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Self-trapped exciton and rare-gas impurity centers in solid Ne

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The structure of the atomic-type self-trapped exciton in solid Ne is studied using a hybrid method in which the inner shells of an atom are represented by the ion-size parameters of Bartram, Stoneham, and Gash, while the two outermost *s,p* shells are treated exactly as in the extended-ion model. The electronic wave function and the lattice relaxation are determined self-consistently by minimization of the total energy of the system. The lattice is found to dilate around the excited Ne atom by an amount corresponding to about five vacancies. The calculated absorption energy of the self-trapped exciton for $\Gamma_1 \rightarrow \Gamma_{15}$ (atomic $3s \rightarrow 3p$) transition is in good agreement with the experimental data of Suemoto and Kanzaki. The impurity centers of rare-gas atoms in a Ne host are also studied by the same method. The results show the existence of a small cavity around the impurity atoms, and account satisfactorily for the changes in the optical transition energies from gas to solid.

I. INTRODUCTION

The electronic structure of rare-gas solids (RGS) has been the subject of extensive investigations experimentally, as well as theoretically.[1] Optical absorption, luminescence, photoemission, and transport measurements have been conducted on pure and doped RGS and yielded a wealth of interesting results.

Recently, Suemoto and Kanzaki[2,3] have observed that the atomic-type self-trapped excitons (a-STE) in solid Ne are surrounded by cavities (which they called the STE bubble) and that the size of the bubble grows as a function of time during the lifetime (~ 560 μsec) of the STE. A similar phenomenon has also been observed for the molecular-type STE.[3] The phenomenon of a bubble around an excited electron is closely related to the earlier observation of the electron bubble in liquid He (Ref. 4) and liquid Ne.[5] It is also intimately related to the observed negative electron affinity in solid Ne.[6] The underlying principle is the following: The excited electron, whether in the conduction band or in a localized defect center such as the STE or an impurity rare-gas atom (e.g., Ar in Ne host), interacts with a large number of surrounding Ne atoms. There are two kinds of interaction. One is the repulsive interaction between the excited electron and the core electrons of the Ne atom due to the requirement of the wave-function orthogonalization. The other is the polarization of the core atoms which always leads to an attractive interaction. For the lighter rare-gas atoms (He, Ne, and marginally also Ar), the repulsive interaction is more important than the effect of the polarization. This explains qualitatively why an excited electron pushes away nearby atoms, thereby creating locally a "vacuum," or why a conduction-band electron (at the bottom of the band) has energy higher than the vacuum level. In the case of the STE in Ne, it has been shown by Song and Leung[7] that the lowering of the electronic energy by removing a nearest-neighbor atom is larger than the vacancy formation energy, so that it is energetically favorable for bubble to exist in Ne.

In an earlier work,[8] a hybrid method was employed to study the Rydberg series of alkali and rare-gas atoms, giving very good results. The method can readily be applied to study defects in insulators. This method consists of dividing the electrons of a lattice atom into two groups: the compact deep-core electrons and the more extended outer shell electrons. The deep core is approximated by the ion-size parameters of Bartram, Stoneham, and Gash,[9] while the interaction terms of the defect electron with the outer shell electrons are calculated exactly. In addition, floating 1*s* Gaussian basis functions are employed, which allow a very efficient calculation of the various terms.

In this paper, we investigate the properties of the a-STE in solid Ne using the hybrid method described above. Also studied are the rare-gas impurities (Ar, Kr, and Xe) in solid Ne which exhibit interesting effects of the lattice similar to the STE bubble of Ne. As the electron-lattice interaction is comparable (or larger) to the lattice deformation energy, we have to minimize the total energy of the system with respect to the electronic wave function and the lattice configuration simultaneously. The details of the method and calculation for the a-STE in Ne are presented in Sec. II. The same method also applies to the study of impurity centers in Ne. In Sec. III we present the results of our calculation for the a-STE in Ne. It is shown that the lattice expands immediately after the excited electron becomes bound to the localized hole; the size of this original cavity corresponds to about five vacancies. The transition energy between the *s*-like and the *p*-like states of the STE bubble is in very good agreement with the observed value of Suemoto and Kanzaki.[3] Subsequently, the size of the bubble grows by capturing vacancies from the bulk of the crystal. The number of the attracted vacancy at equilibrium is estimated from the rate theory point of view, and is in reasonable agreement with the proposed value of Ref. 3. In Sec. IV we present the results of a similar study of the rare-gas impurity atom (Ar, Kr, and Xe) in solid Ne. The energy shifts observed in the absorption (and luminescence) between the free atomic state and in solid Ne are calculated. These compare satisfactorily with the experimental data. The size of the cavity around the excited impurity atom is found to be comparable to that of the STE bubble in Ne. Finally, in Sec. V, we discuss several other possible applications of the method employed in this work.

II. METHOD OF CALCULATION FOR THE a-STE IN Ne

As it has been pointed out earlier,[7] the electron-lattice interaction energy is quite large in comparison with the lattice deformation energy. We therefore evaluate the thermodynamic free energy of the whole system at 0 K. The sum of the energy of the electron in the field of the central Ne^+ ion, its interaction energy with a large number of the surrounding Ne atoms, and the lattice deformation energy is minimized with regard to the electron wave function and the atomic displacements of the Ne atoms. The contribution of the zero-point energy of the lattice is also examined in some cases as described below. The total Hamiltonian is

$$\begin{aligned} H &= H_e(\vec{r},\{\vec{R}_l\})+H_L(\{\vec{R}_l\}) , \\ H_e &= K + V_{\mathrm{PI}} + V_{\mathrm{SC}} + V_{\mathrm{EX}} , \end{aligned} \tag{1}$$

Here H_e is the Hamiltonian for the electron, which depends on the lattice configuration $\{\vec{R}_l\}$, and H_L is the lattice deformation energy. K, V_{PI}, V_{SC}, and V_{EX} are the kinetic energy, the point-ion potential, the screened Coulomb potential, and the exchange interaction, respectively. The electron wave function is taken as a linear combination of three 1s Gaussians whose coefficients are treated as variational parameters, determined by solving the secular determinant. The lattice positions $\{\vec{R}_l\}$ are varied in a discrete way assuming radial displacements up to the 13th shell. (A continuum correction for the remainder of the lattice was found to contribute a negligible term to the energy, and was subsequently dropped.) The minimization is carried out by searching the minimum of the total energy for the various configurations $\{\vec{R}_l\}$. In the following, we give the details for H_e and H_L.

A. Electronic energy

We have used a hybrid version of the one-electron Hartree-Fock method, which is also called the extended-ion model in the study of color centers in ionic crystals. In this method, the occupied core states of the lattice atoms are assumed not to change in any substantial way from those of the free atoms (ions). The Hartree-Fock equation for the defect electron is solved by variational method. This approximation is generally a reasonable one for large band-gap insulators, such as the alkali halides and rare-gas solids. As was discussed in an earlier paper,[8] the deep cores are very compact and can be adequately represented by the first few orders of the ion-size parameters first introduced by Bartram, Stoneham, and Gash.[9] However, it was found that the electrons of the outermost shells (2s and 2p of Ne for example) have quite extended charge density and these have to be treated separately. The overlap integrals, the screened Coulomb, and the nonlocal exchange terms are evaluated exactly for the outermost shells in accordance with the extended-ion model.

The pseudo-wave function ϕ is represented by a set of floating 1s-like Gaussian basis functions. There is no need for using Gaussian functions of higher-order spherical harmonics, since states of different symmetries can be obtained by using a set of 1s Gaussians centered at suitable positions around the defect center. After the outer-shell electron wave functions are expressed in terms of Gaussian functions, all the required integrals can be evaluated in closed analytic form.[10] The use of 1s Gaussian basis functions also proves to be particularly convenient in another respect. In fact after some experience, it is found that these various terms can be fitted quite accurately by simple interpolation formulas over a range of the Gaussian damping factors and the distance between the Gaussian pseudofunction and the ion. A brief description of the interpolation scheme is given in the Appendix. This simplifies substantially the task of evaluating the various terms for the outer shells, while retaining the required accuracy. To determine the equilibrium state of the self-trapped exciton at its lowest bound state (corresponding to the 3s atomic state of Ne^*), we have employed three s-like Gaussians centered at the excited atom (damping factors: $\alpha=0.020$, 0.045, and 0.090 in a.u.). The eigenvector varies with the lattice configuration. The Gaussian damping factors α were determined from a preliminary work with single Gaussians. The number of atoms summed can easily be extended, because of the fast interpolation scheme. We have found it sufficient to sum over the first six shells for the Γ_1 state and somewhat larger for the Γ_{15} state.

The matrix elements of the secular determinant $|H_{ij}-ES_{ij}|=0$ between a pair of Gaussians ϕ_i and ϕ_j, after orthogonalizing to the occupied core states χ_{lm} of the atoms are as follows:

$$\psi_i=\phi_i-\sum_l\sum_m \chi_{lm}\langle\phi_i\,|\,\chi_{lm}\rangle ,$$

$$\begin{aligned} H_{ij} &= \langle\psi_i\,|\,H_e\,|\,\psi_j\rangle \\ &= \langle\phi_i\,|\,(K+V_{\mathrm{PI}}\,|\,\phi_j\rangle \\ &\quad + \sum_l \langle\phi_i\,|\,[V_{\mathrm{SC}}(l)+V_{\mathrm{EX}}(l)]\,|\,\phi_j\rangle \\ &\quad - \sum_l\sum_m E_{lm}\langle\phi_i\,|\,\chi_{lm}\rangle\langle\chi_{lm}\,|\,\phi_j\rangle , \end{aligned} \tag{2}$$

$$\begin{aligned} S_{ij} &= \langle\psi_i\,|\,\psi_j\rangle \\ &= \langle\phi_i\,|\,\phi_j\rangle - \sum_l\sum_m \langle\phi_i\,|\,\chi_{lm}\rangle\langle\chi_{lm}\,|\,\phi_j\rangle . \end{aligned} \tag{3}$$

Here the core energy E_{lm} and wave function χ_{lm} refer to the mth core state of the ion at site $\vec{R}_l$. E_{lm} is related to the free-atom core energy $E_{lm}^{(0)}$ by

$$E_{lm}=E_{lm}^{(0)}+\Delta V_l ,$$

where ΔV_l is the point ion potential at $\vec{R}_l$.

The core wave functions χ_{lm} and the corresponding energies $E_{lm}^{(0)}$ for Ne^+ and Ne are taken from Clementi and

Roetti.[11] Separating the deep core from the outmost s and p shells (SP), and treating them in terms of the zeroth-order ion-size parameters A and B, Eqs. (2) and (3) are rewritten as

$$\begin{aligned} H_{ij} = & \langle \phi_i \mid (K + V_{\mathrm{PI}}) \mid \phi_j \rangle \\ & + \sum_l (A_l - B_l \Delta V_l) \phi_i^*(\vec{R}_l) \phi_j(\vec{R}_l) \\ & + \sum_l \langle \phi_i \mid [V_{\mathrm{SC}}^{(\mathrm{SP})}(l) + V_{\mathrm{EX}}^{(\mathrm{SP})}(l)] \phi_j \rangle \\ & - \sum_l \sum_m {}^{(\mathrm{SP})} E_{lm} \langle \phi_i \mid \chi_{lm} \rangle \langle \chi_{lm} \mid \phi_j \rangle \;, \end{aligned} \qquad (2')$$

$$\begin{aligned} S_{ij} = & \langle \phi_i \mid \phi_j \rangle - \sum_l B_l \phi_i^*(R_l) \phi_j(\vec{R}_l) \\ & - \sum_l \sum_m {}^{(\mathrm{SP})} \langle \phi_i \mid \chi_{lm} \rangle \langle \chi_{lm} \mid \phi_j \rangle \;. \end{aligned} \qquad (3')$$

The third and fourth terms of Eq. (2′) and the third term of Eq. (3′) are evaluated as explained above. The ion-size parameters A and B of Ne^+ and Ne are given in Ref. 8.

After the equilibrium lattice configuration corresponding to the STE in the Γ_1 state is obtained, we calculate the electronic energy of the Γ_{15} state assuming the Franck-Condon approximation. Two pairs of s-like Gaussians ($\alpha_1 = 0.06$ and $\alpha_2 = 0.03$) centered along a cubic axis across the defect center were used. The energy is not very sensitive to the distance of these Gaussians from the center. We found that $d_1 = 0.84$ and $d_2 = 3.00$ (in a.u.) nearly optimal. If we require other excited states belonging to different irreducible representations of the system, we simply would place more $1s$-like Gaussians along various axes around the defect center and diagonalize a larger secular determinant.

The electronic polarization energy is included using the method of Mott and Littleton, in which the dipole moments of the first 13 shells are determined by iteration. It is found that the effect of electronic polarization is quite negligible, especially when there is large lattice expansion around the STE. Similar results were reported earlier for the case of an undistorted lattice.[7] The smallness of the electronic polarization energy for the STE in Ne is due primarily to the fact that the system is electrically neutral. It is also due to the relative compactness of the charge density of the excited electron. In the ground state, about 95% of the electron charge resides inside the bubble. We note that in a similar system, the F center in alkali halides, Gourary and Adrian[12] have also shown that the electronic polarization energy is also quite negligible. By contrast, for the electron bubble in solid Ne, which we have also studied the electronic polarization energy is substantial. It is more important than the lattice elastic energy in determining the equilibrium size of the bubble. (It represents about one-third of the total energy of the electron bubble.)

B. Lattice energy

For the rare-gas solids, there is extensive work on the interatomic potentials. In this work, we have used two different interatomic potentials for the Ne-Ne pair interaction in the solid. One is the potential proposed by Aziz,[13] which is determined to correctly account for a large number of properties of the gas. The other is the (6-12)-type potential presented in Kittel.[14] It turns out that the final results do not depend on the choice of the potential in any substantial way.

We will discuss in some detail the choice of these interatomic potentials at the end of next section. Aziz's potential is as follows:

$$U(r^*) = \epsilon \left[\frac{6}{n-6} (r^*)^{-n} - \frac{n}{n-6} (r^*)^{-6} \right]$$

with

$$r^* = r / r_m$$

and

$$n = 13 + \gamma (r^* - 1) \;,$$

where r is the pair distance and the constants have been determined as

$$\gamma = 5 \;,$$

$$r_m = 3.0739 \text{ Å} \;,$$

$$\epsilon = 41.1863 \text{ K} \;.$$

We have also examined the effect of zero-point energy using a simple approximation. The zero-point energy is given by $(\frac{9}{8}) k \Theta_D$ according to the Debye model. Here Θ_D is the Debye temperature. With the use of such experimental data as the sublimation energy, the lattice constant, and the compressibility, the Debye temperature Θ_D can be expanded in a power series of the local volume change $\Delta v / v$. The change in the local zero-point energy can be represented in such a way as when the total energy of the system is minimized in determining the equilibrium state of the STE bubble. Using this approximation, we have estimated that the inclusion of the zero-point energy leads to at most about 10% increase in the first shell displacement As for the energies, there is less than 1% change when the zero-point energy is included. A more accurate treatment should include the effect of possible local modes of different frequencies in the immediate neighborhood of the excited atom of which we know little at this time. The results reported below are obtained without the zero-point energy correction. This amounts to assuming that the zero-point energy does not vary during the lattice relaxation and that the local modes are neglected.

The second interatomic potential used is of Lennard-Jones type and the parameters for all RGS are given in Kittel.[14] Reliable interatomic potential between Ne^+ and Ne is not readily available. However, because of the large repulsive interaction between the excited electron and the nearby atoms, the radial displacements depend only slightly on this interatomic potential. We have examined two approximations. In the first we used exactly the same potential as that for Ne-Ne. In the other, the Ne^+-Ne potential was obtained by scaling the two parameters of the Ne-Ne potential by constant factors (0.6866 for the attractive part and 0.5474 for the repulsive part), as was done by

Druger and Knox[15] in their study of the self-trapped hole in rare-gas solids. The result is that it introduces a small difference in the first-shell radial displacement (2.01 and 2.00 a.u., respectively, for the cases with and without the scaling). Beyond the first shell, the effect is almost unrecognizable. All the results reported here are obtained with the use of the scaled form for the Ne^+-Ne interaction. The total energy is evaluated for each lattice configuration which undergoes a gradual stepwise relaxation. It is important to consider a large enough cluster (in this work 13 shells are included). The number of atoms around each atom undergoing a relaxation which are counted in the lattice sum is relatively less critical. We found that the first seven shells of atoms (135 atoms) are sufficient in this regard. The electron wave function is optimized at each step by means of the three Gaussian basis functions mentioned above. When the total energy varied by less than 10^{-4} hartree, the minimum is considered to be reached.

III. THE STE BUBBLE IN SOLID Ne

The most interesting result we obtained is that the lattice expands by a considerable amount around the excited atom. The first shell of atoms is displaced radially by about 2 a.u., corresponding to a cavity of volume equivalent to about five vacancies. This means that there is an initial bubble equivalent to about five vacancies immediately after the atom is excited. The dilatation extends over many atomic shells. Important displacements are experienced by those shells which are directionally coupled to the first shell along the (110) axis. Those are the first, the fourth, and ninth, etc., shells. The last shell (the 13th) included in our work experiences about 0.11 a.u. outward shift. A continuum correction to represent the remainder of the lattice represents about 3% of the total deformation energy, and is therefore neglected in the subsequent calculations.

Results obtained with the two sets of Ne-Ne potential are listed in Table I which includes the total energy, the first-shell radial displacement δR, with the electron in the s-like (Γ_1) state and the electronic energies for the Γ_1 and Γ_{15} states at the Γ_1 state lattice configuration. Also listed are the Γ_1 and Γ_{15} state energies with the lattice held in its perfect configuration. By assuming that the hole state energy (in the $2p$ shell of Ne) does not vary in the solid from its value in the gas state, we can evaluate the change in energy for the absorption $2p \rightarrow 3s$ and for the emission $3s \rightarrow 2p$ between the gas and solid phases. We find that the absorption energy is larger in solid by 1.22 eV, while the emission energy is larger in the solid by 0.18 eV than in the gas. The experimental values[16,17] are, respectively, 0.79 and 0.07 eV (after taking the weighted average to take account of the spin degeneracy). If the hole energy before the absorption in the solid is raised somewhat, the agreement improves further.

The different behavior of the Γ_1 and Γ_{15} states is largely due to the difference in the spatial extension of the wave functions. For the more compact Γ_1 state, the wave function approaches that in the gas state after the lattice has dilated. However, the Γ_{15} state is still substantially higher than that in the gas state. Consequently, the $\Gamma_1 \rightarrow \Gamma_{15}$ transition energy is slightly larger in the solid than in the gas, in agreement with the experiment of Suemoto and Kanzaki.[2]

Before we compare the absorption energy calculated here with the experimental data we should note that the presence of a hole in Ne^+ introduces the spin-orbit interaction as well as the exchange interaction between the hole and the electron. In the present work we have not considered the spin-orbit interaction, although the exchange effect was represented. From the atomic spectra tables[18] we have determined the centers of gravity of those states which converge to $J=\frac{3}{2}$ state in the ionizing limit for both $(2p^5 3s)$ and $(2p^5 3p)$ configurations. The weight taken was $(2J+1)$. As was reported in Ref. 7, this gave an excellent overall agreement between the calculated Rydberg energies and the experimental values for the alkali-metal atoms and rare-gas atoms.

In their experimental work on the STE bubble in Ne, Suemoto and Kanzaki[3] have monitored the energy of one particular transition $3s_{12} \rightarrow 3p_{01}$, which is isolated from the others. This line is lower than the center of gravity defined above by 0.17 eV in the gas. In the solid, we have therefore estimated the position of the centers of gravity from that of $3s_{12} \rightarrow 3p_{01}$ by the same shift. These estimated energies of the center of gravity are compared with our calculated values for the free atom and the solid in various lattice configurations. The experiment followed the evolu-

TABLE I. Size of the bubble and the electronic energies of Γ_1 and Γ_{15} states. The bubble size with the electron in the Γ_1 state is indicated by the radial displacment δR_1 of the first-shell atoms. The total energy E_T of the system with the electron in the Γ_1 state is also given. (All are in atomic units.)

	Gas		Solid ($a=8.43a_0$): theory		Dilation + 12[a] vacancies
	Theor.	Expt.	Rigid lattice	Dilated lattice[a]	
$E(\Gamma_1)$	−0.1755	−0.1798	−0.1306	−0.1688	−0.1741
				−0.1670	−0.1733
$E(\Gamma_{15})$	−0.1069	−0.1088	−0.0252	−0.0877	−0.1013
				−0.0840	−0.1005
δR_1				2.01	
				1.82	
$E_T(\Gamma_1)$				−0.1634	
				−0.1607	

[a] The first is for the Aziz (Ref. 13) potential and the second for the (6-12) potential (Ref. 14).

TABLE II. Transient absorption energy for $\langle 3s \rangle \rightarrow \langle 3p \rangle$ of the STE in solid Ne. $\langle\ \rangle$ indicates the center of gravity of the multiplet (see the text for details). The two interatomic potentials used for Ne-Ne give slightly different results. The first is for the Aziz potential (Ref. 13) and the second for the (6-12) potential (Ref. 14). (All in electron volts).

Gas		Solid: theory			Expt.[b]	
Theor.	Expt.[a]	Rigid lattice	Dilated lattice	Dilation + 12 vacancies	Initial	Final
1.87	1.93	2.87	2.21	1.98	2.13	2.07
			2.26	1.98		

[a] Reference 18.

[b] Reference 3.

tion of the transition energy $3s_{12} \rightarrow 3p_{01}$ as a function of the delay time between the electron pulse (excitation of the Ne atoms) and the subsequent laser light pulse, which varied between 5 and 160 μsec. The shift of the absorption energy is toward the longer wavelength, thereby approaching the free atomic value. The authors have interpreted their data in terms of the bubble formation around the excited Ne* atom. Our calculated absorption energy in the presence of the lattice dilatation should therefore be compared with the experimental absorption energy corresponding to the shortest time delay (5 μsec). As can be seen in Table II, the agreement with experiment is very good. Similar good agreement exists also for the case of the free atom (Table II).

After the initial lattice dilatation which is believed to follow the electron localization very fast (within about one period of the lattice vibration), the total energy of the system can still be lowered by capturing the free vacancies in the lattice. The rate and the growth of the bubble is therefore diffusion controlled and shows strong temperature dependence as was observed by Suemoto and Kanzaki.[3] The red shift of the absorption energy per additional vacancy to the first shell is found to be about 0.02 eV from our work. The experiment shows that the $3s_{12} \rightarrow 3p_{01}$ absorption energy varies from 1.957 to 1.902 eV during the growth of the bubble independent of the temperature (between the observed interval of 18 and 28 K). This red shift of about 0.055 eV corresponds therefore to about three extra vacancies attracted to the bubble before the growth stops. This number is in agreement with the results of the analysis given by Suemoto and Kanzaki (who concluded that their data is consistent with the vacancy number between three and seven). They have not realized, however, that the lattice undergoes the large initial dilatation which we have found.

An interesting question is why the bubble stops growing. According to our calculation, the system energy lowers by about 0.02 eV for each additional vacancy captured in the first shell. Thus it is energetically possible for the STE to capture at least 12 vacancies. In fact, the number of vacancies captured in equilibrium depends also on the kinetics of vacancy diffusion. We have made a crude estimate following the usual theory of vacancy cluster formation. By matching the rate of a vacancy jumping into the first shell with that of a vacancy jumping out, we have found that the number of vacancies at equilibrium would be small, somewhere between one and two. This is therefore in qualitative agreement with the analysis presented above.

Another interesting result of the experiment[3] is that the absorption line is relatively sharper at the two ends of the delay time. Suemoto and Kanzaki have argued that during the growth of the bubble there is a statistical distribution in the bubble size and this introduces extra broadening of the absorption line.[19] This seems to be a correct reasoning. The other factor to consider is the crystal-field splitting of the Γ_{15} state in the presence of a small number of vacancies in the first shell. We have estimated that this effect leads to a splitting of about 0.1 eV among the Γ_{15} states. This is about twice as large as the maximum linewidth. We do not understand why this effect on the Γ_{15} state is not observable. It could be that the first-shell atoms undergo substantial rearrangement when vacancies jump in, so that the new arrangement largely cancels the anisotropy.

In an earlier work, Song and Leung[7] have used the pseudopotential theory of Bartram, Stoneham, and Gash[9] to study the a-STE in Ne. In this work, the outermost *s* and *p* electron shells were not represented separately, but were included in the total ion-size effect together with the contributions from the deeper cores. The ion-size parameter *A* was scaled by a factor of 0.53 as in the studies of *F* centers in alkali halides. Although the important point about the large electron energy gain per atom removed was made in that work, the possibility of the lattice dilatation was not investigated then. A mention should be made of a little-known work by Sribnaya *et al.*[20] in which the interaction of the excited electron with the lattice atoms is studied for solid Ne. They have used a simple wave function which was orthogonalized to the first-shell atoms. They found the lattice dilatation which is somewhat larger than our value (3.0 vs 2.0 a.u. in our work). They have not studied the other excited states, and the method used was a direct orthogonalization scheme organized for one specific example.

Another interesting work was done by Kunsch and Coletti[21] who exploited the existence of the potential of Ne$_2^*$ from an *ab initio* calculation of Cohen and Schneider.[22] By extracting out the interatomic potential for Ne-Ne and Ne*-Ne, they obtained the dilatation field around the excited Ne* atom, and also the change in the emission energy $3s \rightarrow 2p$ in solid from the free-atom value. This energy change is in very good agreement with the experiment and the lattice dilatation result is very close to ours (2.22 a.u. for the first shell, which is very close to our 2.01 a.u. with the Aziz potential).

In view of the very large lattice dilatation which we found around the excited atom, one may question the validity of the interatomic potential used. These potentials are determined from a set of lattice properties[14] or gas properties over a wide range of temperature.[13] In particular, the Aziz potential used here was fitted from data including the low-temperature gas diffusion data, which is important in determining the slope of the repulsive potential wall. This portion of the interatomic potential is of particular importance in this work, as the lattice is compressed in the neighborhood of the bubble. The large outward displacement of atoms in the first shell is determined primarily by the interaction between the excited electron and the core electrons of the surrounding atoms. We found that the size of the bubble is practically insensitive to the treatment we made to the Ne^+-Ne interaction, as we reported above. We believe that the uncertainty of the potential for large lattice distortion would have only a small effect on the formation of the large bubble around the STE in Ne.

IV. RARE-GAS IMPURITIES IN SOLID Ne

The influence of an inert host matrix on the properties of various atomic and molecular systems has been the subject of considerable interest.[1] The case of low-concentration rare-gas impurities (Ar, Kr, and Xe) in solid Ne (Refs. 23 and 24) is very similar to the a-STE in Ne just studied. These systems have been studied by optical absorption and luminescence between the various electronic states and the results were compared with the corresponding free-atom data. There are rather large Stokes's shifts, as well as subtle differences between the solid and the gas data. These point to the presence of "bubbles" around the excited impurity atoms. While in the case of the a-STE in Ne, the absorption and emission are between a pair of excited states (3*s* and 3*p* of the central Ne atom), the optical transitions for the impurity centers are between the hole state (in the compact closed shell) and the first excited *s*-like state of the impurity atom (e.g., between 3*p* and 4*s* states of Ar in Ne).

We have studied these impurity centers using the method of Sec. II. Before presenting the results of our work, the following points can be made.

(1) The hole state is from the last closed shell (*p* state) of the neutral impurity atom. This being a relatively compact state, the influence of the inert-gas lattice is believed to be relatively small on the hole state, as was assumed in the preceding section.

(2) Even with the electron in the compact hole state (i.e., when the dopant atom is unexcited), there is a nonnegligible lattice relaxation around the dopant atom, because of the difference in the atomic radii between the dopant and the host atoms. As the electronic energy is very sensitively dependent on the surrounding lattice configuration when the electron is excited to the *s* state, we should determine this relaxation first. This relaxation is much smaller than the large dilatation expected to take place once the electron is in the excited *s*-like state.

(3) According to the Franck-Condon principle, the optical absorption takes place while the lattice is frozen in the initial-state configuration. It is therefore expected that the energy of the optical absorption (e.g., $3p \rightarrow 4s$ in Ar-Ne) will be considerably larger than that of the corresponding transition for the free atom.

(4) For luminescence back to the ground state (e.g., $4s \rightarrow 3p$ in Ar-Ne), the electron is initially in a diffuse excited state. Since the lifetime of the excited state is in general long compared with the lattice relaxation time, the lattice expands around the impurity atom leading to the formation of a cavity, in the same way as the case of the STE studied above. The luminescence energy in the solid is therefore very close to that of the free atom, but slightly larger reflecting the residual effect of the lattice on the relaxed excited electron state.

For the study of impurities in solid Ne, we have followed the same approach as for the a-STE in Sec. III. The ion-size parameter A is 27.70, 38.55, and 61.28, respectively, for Ar^+, Kr^+ and Xe^+. The values of B are 2.52, 4.43, and 10.06 for the three ions. (All are in a.u.) In choosing the interatomic potential, however, we limited ourselves to the (6-12) potentials for the sake of uniformity. The pair potential between the impurity atom and a host atom was also taken as a (6-12) potential, determined along the line proposed by Prigogine[25]: The energy parameter is taken as the geometric average of those for the impurity atom and the host atom, and the radius parameter is taken as the corresponding arithmetic average. This determined the interaction for the pairs Ar-Ne, Kr-Ne, and Xe-Ne. When the electron is excited, the interactions to consider are between the impurity ions (e.g., Ar^+) and the neutral Ne atom. This was treated by scaling the constants in the same way as in the STE work of Sec. III. Again in this case the scaling has only a small effect on the size of the bubble because of the strong electron-lattice interaction.

As the compact hole state is not accessible by the present method, we have calculated the excited *s*-like states under various lattice configurations. We first evaluate the small relaxation of the lattice around the dopant atom with the electron in the ground state. Then a second calculation minimizes the total energy of the system (using three Gaussians for the excited electron) with the electron in the first excited *s*-like state. This part is similar to the STE work of Sec. III, and determines the size of the "bubble."

For comparison's purpose, the following *s*-like excited state energies are obtained using a single optimized 1*s* Gaussian function centered on the impurity atom: (1) E_A, the final-state energy in the absorption for the relaxed lattice (no bubble); (2) E_E, the initial-state energy in the luminescence for the solid (i.e., the energy of the excited state in the bubble); (3) E_G, the initial-state energy in the luminescence for the free atom. These energies are assembled in Table III, which also gives the first-shell radial displacements δR_1^0 and δR_1^*, respectively, with the electron in the ground and the relaxed excited states.

Assuming the hole-state energy is the same for the solid and the free atom, $(E_A - E_G)$ is the difference in the absorption energies in the solid and in the free-atom state, and $(E_E - E_G)$ is the difference in the luminescence energy. The calculated values $(E_A - E_G)$, $(E_E - E_G)$, and the Stokes's shift $(E_A - E_E)$ are listed in Table IV, and compared with the experimental data of Hahn and

TABLE III. First-shell radial displacement with the impurity atom in the ground state (δR_1^0) and in the excited state (δR_1^*). [In Ne-Ne, the result for the (6-12) potential is listed.] The electron energies and the corresponding optimized Gaussian functions (the damping factors α) of the first excited state for the gas state (E_G), the unrelaxed state reached by optical absorption (E_A) in the solid, and the relaxed excited state prior to the emission in the solid (E_E). (All in a.u.)

	Ne-Ne	Ar-Ne	Kr-Ne	Xe-Ne
δR_1^0	0	0.371	0.576	0.860
δR_1^*	1.82	2.239	2.287	2.572
$E_G(\alpha)$	-0.1755	$-0.1483(0.028)$	$-0.1400(0.024)$	$-0.1333(0.020)$
$E_A(\alpha)$	-0.1306	$-0.0908(0.042)$	$-0.0779(0.035)$	$-0.0623(0.026)$
$E_E(\alpha)$	-0.1670	$-0.1352(0.036)$	$-0.1222(0.031)$	$-0.1112(0.026)$

Schwenter.[24] The atomic values are taken from the standard source.[18] For comparison's sake, we have included in this table the corresponding values for the Ne "impurity" in solid Ne, obtained in Sec. III.

The comparison between theory and experiment shows that there is an overall satisfactory agreement. The important facts of a large Stokes's shift and a slightly larger luminescence energy in the solid are well confirmed by our calculation. It is also interesting to compare how the wave function (single optimized Gaussian) varies from atom to atom and from gas to solid (see Table III). The most uncertain quantity is the relaxation of the lattice with the electron in the ground state. The energy of the excited state reached by absorption depends quite sensitively on the ground-state lattice configuration and even slight uncertainties would shift E_A by a substantial amount. The assumption that the hole-state energy is the same for the solid and gas also contributes to the discrepancy between theory and experiment. Since the hole-state energy is slightly higher in the solid (particularly for the heavier impurity atoms), we have probably overestimated the change in the absorption energy ($E_A - E_G$) somewhat.

V. CONCLUSION

We have studied the electronic structure of the a-STE and rare-gas impurities in solid Ne using a hybrid version of the extended-ion model and obtained quite interesting results. The most important result obtained is the existence of a microcavity around the excited atom in solid Ne, similar to the well-known electron-bubble in liquid Ne.[5] Qualitatively speaking this is the effect of the repulsive pseudopotential of the Ne atom. The gain of electron energy when a nearest-neighbor Ne atom is pushed away is large enough to compensate the expense of energy to deform the lattice locally. The change in the spectroscopy between the states of the free atom and those in the solid Ne lattice are also correctly reproduced in the present theory as they are observed experimentally.

In the hybrid scheme used in this work, the deep-core electrons are treated by the ion-size theory of Bartram *et al.*[9] of the lowest order, and the two outermost shells (s and p) are treated exactly within the framework of the one-electron Hartree-Fock method. The exclusive use of the floating basis 1s Gaussian functions allows an efficient and accurate evaluation of the many and various terms of the Schrödinger equation. Further applications of the present approach to other interesting defect systems in rare-gas solids, such as the impurity alkali metals in solid Ne and Ar are now under way. When applied to the study of the conduction bands of solid Ne and Ar (Ref. 26) we have obtained very encouraging results which compare well with other Hartree-Fock band calculations.[27]

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APPENDIX A: INTERPOLATION SCHEME

We present here a brief description of the interpolation scheme for the various integrals of Eqs. (2′) and (3′) which we found very efficient and accurate. First, we convert the Slater orbitals of the outer shell wave functions in terms of linear combinations of Gaussian orbitals by least-squares fit (the number is usually 12). Then the overlap integral, the screened Coulomb, and the nonlocal exchange terms are evaluated exactly by using the analyti-

TABLE IV. The changes in the optical transition energies of the impurity atoms in the free state and in solid Ne: ($E_A - E_G$) for the absorption, ($E_E - E_G$) for the emission, and ($E_A - E_E$) the Stokes's shift (in eV).

	Ne-Ne		Ar-Ne		Kr-Ne		Xe-Ne	
	Theor.	Expt.[a]	Theor.	Expt.[b]	Theory.	Expt.[b]	Theor.	Expt.[b]
($E_A - E_G$)	1.22	0.79	1.56	0.89	1.69	0.53	1.93	0.62
($E_E - E_G$)	0.23	0.07	0.36	0.08	0.48	0.07	0.60	0.17
($E_A - E_E$)	0.99	0.72	1.21	0.81	1.21	0.50	1.33	0.45

[a] Reference 16.

[b] Reference 24.

cal expressions which are available.[10] A set of these exact values are then fitted to simple interpolation forms over a range of the Gaussian damping factor and the distance between the atomic core and the 1*s* Gaussian pseudo-wave-function. The range of the damping factor employed is guided by a preliminary study of the wave functions for a variety of excited states. These include the conduction-band electron, the STE, and the electron bubble in the case of Ne. For most cases we studied, the optimal range of the Gaussian damping factor is about 0.002 to 0.140 (in a.u.) The distance between the atomic core and the 1*s* Gaussian ranges from 0 to about 15 a.u.

In the following we give merely the form of the interpolation formulas.

A. Screened Coulomb energy

We found the following form of the screened Coulomb energy very satisfactory. Here $G(R_1)$ and $G(R_2)$ are the 1*s* Gaussian pseudo-wave-functions centered on R_1 and R_2, and A and β are the parameters fitted

$$\int G(R_1)V_{\text{sc}}(r)G(R_2)d\tau=A\int G(R_1)\frac{e^{-\beta r^2}}{r}G(R_2)d\tau\ .$$

B. Exact exchange energy

We have examined various forms of interpolation including the ones for the exact exchange energy with an *s*- or *p*-type Gaussian core. We found the following form very accurate and convenient:

$$\int G_1(R_1)V_{Ex}(1,2)G_2(R_2)d\tau_1 d\tau_2 =A'\int G(R_1)e^{-\beta' r^2}G(R_2)d\tau\ ,$$

where A' and β' are the parameters of fit.

C. Overlap integrals

The overlap integrals between a 1*s* Gaussian $G(R_1)$ and an *s*- or *p*-core Gaussian orbital are straightforward. The fit can be accomplished by means of one- or two-core Gaussians as follows

$$\int G(R_1)\chi_s d\tau=N_s\int G(R_1)e^{-\alpha r^2}d\tau\ ,$$

$$\int G(R_1)\chi_{p_z} d\tau=N_p\int G(R_1)e^{-\alpha' r^2}z\,d\tau\ .$$

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