

Possibility of Rare-Gas Color Centers in Ionic Crystals*

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It is argued that the defect consisting of a rare-gas atom at a negative-ion vacancy in an ionic crystal should trap an electron to form an electron-excess color center. The basis for this speculation is that the potential for such defects, as for the F center, must approach a Coulomb form at large distances. The principal optical absorptions for these hypothetical rare-gas centers have been calculated in the point-ion approximation for alkali-halide matrices. The transitions are predicted to lie in a range from 0.9 to 1.8 eV, depending on the rare-gas and the host crystal. In all cases, the absorption lies to the low-energy side of the corresponding F band and has an oscillator strength of the order of unity. Although these centers possess bound electronic states, it is not clear that they are "chemically" stable against decay into an F center and an interstitial rare-gas atom. However, from studies of the conversion of U_3 centers to U_2 centers, it is argued that the hypothetical rare-gas centers may be stable in the iodides or bromides of intermediate-weight alkalis. The possibility of observing both substitutional rare-gas atoms and ions by means of α - and β -band-like transitions is also discussed.

I. INTRODUCTION

THE F center, an electron trapped at a negative-ion vacancy in an ionic crystal, has played a central role in the study of the electronic states of defects in solids.¹ The basic feature of the electron-negative-ion vacancy system that leads to a series of bound electronic states is that the vacancy produces a long-range Coulomb potential that is superimposed on the normal periodic crystal field.^{2,3}

This feature of a negative-ion vacancy is not unique, but must also obtain for the class of defects consisting of negative-ion vacancies containing any neutral atom or complex. While the details of the potential for the various defects may differ widely near the central neutral atom or complex, the character of the long-range part is the same as that for the isolated vacancy. Consequently, the energy spectrum of an electron bound to these defects consists in the general case of a series of localized states within the band gap and mixed impurity-crystal "resonance" states for levels degenerate with existing crystal energy bands.

This type of defect together with its bound electron is conventionally viewed as a substitutional negative-ion impurity. Centers involving atoms or complexes with positive electron affinities such as the columns VI and VII elements have been studied in detail in the alkali halides.⁴ Because of their positive electron affinity, these species would normally form stable negative ions in free

space. However, in ionic crystals, a positive electron affinity is not necessary for negative-ion stabilization because of the asymptotic character of the defect potential.

A particularly intriguing series of defect centers formed from atoms with negative electron affinities would be those for the rare gases. Unfortunately, there is no evidence to indicate whether or not such centers actually exist. It is the purpose of this note to consider the properties of these "speculative" substitutional rare-gas centers and to investigate the possibility of their formation.

The primary feature of this class of centers is their simplicity. They consist of a single electron outside a closed shell and, together with the F center, form a defect-center series analogous to the free-atom series of hydrogen and the alkali atoms. Since rare-gas atoms do not form stable free negative ions,⁵ these defects may be viewed as negative rare-gas ions stabilized by an external crystal field. As will be shown, the centers may equally well be viewed as an F center perturbed by the presence of a rare-gas atom within the negative-ion vacancy.

In Sec. II, the electronic structure of the rare-gas centers is developed in the point-ion approximation. The possibility of observing both substitutional rare-gas atoms and ions through their perturbation of the exciton absorption is considered in Sec. III, and the stability of the various centers and possible methods for their formation are discussed in Sec. IV.

II. ELECTRONIC PROPERTIES

A. Theoretical Model

To investigate the low-lying energy levels of an electron bound to a substitutional rare-gas atom at a

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¹ J. H. Schulman and W. D. Compton, *Color Centers in Solids* (The MacMillan Co., New York, 1962).

² N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), p. 114.

³ D. Y. Smith and G. Spinolo, *Phys. Rev.* **140**, A2121 (1965).

⁴ For examples, see Ref. 1 and abstracts of reports to the International Symposium on Color Centers in Alkali Halides, Urbana, Illinois, 1965 (unpublished).

⁵ H. S. W. Massey, *Negative Ions* (Cambridge University Press, Cambridge, England, 1950).

negative-ion vacancy, we have studied the Hartree-Fock problem for a negative rare-gas ion stabilized by an external field. The potential chosen to represent the crystal field was the spherically symmetric component of the potential for a lattice of point ions with one missing negative charge.

This potential has been used with considerable success by Gourary and Adrian in a study of the ground and first optically accessible excited states of the F center.⁶ These authors found that this model potential yielded good values for the F -band energies and gave a theoretical basis for Ivey's "law."⁷ It has been further shown that if the eigenfunctions for this potential are corrected for the crystal environment by orthogonalization to the occupied crystal-ion core states,⁸ good descriptions of the hyperfine interaction and g factor of the ground state^{9,10} and the spin-orbit interaction in the excited state¹¹ are obtained.

From this success in treating the low-lying F -center states, it is reasonable to expect that the point-ion model may be useful for treating the low-lying states of the rare-gas centers, provided the valence electron densities are similar to the corresponding densities for the F center. As will be seen, this is what is predicted by the point-ion model so that the approximation is internally consistent.

On the other hand, this potential neglects higher-symmetry components of the crystal potential,¹² the finite size of the ions,^{9,12,13} and polarization.^{9,9,14} Thus, while experience has shown that energy differences between low-lying states are probably meaningful, the actual eigenvalues are not. Furthermore, while the relative energies of low-lying states may be predicted to fair accuracy, the spacing of levels for diffuse states may be in considerable error.³

To simplify the Hartree-Fock problem, the exact equations were replaced by the computationally simpler Hartree-Fock-Slater equations¹⁵ in which the Slater free-electron exchange approximation¹⁶ is used to evaluate exchange integrals. These equations are particularly convenient for numerical estimates because computer programs for their solution have been developed by

⁶ B. S. Gourary and F. J. Adrian, *Phys. Rev.* **105**, 1180 (1957).

⁷ H. F. Ivey, *Phys. Rev.* **72**, 341 (1947).

⁸ See, for example, R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience Publishers, Inc., New York, 1953), Vol. 1.

⁹ B. S. Gourary and F. J. Adrian, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10.

¹⁰ D. Schmid, doctoral thesis, III Physikalisches Institut der Technischen Hochschule, Stuttgart, Germany, 1966 (unpublished); *Phys. Status Solidi* **18**, 653 (1966).

¹¹ D. Y. Smith, *Phys. Rev.* **137**, A574 (1965).

¹² J. K. Kübler and R. J. Friauf, *Phys. Rev.* **140**, A1742 (1965).

¹³ R. F. Wood and H. W. Joy, *Phys. Rev.* **136**, A451 (1964), and references cited therein.

¹⁴ See also R. S. Knox, *Theory of Excitons* (Academic Press Inc., New York, 1963); especially the discussion of dielectric constants.

¹⁵ F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963).

¹⁶ J. C. Slater, *Phys. Rev.* **81**, 385 (1951).

TABLE I. Calculated and observed energies for the principal $s \rightarrow p(\Gamma_1^+ \rightarrow \Gamma_4^-)$ transitions of the rare-gas speculative centers and the F and U centers in various alkali halides. Energies are given in eV and d , the nearest-neighbor separation, is measured in Bohr units.

Host crystal	NaCl	KCl	RbBr	RbI
d in a_0	5.31	5.93	6.48	6.92
He ⁻ center	1.15	1.08	1.00	0.94
Ne ⁻ center	1.82	1.57	1.38	1.26
Ar ⁻ center	1.37	1.24
Kr ⁻ center	1.31
F center				
Theory ^a	2.38	1.98	1.71	1.53
Theory ^b	2.39	1.99	1.71	...
Experiment	2.770 ^e	2.313 ^c	1.85 ^d	1.69 ^d
U center				
Theory ^a	5.67	5.09	4.68	4.41
Theory ^e	5.50	4.84	4.35	...
Experiment ^f	6.46	5.79	5.12	...

^a Present calculation.

^b B. S. Gourary and F. J. Adrian, Ref. 6.

^c W. Gebhardt and H. Kühnert, *Phys. Letters* **11**, 15 (1964); extrapolated to 0°K.

^d F. Lüty, *Z. Physik* **160**, 1 (1960); measured at -180°C.

^e B. S. Gourary, Ref. 19.

^f R. Hilsch and R. W. Pohl as quoted by H. F. Ivey, Ref. 7; measured at room temperature.

Herman and Skillman.¹⁵ In the present work these programs were employed with the addition of a subroutine which calculated the spherically symmetric component of the point-ion crystal field and added this to the self-consistent field calculated from the electron densities.

To test the reliability of the Slater approximation for this application, the ionization and first excitation energies (neglecting spin-orbit effects) were calculated for the free alkali atoms which are isoelectronic to the negative rare-gas ions. Since the core-state wave functions of the alkalis are known to be almost independent of the state of the valence electron,¹⁷ Koopmans's theorem holds and the excitation energies may be calculated as the difference in eigenvalues of the valence electron.¹⁸ For the alkalis in free space, these methods reproduced the ionization energies and the average $s \rightarrow p$ transition energies to better than 0.2 eV in all cases. This error is of the same order as that found in applying the point-ion approximation to the F -center problem so that the Slater exchange approximation would seem sufficiently accurate considering the other approximations made.

B. Transition Energies

The energies of the principal optical transitions predicted for the rare-gas speculative centers, the F center, and the substitutional H⁻ ion or U center are given in

¹⁷ See, for example, D. R. Hartree and W. Hartree, *Proc. Roy. Soc. (London)* **A166**, 450 (1938); **A193**, 299 (1948); *Proc. Cambridge Phil. Soc.* **34**, 550 (1938).

¹⁸ F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Co., Inc., New York, 1940).

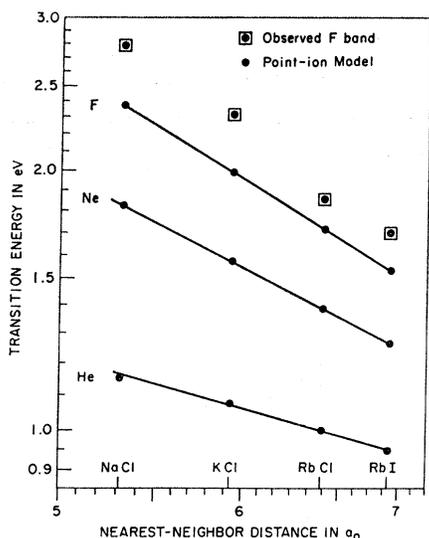


FIG. 1. Calculated energies for the principal $s \rightarrow p$ ($\Gamma_1^+ \rightarrow \Gamma_4^-$) transitions of the rare-gas centers and the F center as a function of lattice spacing for various alkali halides. The results indicate that the rare-gas-center transition energies obey Mollwo-Ivey relations, but with smaller exponents than in the case of the F center.

Table I. The actual eigenvalues for the valence electrons of the F and rare-gas centers are given for reference in the Appendix.

The calculations for the rare-gas centers predict that the principal $ns \rightarrow np$ transitions occur at energies ranging roughly from 0.9 to 1.8 eV for the various systems considered. In all cases, the absorption lies to the long-wavelength side of the corresponding F -center absorption. This "red shift" is largest for the helium centers and least for the krypton centers. The results are summarized in graphic form in Fig. 1, which shows that the rare-gas-center absorptions follow a Mollwo-Ivey relation, but with smaller exponents than in the case of the F center.

An indication of the reliability of these predictions may be had from the results for the F and U centers. For the F center, the point-ion-model predictions underestimate the transition energies by several tenths of an electron volt, or from 10 to 15%. For the U center, two theoretical predictions of the point-ion model are given. The first is for the present calculation and the second is due to Gourary.¹⁹ The two differ because the present work involved the numerical integration of the Hartree-Fock-Slater equations, while Gourary used approximate variational wave functions to solve the two-electron problem. The present results are in somewhat better agreement with experiment than the earlier work, but, as in the case of the F center, the transition energies are underestimated by the order of 10 to 15%. Since the U -center calculations involve both the point-ion and the Hartree-Fock-Slater approximations, they provide a test of the application of the method to

¹⁹ B. S. Gourary, Phys. Rev. **112**, 337 (1958).

TABLE II. Calculated radial positions of the principal maxima in the valence electron density for various defect centers in RbI. Distances are given in terms of the Bohr unit.

	s state	p state
F center	4.65	5.85
He ⁻	5.30	5.75
Ne ⁻	5.15	5.80
Ar ⁻	5.40	6.10
Kr ⁻	5.45	6.15

the speculative centers. From these results, it seems reasonable to expect underestimates of several tenths of an electron volt in the transition energies for the rare-gas centers.

C. Wave Functions

The close similarity of the valence-electron states of the rare-gas centers to those of the F center may be seen from Figs. 2 and 3. In Fig. 2, the F -center $1s$ function and the valence $5s$ wave function for the krypton center in RbI are shown. Aside from oscillations in the neighborhood of the rare-gas atom and a slight change in normalization of the krypton function, it will be seen that the charge distributions are quite similar. The similarity of the excited np valence states of the rare-gas centers to the F -center $2p$ state is even more pronounced. This is shown in Fig. 3 for the krypton center. These results are summarized in Table II, which lists the position of the principal maximum in the radial charge density for various centers in RbI.

The foregoing result depends somewhat on the model potential used. The spherically symmetric component of the point-ion potential used here has a relatively deep central well within the vacancy. The sides of the well rise steeply to a slightly positive value at the second shell of neighbors and then a secondary well lies between the second and sixth shells of neighbors.⁶ The regions of high potential in the vicinity of the second and sixth shells of neighbors are something of a barrier

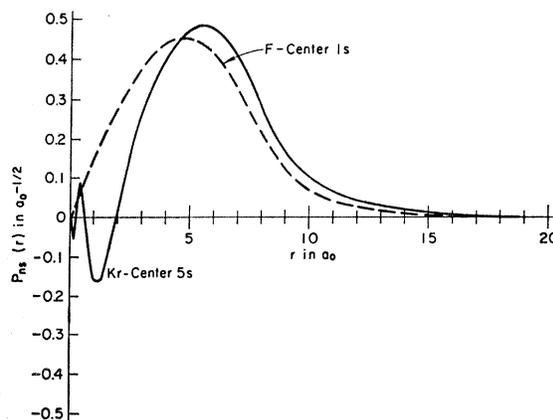


FIG. 2. The ground-state electronic wave functions for electrons bound to F centers and krypton centers in RbI.

to the electron in the energy range of interest here. On the other hand, the various semicontinuum-model potentials have shallower central wells joined to a dielectric-continuum portion near the first shell of neighbors; in all cases the potential increases monotonically and there is no barrier between the central well and the continuum region.⁹ While a qualitatively different result for the semicontinuum model does not seem likely, the wave functions for the rare-gas centers predicted by the latter model would probably show somewhat greater radial extent than found here, particularly in the excited states.

D. Physical Picture

The similarity of the various wave functions suggests that the rare-gas-center valence states may be viewed as a perturbation on the F -center states. Indeed, to a first approximation the speculative-center valence wave functions are those of the corresponding F -center states orthogonalized to the occupied core states of the rare-gas atom. Studies of the physical consequences of the orthogonality condition for wave functions have shown that in such cases the energy-level problem may be at least qualitatively understood in terms of an effective repulsive potential.^{20,21} This potential, the so-called pseudopotential, describes the effect of the Pauli exclusion principle in forbidding the valence electron from occupied core states.

The repulsive effect of the central atom on the eigenvalue of the bound electron is illustrated by the energy-level diagrams for the low-lying states of the F center and the rare-gas centers in RbI shown in Fig. 4. In the case of the ns states of the rare-gas centers, the wave functions must be orthogonal to the occupied $1s, 2s, \dots, (n-1)s$ core states. This leads to a partial exclusion of the electron from the core region and an increase in

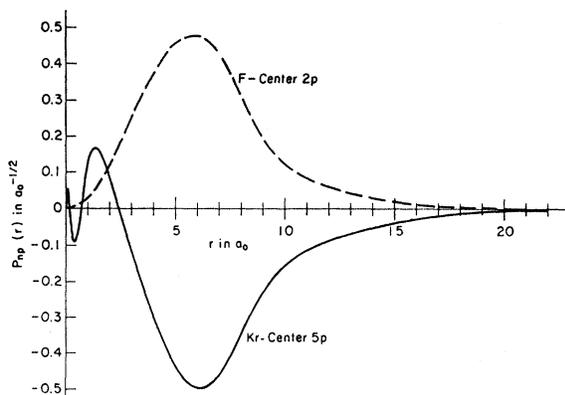


FIG. 3. The first optically accessible excited-state wave functions for electrons bound to F centers and krypton centers in RbI.

²⁰ J. C. Phillips and L. Kleinman, *Phys. Rev.* **116**, 287 (1959).

²¹ D. Y. Smith, unpublished calculations reported at the International Symposium on Color Centers in Alkali Halides, Urbana, Illinois, 1965 (unpublished).

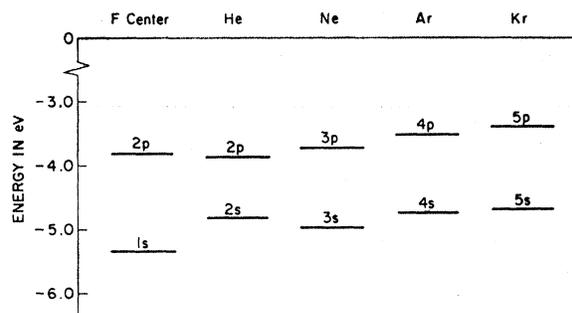


FIG. 4. The eigenvalues of electrons bound to various electron-excess color centers in RbI. The progression of levels from the F center to the krypton center shows the effect of the Pauli exclusion principle on the energy of the outer electron as the number of core electrons is increased.

energy relative to that of the F -center $1s$ state because of the "repulsive core." In general, the greater the number of occupied core states, the greater the repulsion and the greater the increase in energy.²²

The same holds for the np state which must be orthogonal to the $2p, 3p, \dots, (n-1)p$ states of the central atom. The case of the $2p$ state of the helium center is noteworthy in that there is no occupied p core state and thus no repulsive effect. Therefore, since the screened Coulomb field of the neutral helium atom is slightly attractive, the helium $2p$ state lies below that of the F center. A similar effect is observed in atomic lithium.²³

E. Oscillator Strengths

Another interesting comparison with the F center is afforded by the oscillator strength for the principal $s \rightarrow p (\Gamma_1^+ \rightarrow \Gamma_4^-)$ transition. In general, the average oscillator strength for allowed dipole transitions from a set of degenerate states a with spatial degeneracy $2J_a+1$ to a set of degenerate states b is given by²⁴

$$f_{a \rightarrow b} = \frac{2m}{3\hbar^2} \frac{\sum_{\alpha, \beta} E_{\alpha\beta} |\langle \psi_\alpha | \mathbf{r} | \psi_\beta \rangle|^2}{2J_a+1}.$$

Here m is the electron mass and $E_{\alpha\beta}$ is the energy difference between the levels a and b , $(E_b - E_a)$. The sum is taken over all initial and final states, and $\langle \psi_\alpha | \mathbf{r} | \psi_\beta \rangle$ is the matrix element of the dipole operator between states ψ_α and ψ_β .

²² An apparent exception to this occurs for the neon-center $3s$ state which lies 0.18 eV below the helium-center $2s$ state. This is contrary to what would be expected from qualitative arguments based on the Pauli principle and from the behavior of the valence states of the isoelectronic alkali atoms. However, the energy difference involved is less than 4% of the total energy and, considering the approximations used, it is probably not a significant deviation.

²³ C. E. Moore, *Atomic Energy Levels* (U. S. Government Printing Office, Washington, D. C., 1949), Vol. I.

²⁴ H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957); W. B. Fowler and D. L. Dexter, *Phys. Rev.* **128**, 2154 (1962).

TABLE III. Oscillator strengths and related quantities for various defect centers in RbI.

Center	E_{ap} (eV)	$\langle \psi_s z \psi_{pz} \rangle$ in a_0	$f_{s \rightarrow p}$
<i>F</i> center	1.53	2.97	0.97
He ⁻	0.94	-3.22	0.72
Ne ⁻	1.26	-3.20	0.94
Ar ⁻	1.24	-3.34	1.02
Kr ⁻	1.31	-3.37	1.09

The relevant quantities for the various centers in RbI are given in Table III. The values of $\langle \psi_s | z | \psi_{pz} \rangle$ are greater for the rare-gas centers, but the transition energies are smaller. The oscillator strengths range from slightly less than that of the *F* center in the case of the helium and neon centers to slightly more for the argon and krypton centers. The prediction of oscillator strengths greater than unity for some of the rare-gas centers points up the fact that their many-electron character must be considered even when the valence electron is treated as a single electron moving in an effective ion-core field.¹⁸

III. α - AND β -LIKE BANDS

While the negative rare-gas ions should show an optical absorption in the spectral region in which the alkali halides are transparent, absorption due to direct excitation of trapped rare-gas *atoms* would generally be obscured by the fundamental absorption of the host crystal. On the other hand, it may be possible to observe both the ionic and the atomic species through their perturbation of the exciton absorption in analogy to the well-known α - and β -band absorptions.²⁵

The α band is an absorption in the tail of the fundamental absorption and is found in crystals containing large numbers of halogen-ion vacancies. The available evidence suggests that it is due to excitons created in the vicinity of the vacant negative-ion sites.^{26,27} The β band is a similar absorption found in crystals containing a large number of *F* centers, and it has been attributed to excitons created in the vicinity of *F* centers.^{26,27} Analogous perturbations of the exciton absorption should occur for substitutional rare-gas centers.

The position of the α and β bands has been investigated theoretically by Bassani and Inchauspé,^{28,29} and their analysis has been extended to cover the case of rare-gas centers. Briefly, these considerations show that the shift of the exciton absorption is primarily determined by two effects. The first is the amount by which the final state is raised relative to the initial state by Coulomb and exchange interactions with the rare-gas species in the vacancy. The second effect is the change in binding energy of the exciton because it is formed

near a more or less polarizable rare-gas atom or ion. In general, the first effect tends to raise the energy of the transition relative to the normal *F*-center α or β band, while the second tends to lower the transition energy.

Unfortunately, lack of experimental determinations of the interatomic potentials between alkali and rare-gas atoms that are reliable at crystal interatomic separations precluded evaluation of the band positions.^{30,31} Although no quantitative conclusions could be made, extrapolation of potentials derived from scattering experiments^{30,32,33} allowed some crude qualitative estimates.

In the case of the α -band-like transition, the polarization energy is small relative to the Coulomb and exchange effects because of the low polarizability of the rare-gas *atom*. Consequently, it seems probable that for the atomic rare-gas centers these transitions would occur at energies higher than the normal α band and that at least for the heavy rare gases the transitions may well lie beneath the fundamental absorption.²⁷ For β -band-like transitions of ionic rare-gas centers, the high polarizability of the rare-gas *ion* tends to reduce the exciton binding energy. In the case of the helium centers this may be sufficient to overcome the increased Coulomb and exchange interaction with the rare-gas ion and shift the β -band-like transition toward longer wavelengths relative to the *F*-center β band. However, for the heavier rare-gas ions, the shift is almost certainly toward higher energies.

IV. STABILITY OF RARE-GAS CENTERS

Although there has been little work on rare gases as impurities in the alkali halides, an indication of the factors influencing the stability of their substitutional negative ions may be had by considering neighboring elements in the periodic table. The column VI and VII elements have relatively large positive electron affinities ranging from 1.5 to 3.5 eV^{5,34} and form stable negative impurity ions in the alkali halides. The column I elements have positive, though much smaller, affinities that range from 0.3 eV for sodium³⁵ to 0.75 eV for hydrogen.³⁴ Of these elements, the alkalis do not form negative ions in ionic crystals but, because of their low ionization energies, find it more favorable to form positive ions. On the other hand, the high ionization energy of hydrogen is unfavorable to positive-ion formation and hydrogen is observed either as a neutral or

³⁰ H. Pauly and J. P. Toennies, in *Advances in Atomic and Molecular Physics*, edited by D. R. Bates and I. Estermann (Academic Press Inc., New York, 1965), Vol. 1.

³¹ R. B. Bernstein, in *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Co., Amsterdam, 1964).

³² H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, London, 1952).

³³ D. Beck and H. J. Loesch, *Z. Physik* **195**, 444 (1966).

³⁴ L. M. Branscomb, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962).

³⁵ H. Ebinghaus, *Z. Naturforsch.* **19a**, 727 (1964).

²⁵ C. J. Delbecq, P. Pringsheim, and P. Yuster, *J. Chem. Phys.* **19**, 574 (1951); **20**, 746 (1952).

²⁶ D. L. Dexter, *Phys. Rev.* **83**, 1044 (1951).

²⁷ F. Seitz, *Rev. Mod. Phys.* **26**, 7 (1954), Sec. 24.

²⁸ F. Bassani and N. Inchauspé, *Phys. Rev.* **105**, 819 (1957).

²⁹ See also R. Fuchs, *Phys. Rev.* **111**, 387 (1958).

negative-ion impurity.^{36,37} These centers are of particular interest for comparison with possible rare-gas centers and they include:

- (a) the U center—the substitutional H^- ion, H_s^- ;
- (b) the U_1 center—the interstitial H^- ion, H_i^- ;
- (c) the U_2 center—the interstitial H atom, H_i^0 ;
- (d) the U_3 center—the substitutional H atom (anion site), H_s^0 .

The rare gases of column VIII are similar to hydrogen in that their large ionization energies do not favor positive ions. They differ from hydrogen in having a negative electron affinity so that the interstitial negative ion X_i^- is not likely to be stable.

Experimental evidence for the interstitial rare-gas atom X_i^0 exists from studies of diffusion of rare gases in ionic crystals. Although the interpretation of these studies has varied, recent results indicate an interstitial diffusion mechanism in the intrinsic range.³⁸ Since the negative-ion vacancy is larger than an interstitial site, these observations also suggest the existence of the substitutional rare-gas atom in an anion site, X_s^0 .³⁹

The existence of substitutional rare-gas atoms is also suggested by a comparison of the halide-ion and rare-gas radii shown in Table IV. For negative ions, two different groups of radii are given: the “traditional” ionic radii of Pauling and of Goldschmidt and the average “crystal” radii recently determined by Fumi and Tosi from solid-state data.⁴⁰ The latter are roughly 0.2 Å smaller than the “traditional” radii and are probably the best available values for ions in perfect crystals of the NaCl structure. The atomic radii of the rare gases are a revision of values given by Goldschmidt as quoted by Koritnig.⁴¹ For the “traditional” radii it will be seen that the radius of a given halide ion is larger than the atomic radius of the rare gas in the preceding period. In the case of the smaller “crystal” radii the negative ion is, at the least, larger than the rare gas appearing two periods before. In either case it is clear that there are a large number of possible substitutional species if ion size is the determining factor. Furthermore, since Coulomb repulsion between ions neighboring the vacancy is believed to cause outward relaxation

TABLE IV. Ionic and atomic radii for the halides and the rare gases. For the negative ions, the “traditional” radii are those of Pauling and of Goldschmidt while the “crystal” radii are the two sets of values recently determined by Fumi and Tosi from crystal data. The radii for the rare gases are a revision of values given by Goldschmidt as quoted by Koritnig.

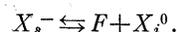
Ion	Traditional radius (Å) ^a	Crystal radius (Å) ^b	Atom	Elemental radius (Å) ^a
H^-	1.54–2.08	...	He	1.22
F^-	1.33–1.36	1.16–1.19	Ne	1.59
Cl^-	1.81	1.62–1.65	Ar	1.91
Br^-	1.96–1.95	1.76–1.80	Kr	2.01
I^-	2.20–2.16	1.97–2.01	Xe	2.20

^a Koritnig, Ref. 41.

^b F. G. Fumi and M. P. Tosi, Ref. 40.

about the vacancy, even more possibilities may exist than the radii for perfect crystals would indicate. However, caution must be used in this type of argument since the actual radius assumed by a species in a given situation depends on the nature of the chemical bonding and the crystal structure involved.

As shown in Sec. II the substitutional rare-gas atoms can trap an electron to form a substitutional ion X_s^- . However, this center could decay into an F center and an interstitial rare-gas atom according to the reaction



In the substitutional site the interaction of the rare-gas atom with the crystal presumably will be less repulsive; this will favor the left-hand side. However, the substitutional rare-gas atom raises the energy level of the trapped electron relative to that of the F center which favors the F -center-interstitial configuration of the right-hand side.

Unfortunately, there is only meager information on these opposing effects so it is only possible to speculate about the energy balance involved. The present calculations indicate that the ground-state energy level of the trapped electron is raised by the order of 0.4 to 1.1 eV relative to that of the F center (see Table V in the Appendix). Although there are no measurements or estimates of the difference in the repulsive interaction energy between substitutional and interstitial lattice sites for rare-gas atoms, an indication of the order of magnitude may be obtained from studies of the U center.

Hayes and Hodby have observed the thermal bleaching of the U_3 center and they attribute this to a U_3 to U_2 conversion ($H_s^0 \rightarrow H_i^0$).³⁷ In KCl an activation energy of 0.43 eV was observed while in NaCl the value was 1.0 eV. The authors associate these energies with the differences in lattice energy between the two possible sites. A more probable interpretation is that these energies represent the height of a barrier through which the hydrogen atom must pass in moving from the substitutional site to an interstitial one. In any event, equal or greater activation energies would be anticipated for the movement of rare-gas atoms all of which have larger atomic radii than hydrogen.⁴¹ This suggests that

³⁶ C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. **104**, 599 (1956).

³⁷ W. Hayes and J. W. Hodby, Proc. Roy. Soc. (London) **A294**, 359 (1966).

³⁸ P. Schmeling and R. Schroerschwartz, Phys. Status Solidi **15**, 325 (1966); P. Schmeling, *ibid.* **11**, 175 (1965); H. P. Mundt and A. K. H. Richter, Z. Naturforsch. **20a**, 267 (1965).

³⁹ Trapping of argon at cation vacancies or vacancy complexes in KCl has been inferred from recent diffusion measurements; see P. Schmeling, J. Phys. Chem. Solids **28**, 1185 (1967). Channeling studies of Rn and Xe trapped in KCl, CaF₂, and UO₂ indicate that at least in ion-bombarded crystals the heavy rare gases are primarily trapped as complex defects not at normal lattice sites; see H. J. Matzke and J. A. Davies, J. Appl. Phys. **38**, 805 (1967).

⁴⁰ F. G. Fumi and M. P. Tosi, J. Phys. Chem. Solids **25**, 31 (1964); M. P. Tosi, *ibid.* **25**, 45 (1964).

⁴¹ S. Koritnig, in *Landolt-Börnstein Tables* (Julius Springer, Berlin, 1955), Vol. 1, Part 4. See also F. Laves, Naturwiss. **25**, 721 (1937).

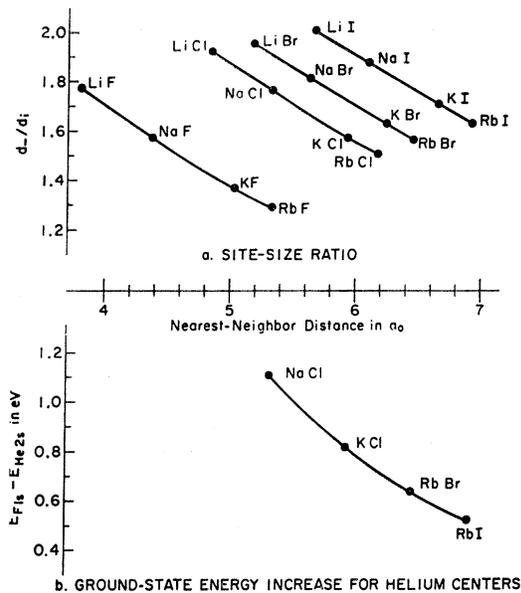


FIG. 5. Factors governing the equilibrium between rare-gas negative-ion centers and the F -center-interstitial rare-gas atom configuration. (a) The ratio of the "diameter" of a negative-ion vacancy, d_- , to the minimum "diameter" of an interstitial site, d_i , assuming no lattice relaxation and the Goldschmidt radii. The Fumi-Tosi "crystal" radii yield similar curves, but ratios that are roughly 10 to 15% less. (b) The calculated increase in ground-state energy of the electron bound to the helium rare-gas center relative to the F -center ground state.

at least in some cases the barrier height between substitutional and interstitial sites exceeds the change in energy of the bound electron which in turn suggests that a rare-gas center, once formed, should be stable at low temperatures. At high temperatures the relative energies of the sites determine the stability, but little can be inferred from the U -center experiments on this point.

Since the repulsive interaction of an impurity atom with the lattice increases rapidly as the internuclear spacing decreases, the difference in repulsive energy between a substitutional site and an interstitial site should be a rapidly varying function of the relative size of the sites with large ratios of substitutional-site to interstitial-site sizes strongly favoring substitutional rare-gas centers. The dependence on lattice parameter of these ratios as calculated from the Goldschmidt radii is given in Fig. 5(a). On the other hand, the increase in energy of the ground state of the electron bound to a rare-gas center relative to the F -center ground state also depends on lattice parameter as shown in Fig. 5(b). Since this provides the driving force for the dissociation of the rare-gas centers, it partially offsets the effect of the site-size ratio. A comparison of the two parts of Fig. 5 thus suggests that the optimum conditions for stable negative-ion rare-gas centers probably occur for the iodides or bromides of sodium, potassium, and perhaps rubidium.

The most straightforward method of forming the rare-gas centers in an alkali halide would be additive

coloration with alkali vapor in the presence of the rare gas under high pressure followed by a quench to freeze in the defects. This method has been successful in the formation of U centers^{36,42} and may be effective in this case if the centers are stable. An alternative method would be to diffuse the rare gas into the uncolored crystal and then x irradiate to produce vacancies into which the dissolved gas atoms could diffuse. Both of these methods depend on the diffusivity and solubility of the rare gases in the alkali halides and it is not obvious, even if the rare-gas centers are stable, that these quantities are such that an observable concentration of centers can be produced.

Other possibilities are to form the centers by bombardment with positive rare-gas ions⁴³ or by nuclear reactions that form the rare gas in the crystal. The latter method includes neutron activation of the alkalis⁴⁴ or the use of β^- -active halides which decay into rare gases. On the other hand, both bombardment and nuclear reactions generally create unwanted radiation damage which complicates the interpretation of results.

V. CONCLUSIONS

It has been argued that the defect consisting of a rare-gas atom at a negative-ion vacancy in an ionic crystal should trap an electron to form an electron-excess color center. The basis for this speculation is that the potential for the substitutional atom-vacancy system approaches that of a point charge in a dielectric medium at large distances.

The principal optical transitions for this class of centers have been calculated to lie in the range from 0.9 to 1.8 eV depending on the rare gas and the host crystal. The oscillator strength is found to be of the order of unity.

These hypothetical centers are particularly interesting because of their similarity to the F center. In principle they provide a series of centers differing somewhat in electronic properties, defect mass, and electron-lattice interaction. If they can be produced, they should provide valuable tests for the theory of electron-excess centers. For example, the centers have electronic levels between those of the F center and the conduction band which is an energy region of interest in relation to differences in the predictions of various theories.

Since the mass of the defect can be chosen lighter than that of the ion it replaces, local phonon modes are to be expected and infrared studies of the rare-gas centers would be an interesting extension of recent studies of the U center.⁴⁵ The centers might also shed new light on the

⁴² H. Rögner, *Ann. Physik* **29**, 386 (1937).

⁴³ R. Kelly and H. J. Matzke, *J. Nucl. Mat.* **17**, 179 (1965).

⁴⁴ See, for example, S. Kalbitzer, *Z. Naturforsch.* **17a**, 1071 (1962).

⁴⁵ See, for example, B. Fritz, U. Gross, and D. Bäuerle, *Phys. Status Solidi* **11**, 231 (1965); W. Barth and B. Fritz, *ibid.* **19**, 515 (1967); H. Bilz, B. Fritz, and D. Strauch, *J. Phys. (Paris)* **27**, Suppl. C2-3 (1966).

relaxation process in the excited states of color centers. The point is that the ions neighboring the rare-gas atom presumably would be more constrained than in an F center and their role in relaxation should be reduced.⁴⁶ Other points of interest include the possibility of α - and β -band-like transitions, sensitized luminescence, ESR and ENDOR spectra, fine structure in absorption and emission, and so on.

While all the potentialities associated with the rare-gas centers are quite intriguing and postulation of hypothetical centers is great sport, it must be stressed that they are pure speculation. Certainly the fact that many crystals have been grown under inert-gas atmospheres and no such color centers reported indicates that the centers, if they can be stabilized at all, are not to be had simply for the asking.

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APPENDIX

In Table V, the eigenvalues predicted by the present calculation for the F and rare-gas centers are listed for comparison with previous studies. Since the point-ion approximation is a drastic simplification, the actual values have little meaning. However, the energy differences between low-lying states has been shown to be in good agreement with experiments for the F center so that the neglected terms seem to have similar effects on both the low-lying s and p states.⁶

An important feature of these results is that the ground-state eigenvalues for the electron bound to the

TABLE V. Valence-electron eigenvalues for the F and rare-gas speculative centers in the point-ion approximation for various host materials. All energies are in eV.

Center	State	Eigenvalues (eV)			
		NaCl	KCl	RbBr	RbI
F	1s ^a	-6.50	-6.00	-5.61	-5.34
	1s ^b	-6.48	-5.96	-5.58	...
	2p ^a	-4.12	-4.02	-3.90	-3.81
	2p ^b	-4.08	-3.97	-3.86	...
He	2s	-5.39	-5.18	-4.98	-4.81
	2p	-4.24	-4.11	-3.97	-3.87
Ne	3s	-5.71	-5.43	-5.18	-4.99
	3p	-3.89	-3.86	-3.80	-3.73
Ar	4s	-5.22	-5.08	-4.91	-4.77
	4p	°	°	-3.54	-3.53
Kr	5s	-4.84	-4.71
	5p	°	-3.40

^a Present calculation.

^b B. S. Gourary and F. J. Adrian, Ref. 6.

[°] The integration routine for the radial Schrödinger equation failed to converge.

rare-gas centers always lie above those of the corresponding F centers. The rare-gas-center states are therefore predicted to lie within the gap between the crystal valence and conduction bands, and are not degenerate with occupied crystal states as is, in general, possible.

Two results are given for the F center. The first is for the present work and the second is taken from the work of Gourary and Adrian. The results differ slightly because Gourary and Adrian used variational wave functions with a limited number of parameters for solving the eigenvalue problem while numerical integration was used in the present work.

In a number of cases, solutions for excited electronic states of the rare-gas centers were not obtained because of the failure of the integration subroutine to converge. These solutions exist, but the numerical techniques used were not sufficient to integrate Schrödinger's equation with the jagged point-ion potential when the eigenvalues were small.

⁴⁶ W. B. Fowler, Phys. Rev. **135**, A1725 (1964).