moments and nuclear spins, while $a_s(x)$ is the hyperfine constant for either La or Lu. Using the accepted values of μ and I and the data in Table II for $a_s(x)$, we find that the derived value for a_s(Tb) is 303 and 476×10^{-4} cm^{-1} obtained using the data for La and Lu, respectively. These values are in good agreement with the value of 450×10^{-4} cm^{-1} obtained from the data on the Tb center provided the $J = \frac{13}{2}$ manifold is taken as the ground state. Therefore, we conclude from both the g and A values that the ground state of the ionized center in Tb doped CaF$_2$ arises from the $J = \frac{13}{2}$ manifold.

[1]D. L. Staebler and Z. J. Kiss, Appl. Phys. Letters **14**, 93 (1969); Z. J. Kiss, IEEE J. Quantum Electron. **QE-5**, 12 (1969).

[2]D. L. Staebler and S. Schnatterley, preceding paper, Phys. Rev. B **3**, 516 (1971).

[3]W. Hayes and J. W. Twidell, J. Chem. Phys. **35**, 1521 (1961).

[4]Z. J. Kiss and P. N. Yocom, J. Chem. Phys. **41**, 1511 (1964).

[5]J. Arends, Phys. Status Solidi **7**, 805 (1964); W. Hayes and J. P. Stott, Proc. Roy. Soc. (London) **A301**, 313 (1967).

[6]D. S. McClure and Z. J. Kiss, J. Chem. Phys. **39**, 3251 (1963).

[7]R. Alig, following paper, Phys. Rev. B **3**, 536 (1971).

[8]Barry S. Gourary and Frank J. Adrian, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1960), Vol. 10, p. 127.

[9]In these materials, D. Staebler and Z. J. Kiss have observed the presence of optical absorption bands due to Ce^{2+} after the crystals have been irradiated with blue light ($\lambda \le 400$ Å). The energy levels of Ce^{2+} in CaF$_2$ have been reported by R. Alig, Z. J. Kiss, J. P. Brown, and D. S. McClure, Phys. Rev. **186**, 276 (1969).

[10]Y^{2+} has not been identified by us in these crystals. EPR of Y^{2+} has been reported by J. R. O'Connor and J. H. Chen, Appl. Phys. Letters **5**, 100 (1964).

[11]An EPR spectrum recently observed in irradiated CaF$_2$:Gd^{3+} is probably that due to the stable center associated with Gd. A. J. Bevolo and S. Lee, Phys. Rev. Letters **24**, 1276 (1970).

[12]W. Hayes and J. W. Twidell, Proc. Phys. Soc. (London) **82**, 330 (1963).

[13]Halis Odabasi, J. Opt. Soc. Am. **57**, 1459 (1967).

[14]N. F. Ramsey, in *Handbook of Physics*, 2nd ed., edited by E. U. Condon and H. Odishaw (McGraw-Hill, New York, 1957), pp. 9–98.

[15]G. J. Ritter, Phys. Rev. **126**, 240 (1962).

[16]A. Steudel, Z. Physik **152**, 9 (1958).

[17]P. A. Forrester and C. F .empstead, Phys. Rev. **126**, 923 (1962).

[18]B. G. Wybourne, *Spectroscopic Properties of Rare Earth* (Interscience, New York, 1965).

[19]J. M. Baker, W. Hayes, and M. C. O'Brian, Proc. Roy. Soc. (London) **A254**, 273 (1960).

[20]M. S. Weber and R. W. Bierig, Phys. Rev. **134**, A1492 (1964).

[21]S. D. McLaughlan and P. A. Forrester, Phys. Rev. **151**, 311 (1966).

[22]J. H. Beaumont and W. Hayes, Proc. Roy. Soc. (London) **A309**, 41 (1969).

[23]E. S. Sabisky and C. H. Anderson, Phys. Rev. **159**, 234 (1967).

Theory of Photochromic Centers in CaF$_2$

R. Casanova Alig

RCA Laboratories, Princeton, New Jersey 08540

(Received 23 July 1970)

On the basis of recent optical and EPR work, it has been suggested that the ionized and thermally stable photochromic centers in CaF$_2$ consist of one and two electrons bound at an anion vacancy adjacent to a trivalent impurity cation. For the ionized center, we have shown that the energy levels and wave functions of the isolated F center are not strongly perturbed by the introduction of the impurity ion. Since the divalent ions of the impurities which are found to form these centers, i.e., Y, La, Ce, Gd, Tb, and Lu, have low-lying s and d valence orbitals which overlap the F-center wave functions, we have investigated the defect-impurity orbitals which may be formed from a linear combination of F electron orbitals and these impurity orbitals. The predictions based on this defect-impurity orbital description are found to be consistent with the optical and EPR data for the stable and ionized photochromic centers.

I. INTRODUCTION

During the past few years there have been a number of studies of the optical properties of colored CaF$_2$ crystals containing impurity cations. One of the earliest of these studies was that of Scouler and Smakula[1] in which the optical absorption of CaF$_2$ doped with YF$_3$ and NaF was measured after coloration by electron irradiation at selected temperatures; in a number of cases new absorption bands

appeared in the visible portion of the spectrum. While there has been little subsequent study of the optical properties of colored CaF_2 doped with NaF, there have been a number of papers[2,3] in which the coloration of CaF_2 containing Y impurities is discussed. More recently it has been found that crystals of additively colored CaF_2 doped with the fluorides of certain rare earths, specifically, La, Ce, Gd, Tb, and Lu, also exhibit optical-absorption bands in the visible region of the spectrum which are thermally stable at room temperature[4,5]; in addition, these crystals, as well as those containing Y impurities, are found to be photochromic.[5-7]

It has been noted[3,8] that the infrared luminescence associated with visible irradiation of the absorption bands of colored YF_3-doped CaF_2 is partially polarized and that the luminescent centers are oriented along the [111] direction. In addition, two of the more prominent bands in the visible portion of the thermally stable absorption spectrum of colored CaF_2 doped with Y or one of the rare earths mentioned above are found to exhibit a linear dichroism[9] consistent with an anisotropic center having a symmetry axis along the [111] direction. Of these two absorption bands, the band occurring at shorter wavelengths is found to be due to an absorption dipole oriented along the symmetry axis while the band at longer wavelengths is found to be due to two orthogonal absorption dipoles perpendicular to the symmetry axis.[9] Upon irradiation of the crystal in the photochromic band, i. e., irradiation with light of the wavelength of the higher-energy absorption band, these two absorption bands disappear and the characteristic absorption bands of the switched photochromic spectrum appear; this spectrum is not thermally stable at room temperature. In addition to the absorption bands of the switched photochromic state,[10] this spectrum contains two absorption bands which are in many ways similar to the two thermally stable absorption bands except that they are shifted to shorter wavelengths; in particular, they exhibit a linear dichroism similar to that just described.[5] It is presumed that these two absorption bands arise from an ionized form of the color center responsible for the two thermally stable absorption bands.

It has been suggested[8,9] that the color center responsible for the optical phenomena described above consists of an F center perturbed by an impurity cation substitutionally replacing one of the Ca^{2+} ions nearest the vacancy center. This model would, of course, have the required [111] symmetry. It has been recently confirmed[11] by EPR techniques and by a combination of linear- and circular-dichroism measurements[5] that the center responsible for the absorption bands in the thermally stable spectrum consists of two electrons trapped at an anion vacancy associated with a trivalent impurity cation in one of

the sites nearest the vacancy center. At the same time it was also confirmed that the pair of absorption bands appearing in the switched photochromic spectrum do indeed arise from an ionized form of this center, i. e., one electron trapped at an anion vacancy adjacent to a trivalent impurity cation.

The F center, which consists of an electron bound to an anion vacancy, has been identified,[12] in additively colored CaF_2, as the source of an optical-absorption band at 3750 Å. The symmetry of the potential acting on the F electron in CaF_2 is T_d; the optical absorption arises from a transition of the F electron from the s-like ground state transforming as A_1 to the p-like excited state transforming as T_2. The introduction of an impurity cation on a lattice site nearest the vacancy center will reduce the symmetry of the potential acting on the trapped electron to C_{3v}. The electron orbitals of this modified F center will transform according to the A_1, A_2, and E representations of C_{3v} in a manner analogous to the transformation of the electron orbitals of the heteronuclear diatomic molecule according to the representations σ^+, σ^-, π, etc., of $C_{\infty v}$. The orbital ground state of this center transforms[5] according to the A_1 representation. Transitions between the ground state and the excited levels transforming as A_1 and E will be characterized by the labels $F_{\parallel}$ and $F_{\perp}$ respectively. The optical absorption associated with these transitions will consist of bands polarized in the plane perpendicular to the vacancy-impurity axis ($F_{\perp}$) and along the vacancy-impurity axis ($F_{\parallel}$).

In this paper we shall devote the greater part of our attention to the system consisting of a single electron trapped at an anion vacancy adjacent to a trivalent impurity ion, i. e., to the ionized photochromic center. Because of its similarity we shall also treat the system consisting of an alkali-metal cation impurity, in particular Na^+, adjacent to an anion vacancy with a trapped electron. The Hamiltonian operator for the electron trapped at this vacancy-impurity center is

$$H = -(\hbar^2/2m)\nabla^2 + V(\vec{r}) + [V'(\vec{r}) - V(\vec{r})] , \qquad (1)$$

where $V(\vec{r})$ is the potential energy of an electron trapped at an anion vacancy in an otherwise perfect crystal and $V'(\vec{r})$ is the potential energy of an electron trapped at an anion vacancy adjacent to an impurity cation in an otherwise perfect crystal. The wave functions or defect-impurity orbitals $\psi_n(\vec{r})$ for this electron can be written by analogy to the formation of molecular orbitals by the linear combination of atomic orbitals[13] as

$$\psi_n(\vec{r}) = N_n^{-1} \sum_{i=1}^{\infty} [a_{Fni}\psi_{Fi}(\vec{r}) + a_{Ini}\psi_{Ii}(\vec{r})] , \qquad (2)$$

where N_n normalizes the wave function and where $\psi_{Fi}(\vec{r})$ and $\psi_{Ii}(\vec{r})$ are the respective wave functions

of an electron bound to an isolated anion vacancy
(F center) and to an isolated impurity ion (hence, an
impurity ion with one less unit of positive charge)
in an otherwise perfect crystal. The electronic
energies and the associated defect-impurity orbital
wave functions are obtained, of course, by minimiz-
ing $\langle \psi_n(\vec{r}) | H | \psi_n(\vec{r}) \rangle$ with respect to a_{Fni} and a_{Ini}.
This leads to the set of equations

$$\sum_{i=1}^{\infty} [a_{Fni}\langle \psi_{Fj} | H - E_n | \psi_{Fi} \rangle + a_{Ini}\langle \psi_{Ij} | H - E_n | \psi_{Fi} \rangle] = 0 ,$$

$$\text{(3)}$$

$$\sum_{i=1}^{\infty} [a_{Fni}\langle \psi_{Fj} | H - E_n | \psi_{Ii} \rangle + a_{Ini}\langle \psi_{Ij} | H - E_n | \psi_{Ii} \rangle] = 0 ,$$

where j runs from 1 to ∞ and E_n is the energy as-
sociated with $\psi_n(\vec{r})$.

The evaluation of the matrix elements $\langle \psi_{Fi} | H | \psi_{Fj} \rangle$
is simply a perturbation calculation on the F-center
wave functions, the perturbation being just the third
term in Eq. (1); this calculation is discussed in
Sec. III of this paper. One expects that the pres-
ence of a charged impurity ion in a nearest-neighbor
site to the vacancy center will have a strong effect
on the F-electron energies and wave functions. One
also expects that in the case of a trivalent impurity,
the additional positive charge on the impurity will
lower the energy of the A_1 level derived from the
p-like F-center excited state with respect to the E
level derived from the same state. This prediction
is quite disconcerting, for we noted earlier that
the experimental ordering of the energy levels is
reversed. We shall show in Sec. III that when one
takes into account the displacements of the ions
surrounding the impurity ion and the finite sizes of
the impurity ion and the ions surrounding the im-
purity, these contributions tend to cancel the effect
of the additional charge on the impurity ion. Thus,
the energy levels of the perturbed F-center system
do not differ greatly from the energy levels of the
unperturbed F center and there is little admixture
of the s- and p-like wave function on the perturbed
center.

The defect-impurity orbital description of the va-
cancy-impurity system is given in Sec. II. The
reader will note that the order of presentation of
this calculation is reversed from that in which it
was carried out. This was done because the defect-
impurity orbital description is more qualitative and
the results are more interesting. This description
yields tentative explanations for the thermal stability
of the photochromic centers, for the existence of
another $F_\perp$ transition at shorter wavelengths than the
$F_\parallel$ transition in the photochromic centers, and for
the anomalous oscillator strengths of the absorption
bands of the photochromic centers. It also yields
predictions for the optical transition energies, for
the isotropic hyperfine constant, and for the g-factor

anisotropy, which are consistent with those observed
experimentally.

II. DEFECT-IMPURITY ORBITAL DESCRIPTION

The defect-impurity orbital $\psi_n(\vec{r})$ defined in Eq.
(2) is a linear combination of the F-electron orbit-
als centered on the vacancy and the atomic orbitals
centered on the impurity. As was mentioned in the
Introduction, it might be thought that the F-electron
wave functions will be strongly admixed by the pres-
ence of a charged impurity ion and that the F-elec-
tron energy levels will be severely perturbed; in
Sec. III this is shown not to be the case for the tri-
valent impurity ions considered here. The energies
of the atomic orbitals centered on the impurity will
be perturbed from their free-ion values not only by
the cubic crystal field of the CaF_2 lattice, but also
by the presence of the adjacent anion vacancy which
will introduce an additional trigonal field.

The overlap integrals $\langle \psi_{Fi} | \psi_{Ij} \rangle$ and the resonance
integrals $\langle \psi_{Fi} | H | \psi_{Ij} \rangle$ will, of course, be quite im-
portant in the determination of the amount of co-
valent bonding between the anion vacancy and the
impurity. In addition the relative energy separa-
tions between the orbitals of the F electron and
those of an additional electron on the impurity will
be important in this calculation and, furthermore,
these energy separations will be significant in the
selection of those orbitals between which covalent
bonding can be expected to occur. In the case of
an alkali-metal impurity ion we expect to find no
energy levels of the alkali-metal atom impurity
below the CaF_2 conduction band because the binding
energy of an electron in a free alkali-metal atom
is considerably less than the Madelung potential
energy (20 eV) of an electron at a cation site in
CaF_2. Thus, we expect the energy levels of an F
center modified by an adjacent Na^+ impurity ion to
be just those given in Sec. III, that is, there is
little covalent contribution to the bonding energy.
In the case of a trivalent impurity ion of one of the
rare earths or Y, however, it is indeed likely that
there will be energy levels of the divalent impurity
ion below the CaF_2 conduction band because the bind-
ing energy of an electron in the free divalent ions of
these atoms (see Fig. 1) is comparable to the Made-
lung potential energy of an electron at a cation site
in CaF_2. In fact these rare-earth impurities are
known[10,14] to exist in the divalent state in CaF_2.

If one views the center consisting of an electron
trapped at an anion vacancy adjacent to a trivalent
impurity ion of one of the rare earths or Y as a di-
valent impurity ion with an adjacent anion vacancy,
the energy levels and wave functions of this defect-
impurity center will be those of the divalent ion in
a cubic crystalline field modified by a superimposed
trigonal field. The energy levels and wave functions
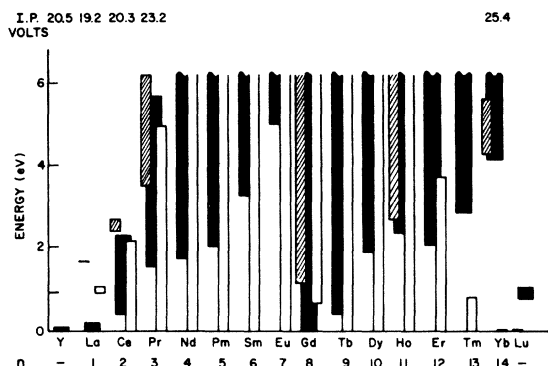of the divalent ions of these atoms in the cubic crys-

FIG. 1. Diagram of $4f^n$ (white), $4f^{n-1} 5d$ (black), and $4f^{n-1} 6s$ (shaded) configurations of the free divalent rare-earth ions. Analogous configurations of the free divalent Y and Lu ions are also shown. Ionization potentials in eV of these divalent ions are shown at top of figure. Sources of these data are given in Ref. 15.

talline field of CaF$_2$ are not well known; indeed, the energy levels and wave functions of the free divalent ions of these atoms have not been fully ascertained. Because so little quantitative information is available about the electronic orbitals centered on the impurity ion, it is clear that our calculation of the electron orbitals of the vacancy-impurity center must be highly approximate.

The distribution of energy levels of the lower-lying electronic configurations of the free divalent yttrium and rare-earth ions[15] is shown in Fig. 1. It is clear from this figure that the $4f^{n-1} 5d$ and the $4f^{n-1} 6s$ configurations either lie close to or contain the ground states of the free divalent ions of the rare earths lying near the beginning or the middle of the rare-earth series. A similar statement can be made regarding the $5d$ and $6s$ configurations of Lu^{2+} and the $4d$ and $5s$ configurations of Y^{2+}. If we assume that the centers of gravity of these lower-lying configurations are shifted uniformly when the divalent ions are placed in a cubic crystalline field[16] and that the f electrons are shielded from the crystal field, then the levels of the $4f^n$ and $4f^{n-1} 6s$ configurations[17] will not be greatly changed by the crystal field. The levels of the $4f^{n-1} 5d$ configuration will be split into two sets of levels transforming as t_{2g} and e_g of the cubic symmetry group O_h; these two sets of levels will be separated by an energy 10 Dq, where[10,18] Dq is of order 0.2–0.25 eV. Due to the eightfold coordination of the fluorine ions about the divalent rare earth, one expects the levels transforming according to e_g to lie at lower energies. This has been observed[10,19] for La^{2+}, Ce^{2+}, and Yb^{2+} on cubic sites in fluorite structures. These e_g levels will not be split by the addition of the trigonal field and we shall assume that they are

not strongly admixed with the t_{2g} levels by the trigonal field.

These e_g orbitals can overlap the p_x and p_y orbitals of the F electron, i. e., the p orbitals oriented perpendicular to the vacancy-impurity axis, to form E bonds (π bonds in the notation appropriate to the free diatomic molecule) and the $4f^{n-1} 6s$ orbitals can overlap the p_z and s orbitals of the F electron to form A bonds. It should be noted that the e_g orbitals do not overlap the p_z orbital of the F electron. The orbitals transforming according to t_{2g} of the $4f^{n-1} 5d$ configuration and the orbitals of the $4f^n$ configuration will, of course, overlap the F-electron wave functions to form both A and E bonds. We shall assume, however, that the orbitals of the $4f^n$ configuration are so tightly bound to the ion core that they do not contribute significantly to the bonding.

It is not at all clear where the energy levels of the divalent impurity ion lie relative to those of the F electron. We do note, however, that in addition to the previously mentioned photochromic $F_\perp$ absorption band at longer wavelengths than the $F_\parallel$ absorption band, there exists[5] a second photochromic $F_\perp$ absorption band at shorter wavelengths than the $F_\parallel$ band. The energies of these two $F_\perp$ absorption bands in the ionized photochromic center are found[5] to be about equally spaced above and below the absorption-band energy of the unperturbed F center in CaF$_2$. Since two overlapping atomic orbitals at the same energy form bonding and antibonding molecular orbitals which are shifted to lower and higher energies than the atomic orbital energy, we shall assume that the energy of the $4f^{n-1} 5d e_g$ orbitals on the impurity ion is approximately the same as the energy of the p state of the F electron. If this is the case, then these e_g orbitals on the impurity and the p_x and p_y orbitals of the F center contribute equally to the formation of the E bonds.

The energies of the remaining impurity levels may now be ascertained from the data shown in Fig. 1, keeping in mind, of course, that the $4f^{n-1} 5d$ levels transforming according to e_g will be lowered by the crystal field to about 1.5 eV below the bottom of the $4f^{n-1} 5d$ configuration shown in Fig. 1. The $4f^{n-1} 6s$ and the $4f^{n-1} 5d t_{2g}$ levels will then lie near to, but somewhat higher in energy than, the $4f^{n-1} 5d e_g$ levels. Thus, the degree of covalency of the A bond between the $4f^{n-1} 6s$ and $4f^{n-1} 5d t_{2g}$ impurity orbitals and the F-electron s orbital will be small compared to the E bonds despite the large-overlap integrals of these orbitals. Since the $4f^{n-1} 5d t_{2g}$ levels lie 2 or 3 eV above the $4f^{n-1} 5d e_g$ levels, we shall neglect the contribution of these t_{2g} levels to the E bonds. A schematic diagram of the resulting defect-impurity orbitals is shown in Fig. 2.

The order and separation of the defect-impurity

orbital energy levels shown in Fig. 2 are consistent with the results of a very crude numerical calculation[13] of these levels. In particular, atomic radial wave functions[20] were used to describe the impurity orbitals and hydrogenic wave functions were used to describe the F electron. Valence-state ionization energies were used to approximate the diagonal matrix elements and the Mulliken-Wolfsberg-Helmholtz approximation[21] was used to evaluate the resonance integrals. Overlap integrals were estimated from available tables.[22] The energies of the s and p states of the F electron were taken[23] to be 8 and 4 eV below the bottom of the conduction band, while the energies of the $4f^{n-1} 6s$ and $4f^{n-1} 5dt_{2g}$ orbitals were taken to be at the bottom of the conduction band. The $5de_g$ energy-level assignment is consistent with this calculation.

All the preceding discussion has been restricted to the ionized photochromic center. The thermally stable center is formed from the ionized center by the addition of another electron. The optical properties of this neutral center are quite similar to those of the ionized center; this observation is con-
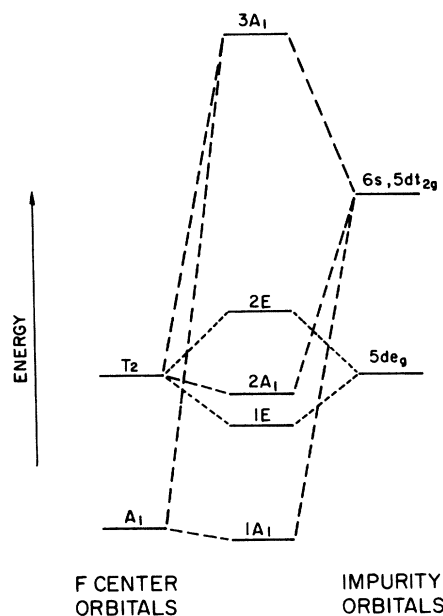

FIG. 2. Schematic diagram of the defect-impurity orbital energy levels of the ionized photochromic center (C_{3v} symmetry). Energy levels of the isolated F center (T_d symmetry) are shown on left and crystal-field energy levels of the isolated divalent impurity ion (O_h symmetry) are shown on right. Each level is designated with the representation according to which it transforms; if several levels transforming according to the same representation appear, they are numbered in ascending energy. Separations in energy of defect-impurity orbitals shown here are consistent with results of a very crude numerical calculation of the energies.

sistent with the building up of the electronic configurations by placing each added electron into the empty orbital with the lowest energy. The spin of the added electron pairs with the spin of the $1A_1$ electron of the ionized center to strengthen the bond between the anion vacancy and the impurity via the exchange interaction. Thus, although we certainly expect the two-electron center to be more stable thermally than the ionized center because the two-electron center is electrically neutral, we have additional support for this expectation from this electron pairing.

This defect-impurity orbital model for the ionized photochromic center accounts for the shift of the lower-energy $F_\perp$ transition to a wavelength longer than that of the F center in CaF_2 as well as for the existence of a second $F_\perp$ transition at a wavelength shorter than that of the F center. In addition, as has previously been pointed out,[5] this model accounts for the decrease in the energy separation of the two $F_\perp$ bands with increased lattice constant; this reduced separation has been observed[5] as a function of increasing temperature and by replacing[24] CaF_2 with SrF_2. In the stable photochromic center and, within experimental error, in the ionized photochromic center, the area under the absorption band, i. e., the zeroth moment of the line-shape function,[25] of the lower-energy $F_\perp$ transition, is found to be equal to the area under the absorption band of the $F_{\|}$ transition.[5] If the excited-state wave functions of these photochromic centers were derived solely from the wave functions of the F center, the area under the absorption band of the $F_\perp$ transition would be twice that of the $F_{\|}$ transition. The formation of an E bond between the p orbitals of the F center and the $4f^{n-1} 5de_g$ orbitals of the impurity, however, reduces the area under the abosrption band of the lower energy $F_\perp$ transition predicted by this model by a factor of 2.

Using the conclusion that the A_1 ground state of the ionized photochromic center is composed largely of the $1s$-like ground-state wave function of the F center (see Fig. 2), one may make rough predictions of the isotropic hyperfine constant and the anisotropy of the g factor for these ionized centers. These predictions are of particular interest since experimental measurements of these quantities exist.[11] The isotropic hyperfine constant due to a nucleus at site γ is[26]

$$a_\gamma = (16\pi \mu_B \mu_\gamma / 3I_\gamma) A_\gamma |\psi(\vec{r}_\gamma)|^2 , \qquad (4)$$

where μ_B is the Bohr magneton, μ_γ and I_γ are the magnetic moment and spin of the nucleus at site γ, and $\psi(\vec{r}_\gamma)$ is the envelope of the defect-impurity ground-state orbital evaluated at site γ. The amplifying factor A_γ accounts for the fact that the wave function of the trapped electron is orthogonal to the core orbitals of the ion at site γ.[26,27] Assuming that

the defect-impurity ground-state orbital is composed solely of the ground state of the F center and using approximate wave functions,[20,23] we calculate the isotropic hyperfine constant due to the impurity ion in these ionized photochromic centers to be 0.034 cm^{-1} when the impurity is La^{3+} or Lu^{3+} and 0.008 cm^{-1} when the impurity is Y^{3+}; the observed[11] values are 0.021 and 0.03 cm^{-1} for La^{3+} and Lu^{3+}, respectively.

An anisotropy in the g factor, which results from a nonzero spin-orbit interaction,[28] can be quantitatively defined as $(g_\| - g_\perp)/g_\|$, where $g_\|$ and $g_\perp$ are the diagonal elements of the g tensor. A nonzero anisotropy may arise from an admixture of F-center states having nonzero angular momentum into the defect-impurity ground state or from orthogonalizing the defect-impurity ground state orbital to the ionic core states. In this latter case the anisotropy arises, of course, because the impurity-core states differ from the Ca^{2+} core states. An estimate of the anisotropy arising from the admixture of p-like F-center functions into the ground state shows that the anisotropy cannot be much "greater than 10^{-4}. A rough calculation[29] based on the admixture of ionic states into the defect-impurity" ground state indicates that, for the ionized photochromic center containing a La^{3+} impurity ion, the anisotropy in the g factor should be about 0.03 due to the large spin-orbit coupling constant for a $5p$ electron on this ion. The experimental value[11] of the g-factor anisotropy for the ionized photochromic center containing La is 0.017, a value with which the latter calculation is consistent.

It is apparent from the discussion of both this section and the next that the properties of the impurity ion play a very significant role in the calculation of the energy levels of the photochromic centers. It is therefore somewhat strange that the experimental transition energies of these photochromic centers do not depend more strongly on the choice of the impurity ion;[30] the reasons for this lack of variation are not clear. It should also be emphasized that the fact that the electronic ground state of the defect-impurity orbital shown in Fig. 2 lies at a lower energy than the electronic ground states of the isolated F center and the isolated divalent impurity does not imply that the defect-impurity system should be more stable thermally than the isolated systems. The reason for this is that several contributions to the total energy of these systems, e. g., the ion-ion repulsion energy and the lattice distortion energy, have not been treated fully in this discussion. Finally the reader will observe that the energy levels of Fig. 2 predict that the $F_\|$ transition will occur at lower energies than the F band while it is observed[5] that the $F_\|$ transition in the ionized center occurs at higher energies than the F band. Our prediction that the $F_\|$ transition

energy is less than the F-band energy arises from the assertion that matrix elements of the third term of Eq. (1) between F-center wave functions vanish; this assertion was based on an approximate calculation and cannot be considered rigorously correct.

III. PERTURBATION DESCRIPTION

In this section we shall discuss the matrix elements $\langle \psi_{Fi} | H | \psi_{Fj} \rangle$ of Eq. (3). Since the first two terms of H in Eq. (1) are just the F-center Hamiltonian, the evaluation of these matrix elements is identical to a perturbation calculation where the perturbation, i. e., the effect of the impurity, is given by the third term of Eq. (1). In this context, the problem is somewhat analogous to the problem of the F_A center[31] encountered in the alkali halides. This center consists of an F center with an adjacent cation replaced by an alkali impurity ion of smaller size. The analogy between the center described in this paper and the F_A center would, of course, be more nearly complete if the impurity ion were divalent, were of smaller size than the Ca^{2+} ion, and possessed only filled electronic shells.

We shall treat this perturbed F center in a manner analogous to that used in treating[32] the F_A center in the alkali halides. For simplicity we shall restrict our attention to those impurity ions with filled electronic shells, i. e., to Y^{3+}, La^{3+}, Lu^{3+}, and to the alkali ion Na^+. The following contributions to the perturbation $V'(\vec{r}) - V(\vec{r})$ on the F-electron energy levels will be considered: (a) that due to an additional charge at the impurity site, (b) that due to the displacements and polarizations of the ions surrounding the vacancy, and (c) that due to the finite size of the impurity and the other ions surrounding the vacancy.

We shall take the wave functions describing the trapped electron at the unperturbed F center to be of the form

$$\Phi_{lm}(\vec{r}) = f_l(r) Y_{lm}(\theta, \phi), \qquad (5)$$

where $l = 0$ and 1 correspond to the ground and excited states; i. e., we take the ground state to be s-like and the excited state to be p-like. We restrict ourselves to these orbitals because they account for the prominent absorption band in the F center and because they are the only orbitals for which accurate radial wave functions are readily available. We shall approximate the radial wave functions by the Gourary and Adrian[26] type-III wave function in the ground state and type-II wave function in the excited state. The variational parameters and energy levels associated with these wave functions for CaF_2 are given in Refs. 23 and 33; our results do not depend significantly on which source is used.

Initially we shall treat the ions in the crystal as point charges. We shall first assume that a nega-

tive ion and an adjacent positive ion in a perfect
CaF_2 crystal are removed and replaced by an elec-
tron and an impurity cation of valence q, respec-
tively, while the positions of the other ions in the
crystal remain unchanged. The additional Coulomb
potential acting on the F electron will be

$$V_c(\vec{r}) = -(q-2)/|\vec{r}-\vec{r}_1| \, , \qquad (6)$$

where $\vec{r}$ is the position of the F electron and $\vec{r}_1$ is
the position of the impurity cation. The changes
in the energy levels of the F electron due to this
perturbation are shown in Figs. 3 and 4 for the
selected impurity ions.

In a real crystal the ions surrounding the impur-
ity-defect complex will certainly be polarized and
displaced from their respective lattice sites. It
has previously been pointed[34] out that, due to the
absence of a center of symmetry, the distortion
about such a center can be quite complex. For ex-
ample, if we limit the ions which can undergo dis-
placements from their respective lattice sites to
those ions which are nearest neighbors to the im-
purity or first- or second-nearest neighbors to the
vacancy, there are six different displacements as-
sociated with these 14 ions. Also, due to the lack
of central symmetry, the directions of these dis-
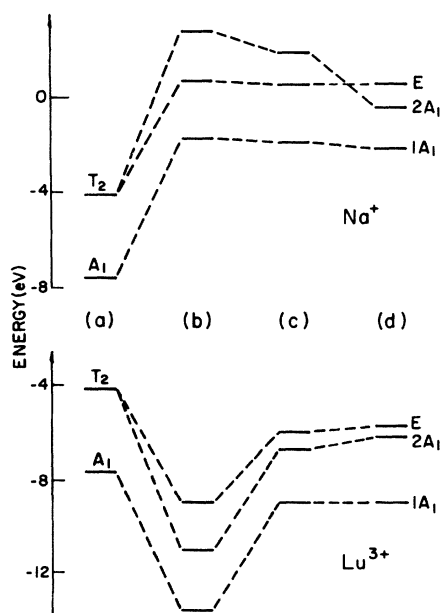placements cannot be predicted *a priori*. To ob-

FIG. 4. Same as Fig. 3 for Y^{3+} and La^{3+} impurities.

FIG. 3. Changes in the F-center energy levels due to
presence of a Na^+ or Lu^{3+} substitutional impurity cation
adjacent to an F center in CaF_2. Energy levels of the
unperturbed F center are shown in (a) and the changes
are due to: (b) additional charge on the impurity, (c)
Stark splitting associated with lattice distortion about
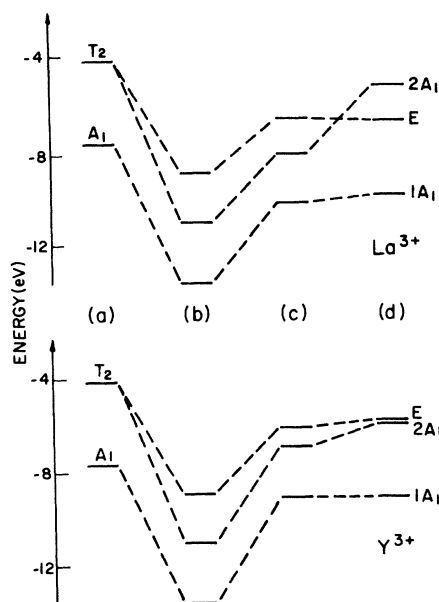the center, and (d) finite size of ions in crystal.

tain an estimate of these displacements we shall
adopt the following artificial procedure. We shall
first calculate the displacements and induced di-
poles on the ions surrounding an isolated impurity
cation in CaF_2. We shall then remove one of the
anions neighboring the impurity and replace it with
an electron of which the wave function is centered
on the lattice site of the absent anion; the positions
of all the other ions in the crystal will be held fixed
during this operation. We next ascertain the equi-
librium position of the impurity ion along the va-
cancy-impurity axis while holding all the other ions
in the crystal fixed to the positions they occupied
prior to the introduction of the F electron. Finally,
we add vectorially to these displacements those that
would occur in the absence of the impurity ion, i. e.,
those associated with an isolated F center. The
only justification for this procedure is that it orders
the introduction of the various displacements accord-
ing to their relative magnitudes and that it is math-
ematically tractable.

A general formulation of the application of the
Born model to the calculation of the energy required
to form a point defect in an ionic crystal and of the
displacements and induced dipoles associated with
this defect, with special emphasis on CaF_2, has
been given by Franklin[35]; the Mott-Littleton[36] tech-
nique of coupling the ions neighboring the defect to
the more distant ions in the crystal is used in this
approach. We shall apply the formalism given by
Franklin, with certain approximations to simplify
the calculations, to the case of a monovalent or

trivalent substitutional impurity cation in CaF$_2$. Following Mott and Littleton, we divide the crystal into two regions, where region I contains the impurity and the eight fluorine ions adjacent to the impurity, and region II comprises all the rest of the crystal. The total energy W required to create the substitutional impurity was minimized with respect to σR, the electrostatic displacement, and to mea, the induced dipole moment, of the ions in region I. The quantities R and a refer to the anion-cation separation and the anion-anion separation in this lattice. Parameters[35] appropriate to CaF$_2$ were used in these calculations together with differences in the effective ionic radii of the impurity and host cations taken from Ref. 37. The results of these calculations are given in Table I.

An estimate of the lattice distortion about an isolated F center can be obtained by minimizing the total energy of the F electron-lattice system with respect to displacements of the ions neighboring the anion vacancy. The contributions to the energy change associated with a radial displacement of the cations nearest the vacancy center are discussed for the F center in the alkali halides in the appendix of Ref. 32; this discussion is easily extended to the alkaline earth fluorides. Since an anion vacancy in the alkaline earth fluorides is surrounded by six fluorine ions which are only 15% more distant from the vacancy center than the four calcium ions, we must allow for displacements of these anions as well as for displacements of the nearest-neighbor cations. We shall permit the four Ca^{2+} ions nearest the vacancy center to be displaced radially inward by an amount σR and the six nearest fluorine ions to be displayed radially inward by an amount δa; the remaining ions in the lattice were kept fixed on their respective lattice sites. The equilibrium values of σ and δ for CaF$_2$ were found to be -0.021 and 0.029, respectively. Nearly identical values of these equilibrium displacements were calculated for SrF$_2$ and BaF$_2$.

TABLE I. First three rows of this table contain the following calculated data for the indicated isolated substitutional-impurity ion in CaF$_2$: equilibrium inward radial displacements $\sigma_0 R$ from their respective lattice sites of the eight F^- ions nearest the impurity, the dipole moments (directed outward) $m_0 ea$ induced on these anions, and the energy W in eV required to create these isolated substitutional impurities in CaF$_2$. The last row contains the equilibrium displacement $\epsilon_0 R$ of the impurity ion from its lattice site toward the vacancy center in the combined defect-impurity center.

	Na$^+$	Lu^{3+}	Y^{3+}	La^{3+}
σ_0	-0.09	0.11	0.10	0.06
m_0	-0.02	0.02	0.03	0.03
W	15.5	-28.0	$-27.$	$-23.$
ϵ_0	-0.02	-0.7	-0.07	-0.04

Estimates of the displacement of an ion surrounding the defect-impurity complex are given by the vector sum of the displacements of that ion associated with the isolated impurity and with the isolated F center. An estimate of the impurity displacement may be obtained by minimizing the total energy of the distorted lattice with respect to a displacement ϵR of the impurity ion toward the vacancy center. This calculation differs from that used to obtain the equilibrium displacements of the ions surrounding the isolated F center in that only one ion is free to move and that the coupling between the impurity and the induced dipole moments on the surrounding ions must be retained. In the actual calculation of the equilibrium value of ϵ the displacements associated with the isolated F center were neglected; the results of this calculation are shown in Table I.

The difference in the point-ion potentials of the distorted and undistorted lattices contributes to the perturbation $V'(\vec{r}) - V(\vec{r})$. The first-order energy corrections due to this perturbation were obtained using the wave functions given in Eq. (5). These results are shown in Figs. 3 and 4. A simple calculation indicates that the order of magnitude of the energy changes resulting from the induced dipoles on the ions surrounding the defect-impurity center is 0.3 eV; this energy is regarded as being negligibly small in this calculation.

The introduction of the impurity ion at a site adjacent to the F center results not only in changes in the point-ion potential of the F electron, but also in changes in the interaction of the F electron with the filled ion-core states in the crystal. We shall refer to the contribution to the energy of the F electron arising from its interaction with these ion-core states as the ion-size correction. This ion-size correction includes the repulsive potential arising from the requirement that the F-electron wave functions be orthogonal to all the occupied orbitals in the crystal and the contributions to the energy of the F electron remaining in the Hartree-Fock potential after the point-ion potential has been removed, that is, the screened Coulomb potential inside the ioncores and the exchange potential of the F electron with the ion-core electrons. This correction to the F electron energy is discussed in Refs. 23 and 32, where it is shown that in the approximation the variations of $\Phi_{lm}(\vec{r})$ over the region of the ion-cores are neglected, the ion-size correction is given by

$$E'^{IS}_{lm} = \sum_{\gamma=1}^{N} [A_\gamma + B_\gamma(E_{lm} - U_\gamma)] |\Phi_{lm}(\vec{r}_\gamma)|^2 . \quad (7)$$

The sum in Eq. (7) is to be carried out over all the indicated lattice sites in the crystal, with the vacancy center being denoted by $\gamma = 1$. There are N ions in the crystal. The coefficients A_γ and B_γ are constants associated with the ion at site γ; the val-

ues of these coefficients for the alkali, alkaline earth, and halide ions are tabulated in Ref. 23. The energy associated with the F-electron wave function $\Phi_{lm}(\vec{r})$ is denoted by E_{lm}, the potential energy of an electron at the site γ due to all the other ions in the crystal is denoted by U_γ, and $\vec{r}_\gamma$ denotes the position of lattice site γ. The validity of the approximations made in obtaining Eq. (7) are discussed in Ref. 32. We shall assume that Eq. (7) is a good approximation for the ion-size correction energy of an F electron in CaF_2.

The change in the ion-size correction energy due to the introduction of the impurity ion and to the resulting lattice distortion can easily be broken into three parts, one of which is the change due to the replacement of the core states of Ca^{2+} with those of the impurity. Since the ion-size correction energy of the F electron depends on the difference of the F-electron energy and the energies of the occupied core states,[32] there will be an energy change due to the shift in the energy of the F electron relative to the shifts in the energy of the core states. Finally there will be an energy change due to the lattice distortion.

The energy changes resulting from each of these three contributions to the change in the ion-size correction were calculated for selected impurity cations adjacent to an F center in CaF_2; the results of these calculations are shown in Figs. 3 and 4. The coefficients A_γ and B_γ for the trivalent impurities considered here were obtained using the approximate expressions

$$A_\gamma = 2\pi q R_{0\gamma}^2 , \quad B_\gamma = \pi R_{0\gamma}^3 , \tag{8}$$

where $R_{0\gamma}$ is an effective ionic radius[37] for the ion at site γ. Similar approximate expressions are given in Ref. 23. The sums over the lattice sites are easily evaluated since the F-electron wave functions decay exponentially in the region of the crystal beyond the sphere defined by the cations nearest the vacancy center, i. e., they are well localized about the vacancy center. In this approximate calculation we have terminated the sums on the shell of fluorine ions nearest the vacancy center.

In the calculations described above, only contributions to the diagonal matrix elements were taken into account. The large changes in the diagonal

energies shown in Figs. 3 and 4 certainly indicate that the off-diagonal matrix elements cannot be ignored. However, one also notes from Figs. 3 and 4 that the contributions to the diagonal matrix elements from the point-ion-lattice distortion and from the changes in the ion-size correction tend to cancel the contribution from the additional charge on the impurity. One might expect that a similar cancellation occurs for the off-diagonal matrix elements. The only off-diagonal matrix element between the s and p states we have been considering that is not identically zero by symmetry considerations is that between the states $\Phi_{00}(\vec{r})$ and $\Phi_{10}(\vec{r})$; for this off-diagonal matrix element such a cancellation does indeed occur. In particular, while the contribution to this off-diagonal matrix element from each of the three sources mentioned above is of order 1.5 eV, the total off-diagonal matrix element is less than 0.3 eV for all four examples considered here. While the exactness of this cancellation is certainly greater than can be expected from such a crude calculation, it is nevertheless clear that this off-diagonal matrix element makes little contribution to the energy levels and that there is no significant mixing of the F center s and p wave functions.

A color center consisting of an F center perturbed by an adjacent monovalent or trivalent impurity cation in CaF_2 is not neutral and therefore we do not expect it to be thermally stable. This is indeed the case for the ionized photochromic center. Although one might conclude from the energy levels shown in Fig. 3 for an F center perturbed by an adjacent Na^+-impurity ion that this center is responsible for the 6050 Å absorption band observed by Scouler and Smakula[1] in electron-irradiated Na-doped CaF_2, these observations regarding thermal stability lead us to suspect that such an identification would be incorrect. Studies of the dichroic properties of the optical absorption of colored Na-doped CaF_2, as well as studies of the EPR resonances of this material are needed before any definite conclusions can be reached.

ACKNOWLEDGMENTS

[1]W. J. Scouler and A. Smakula, Phys. Rev. 120, 1154 (1960).
[2]J. R. O'Connor and J. H. Chen, Phys. Rev. 130, 1790 (1963).
[3]V. A. Arkhangelskaya, Ya. E. Kariss, and P. P. Feofilov, Opt. i Spektroskopiya 18, 330 (1965) [Opt. Spectry. (USSR) 18, 184 (1965)].
[4]J. L. Merz and P. S. Pershan, Phys. Rev. 162, 217 (1967).

[5]D. L. Staebler, Ph. D. thesis, Princeton University 1970 (unpublished); D. L. Staebler and S. E. Schnatterly, preceding paper, Phys. Rev. B 3, 516 (1971).
[6]D. L. Staebler and Z. J. Kiss, Appl. Phys. Letters 14, 93 (1969).
[7]Z. J. Kiss, IEEE J. Quantum Electron. QE-5, 12 (1969).
[8]P. Gorlich, H. Karras, G. Kotitz, and R. Rauch, Phys. Status Solidi 27, 109 (1968).

[9] D. L. Staebler, S. E. Schnatterly, and W. Zernik, IEEE J. Quantum Electron. QE-4, 575 (1968).

[10] R. C. Alig, Z. J. Kiss, J. P. Brown, and D. S. McClure, Phys. Rev. 186. 276 (1969).

[11] C. H. Anderson and E. S. Sabisky, preceding paper, Phys. Rev. B 3, 527 (1971).

[12] J. Arends, Phys. Status Solidi 7, 805 (1964); A. M. Stoneham, W. Hayes, P. H. S. Smith, and J. P. Stott, Proc. Roy. Soc. (London) A306, 369 (1968).

[13] C. J. Balhausen and H. B. Gray, *Molecular Orbital Theory* (Benjamin, New York, 1965).

[14] D. S. McClure and Z. J. Kiss, J. Chem. Phys. 39, 3251 (1963).

[15] Data regarding the energy levels of the free divalent ions were obtained from the following sources: Y^{2+} – W. F. Meggers and H. N. Russell, J. Res. Natl. Bur. Std. 2, 735 (1929); La^{2+} – H. Odabasi, J. Opt. Soc. Am. 57, 1459 (1967); Ce^{2+} – J. Sugar, *ibid.* 55, 33 (1965); Pr^{2+} – J. Sugar, *ibid.* 53, 831 (1963); Sm^{2+} – A. Dupont, *ibid.* 57, 867 (1967); Gd^{2+} – W. R. Callahan, *ibid.* 53, 695 (1963); Ho^{2+} – J. H. McElaney, *ibid.* 57, 870 (1967); Yb^{2+} – B. W. Bryant, *ibid*, 55, 771 (1965); Lu^2: W. F. Meggers and B. F. Scribner, J. Res. Natl. Bur. Std. 5, 73 (1930). Data not available from these sources were taken from G. H. Dieke and and H. M. Crosswhite, Appl. Opt. 2, 675 (1963).

[16] This assumption may not be entirely justified due to the large radial extent of the wave functions of these s and d electrons. See C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill, New York, 1962), p. 59.

[17] In the following discussion we shall use configuration designations appropriate to the rare-earth ions. The discussion may be adapted to Y^{2+} by replacing the designations $4f^{n-1}5d$ and $4f^{n-1}6s$ by $4d$ and $5s$ and ignoring all statements regarding the $4f^n$ configurations and to Lu^{2+} by replacing the designations $4f^{n-1}5d$ and $4f^{n-1}6s$ by $5d$ and $6s$.

[18] E. Loh, Phys. Rev. 184, 348 (1969).

[19] W. Hayes and J. W. Twidell, Proc. Phys. Soc. (London) 82, 330 (1963); T. S. Piper, J. P. Brown, and D. S. McClure, J. Chem. Phys. 46, 1353 (1967).

[20] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

[21] M. Wolfsberg and L. Helmholz, J. Chem. Phys. 20, 837 (1952); see also P. W. Smith, R. Stoessiger, and A. G. Wedd, Theoret. Chim. Acta. (Berlin) 11, 81 (1968) for the application of this approximation to systems in which the fields due to the neighboring ions are significant. Note also that the F-center wave functions are not atomic orbitals and hence do not obey the virial theorem. The parameter F was set equal to 2 in these calculations.

[22] R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, J. Chem. Phys. 17, 1248 (1949); H. H. Jaffe, *ibid*, 21, 258 (1953).

[23] R. H. Bartram, A. M. Stoneham, and P. Gash, Phys. Rev. 176, 1014 (1968).

[24] D. Staebler and R. Duncan (unpublished).

[25] C. H. Henry, S. E. Schnatterly, and C. P. Slichter, Phys. Rev. 137, A583 (1965).

[26] B. S. Gourary and F. J. Adrian, Phys. Rev. 105, 1180 (1957); see also *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1960), Vol. 10, p. 127.

[27] J. A. Krumhansl, Phys. Rev. 93, 245 (1954).

[28] M. H. L. Pryce, Proc. Phys. Soc. (London) A63, 25 (1950).

[29] W. E. Blumberg and T. P. Das, Phys. Rev. 110, 647 (1958). The overlap integrals were estimated using Ref. 22.

[30] Although the transition energies of the photochromic centers are not strongly dependent on the specific impurity, they do tend to decrease as the ionic radius of the impurity is increased. See Ref. 5.

[31] F. Luty, *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968), Chap. 3.

[32] R. C. Alig, Phys. Rev. B 2, 2108 (1970).

[33] H. S. Bennett and A. B. Lidiard, Phys. Letters 18, 253 (1965).

[34] J. R. Reitz and J. L. Gammel, J. Chem. Phys. 19, 894 (1951).

[35] A. D. Franklin, J. Phys. Chem. Solids 29, 823 (1968).

[36] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. 34, 485 (1938).

[37] R. D. Shannon and C. T. Prewitt, Acta Cryst. B25, 925 (1969).