimental value. On the contrary, the value $\chi = 1.88$ Å^{-1} is obtained when the calculations are performed with the free-electron mass. This seems to rule out the free-electron hypothesis for the F center and to favor the band-mass approximation.

Let us now consider the mean kinetic energy related to the ratio μ_1/μ_0. It is reasonable to think that the F-center wave function is real. Its expression, compatible with the charge distribution Eq. (3.12), is then

$$\Psi(\vec{r}) = A^{1/2}(1+ar)^{1/2}e^{-\chi r/2}. \tag{3.16}$$

This leads to the following relation for the expectation value of the kinetic energy:

$$\langle p^2/2m\rangle = \tfrac{1}{2}\pi\hbar^2 m^{-1}A \times[3a\chi^{-2}+\chi^{-1}+a^{-1}e^{\chi/a}E_1(\chi/a)], \qquad (3.17)$$

where E_1 denotes the exponential integral function

$$E_1(x)=\int_x^{\infty} t^{-1}e^{-t}\,dt \quad (x>0). \qquad (3.17')$$

Since the parameters a, χ, and A are known (see Table III), it is possible to evaluate numerically the expression (3.17) and to compare the result with the value deduced from the ratio μ_1/μ_0. This comparison is given in Table IV.

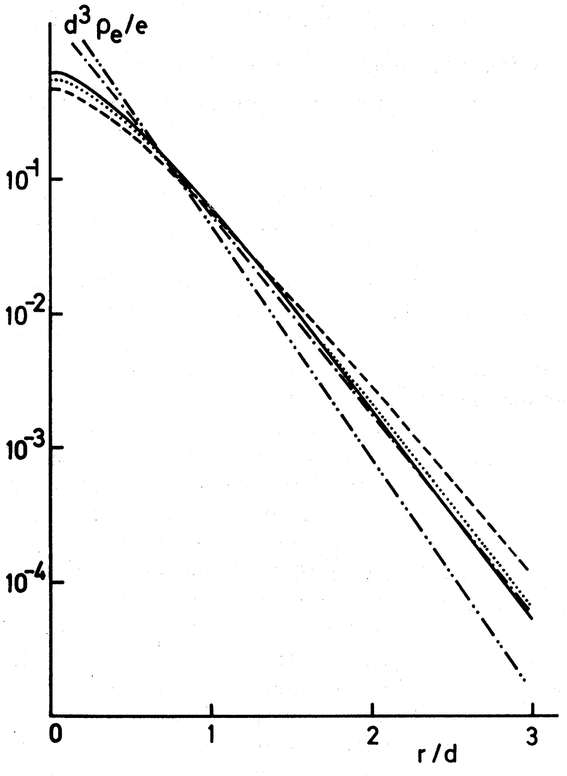

FIG. 1. Reduced electron charge density $\rho_e(\vec{r})$ [Eq. (3.12)] vs the ratio r/d for KBr (dashed line), KCl (solid line), and RbCl (dotted line). Here the reduced charge density is expressed in units e/d^3, where d is the nearest-neighbor distance and e is the electron charge. Fourth curve (dash-dotted line) gives the mean-square fitting of Kersten's experimental data for KCl using the expression $e\chi^3(8\pi)^{-1}e^{-\chi r}$ for the electron charge density. Fifth curve (dash-double dotted line) gives the charge density predicted by the point-ion model of Gourary and Adrian (Ref. 26) with wave function type I.

TABLE IV. Mean kinetic energy (in eV) computed with Eq. (3.16) for the wave function with the set of values of a, χ, and A obtained using the band-mass approximation (a); and with the set of values obtained when the band mass is replaced by the free-electron mass (b); (c) is the "experimental" value deduced from μ_1/μ_0 (see Table II).

	KBr	KCl	RbCl
(a)	1.77	1.99	1.78
(b)	1.72	1.94	1.73
(c)	1.54	1.74	1.56

Let us now use the present method in order to test the validity of the charge distribution deduced from the usual wave function found in the literature[5] for the F-center ground state. This wave function depends upon a single parameter $\bar{\chi}$, so that it leads to the following charge density:

$$\rho(\vec{r}) = e[(\tfrac{1}{2}\bar{\chi})^3/7\pi](1+\tfrac{1}{2}\bar{\chi}r)^2 e^{-\bar{\chi}r}. \qquad (3.18)$$

Our Laguerre representation [Eq. (3.12)] of the charge distribution being linear in r does not allow a comparison with Eq. (3.18). Therefore, it is better for the present purpose to introduce a slightly different expression which is a function of two parameters $\bar{a}$ and $\bar{\chi}$ ($\bar{A}$ is just a normalization constant),

$$\bar{\rho}_e(\vec{r}) = e\bar{A}(1+\bar{a}r)^2 e^{-\bar{\chi}r}. \qquad (3.19)$$

Proceeding in the same way as above, one obtains the following relations analogous to Eqs. (3.13), (3.14), and (3.15):

$$4\pi\bar{A}[2\bar{\chi}^{-3}+2\bar{a}(3!)\bar{\chi}^{-4}+\bar{a}^2(4!)\bar{\chi}^{-5}]=1, \qquad (3.20)$$

$$\langle r^2\rangle = 4\pi\bar{A}[(4!)\bar{\chi}^{-5} +2\bar{a}(5!)\bar{\chi}^{-6}+\bar{a}^2(6!)\bar{\chi}^{-7}], \qquad (3.21)$$

$$\langle\rho(\vec{r})\rangle/e\epsilon_\infty = -\bar{A}/\epsilon_0+(1/\epsilon_0-1/\epsilon_\infty)4\pi\bar{A}^2 \times[2(2\bar{\chi})^{-3}+4\bar{a}(3!)(2\bar{\chi})^{-4} +6\bar{a}^2(4!)(2\bar{\chi})^{-5} +4\bar{a}^3(5!)(2\bar{\chi})^{-6}+\bar{a}^4(6!)(2\bar{\chi})^{-7}]. \qquad (3.22)$$

In Table V, the solutions of these equations for KBr and KCl are reported and compared with the theoretical predictions due to Schmid[5] and Renn.[25]

TABLE V. Numerical values of the parameters $\bar{a}$ and $\frac{1}{2}\bar{\chi}$ (in Å^{-1}) appearing in the charge distribution Eq. (3.19).

	Schmid	Renn	Present work
KBr $\bar{a}$	0.655	0.92	0.492
$\frac{1}{2}\bar{\chi}$	0.655	0.92	0.605
KCl $\bar{a}$	0.675	0.96	0.614
$\frac{1}{2}\bar{\chi}$	0.675	0.96	0.705

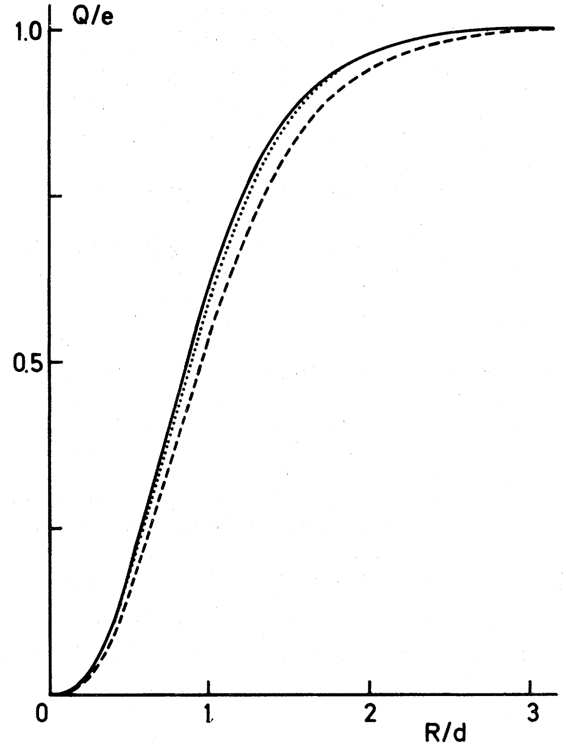

FIG. 2. Quantity Q/e (charge contained in a sphere of radius R centered on the vacancy, in units of electron charge) versus the ratio R/d (d is the nearest-neighbor distance), for KBr (dashed line), KCl (solid line), and RbCl (dotted line).

The values of $\bar{a}$ and $\frac{1}{2}\bar{\chi}$ obtained in the present work are rather close to each other; this shows that the usual trial wave function containing a single parameter is a reasonable approximation to describe the F-center ground state.

IV. CONCLUSIONS

Table IV shows that the kinetic energy computed with the wave function (3.16) is around 10% larger than the value deduced from μ_1/μ_0. This is a good agreement, since the moments are presumably determined with a limited accuracy, the high-energy part of the spectrum not being well known. This agreement is a strong argument in favor of the model used in the present paper. An especially important conclusion is that the energy tail of the F-center absorption spectrum is probably not as strong as one could fear.

Our results, by themselves, do not allow one to decide which value must be used for the mass of the electron in the F center: both the band mass and the free-electron mass give nearly the same value for the kinetic energy. However, it is shown (Fig. 1) that the charge distribution obtained in the present work is in good agreement with Kersten's experimental data for KCl, when the value of the band mass is used in the theory. This is a further argument in favor of the validity of the assumptions used in the present work.

On the other hand, the agreement is poor when the free-electron mass is used in place of the band mass. This seems to prove that the mass to be used to describe the motion of the electron is the band mass rather than the free-electron mass.

For the sake of comparison, the charge distribution predicted by the point-ion model of Gourary and Adrian[26] is also represented in Fig. 1 for KCl. The agreement with experiment is less good, the slope being somewhat too large. In this comparison, the wave function called type I in Ref. 26 has been used. The wave function II and III are more rapidly decreasing with distance from the center, so that the agreement is still worse.

Making use of the expression (3.12) for ρ_e, one can calculate the charge Q due to the electron cloud of the center and contained in a sphere of radius R centered on the position of the vacancy. This charge is given by

$$Q=4\pi\int_0^R r^2\rho_e(r)\,dr. \tag{4.1}$$

The result is shown in Fig. 2. In the case of KCl, one finds $Q\simeq 0.6e$ for a radius R equal to the nearest-neighbor distance. This is in agreement with the conclusion obtained by Schmid.[5]

An important conclusion concerns the large value of the coefficient a in the expression (3.12) of the electron charge distribution. As a consequence, the F centers studied here are far from being hydrogenlike. It seems that the electron is repelled outwards and spends an important part of its time on the first-neighbor ions of the vacancy. This is not surprising since these ions have a positive charge. Of course, our results for distances from the vacancy smaller than the interionic distance are only qualitative.

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