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Ejection of atoms upon self-trapping of an atomic exciton in solid argon

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Molecular-dynamics calculations are performed to describe the sputtering (desorption) of solid argon induced by the formation and trapping of atomic excitons. Upon self-trapping, a cavity is found to form around the atomic exciton in the bulk and the excited atom is desorbed if it traps on the surface. The calculated shift in the atomic lines of the photoabsorption spectrum of the self-trapped species and cavity radius are sensitive to the choice of the potential describing the interaction between the excited atom and the ground-state atom. It is found that ground-state atoms are not ejected by atomic exciton trapping and the calculated kinetic energies of the excited atoms ejected, which are sensitive to both the potential and the crystal configuration, are of the order of or less than 0.1 eV.

INTRODUCTION

The sputtering (desorption) induced by electronic excitations produced in rare-gas solids has been of considerable recent interest and the principal underlying mechanisms have been described. Ions, electrons, and photons incident on solid argon can produce excitons and holes. The holes eventually recombine with electrons, also forming excitons. The excitons formed in this way undergo a series of relaxation processes and eventually "self-trap" as atomic- or molecular-type excitons associated with the first excited *P* state of the atom.[1] The first is a localized, excited argon on a normal crystal site and the second is an excited argon atom, which bonds preferentially with one neighbor. In both cases "trapping" results in lattice distortion about the localized exciton. The absorption spectra show a shift of about 0.4 eV for the atomic-type exciton in solid argon from the gas-phase absorption.[2] This lattice energy can, in principle, cause the ejection of an atom[3] since the bulk cohesive energy of solid argon is only 0.08 eV. It is the purpose of this paper to examine the self-trapping and ejection process using a molecular-dynamics calculation and to evaluate the kinetic energy of the ejected atoms for comparison to recent measurements.

Reimann, Brown, and Johnson[4] observed the sputtering and luminescence of solid argon produced by MeV-energy light ions and found that the so-called *W* band at about 11.3 eV comes at least partly from desorbed excited dimers. Coletti, Debever, and Zimmerer[3] studied the correlation between the intrinsic luminescence and desorption of solid argon excited by slow electrons. They observed a sharp threshold in both the desorption and the luminescence as a function of increasing electron energy. This threshold was associated with the creation of an exciton by inelastic scattering of the incident electron to the bottom of the conduction band. They also pointed out that due to the negative electron affinity of Ne and Ar, self-trapped excitons interact repulsively with their neighbor so that a "cavity" (or bubble) is formed around the localized excitation. If such a process happens on the surface, the self-trapped exciton could be ejected from the surface, thus minimizing the elastic strain of the crystal and the surface energy. The observed $^3P_1$ luminescence line in their experiment, which coincides with the position of the free-atom $^3P_1$ line, gives direct evidence for the desorption of excited atoms. Kloiber *et al.*[5] measured the partial photostimulated desorption (PSD) yields of neutral atoms from solid neon. By selectively exciting a particular energy state of atomic exciton with photons, they were able to isolate the luminescence resulting from individual atomic exciton states and observe the surface and the bulk luminescence separately. Their emission luminescence spectra also indicate that the lines corresponding to $^3P_1$ and $^1P_1$ are due to desorbed excited atoms. They also suggest that trapping at the surface leads to the excited-atom desorption. Feulner *et al.*[6] use synchrotron radiation to excite monolayer and multilayer films of argon atoms on Ru(001). These PSD yields show a threshold at a photon energy of 11.8 eV, corresponding to the lowest surface atomic exciton absorption energy of the argon solid ($n=1$). These experiments demonstrate that desorption can be induced directly by atomic excitons.

Although a significant amount of work has been done, and some theoretical calculations of the spectral line shift and cavity size have been performed for atomic excitons in solid Ne, there has not been to our knowledge any calculation to describe quantitatively the sputtering induced by the self-trapped atomic exciton in solid argon. Features that would be desirable to model should include the kinetic energy of the sputtered atoms, the effect of the crystal environment, and the state of the sputtered atoms (ground state or excited state). Also a more accurate calculation of cavity expansion for solid argon than the Hooke's law approximation[7] is needed. The lattice-distortion effect is largest in Ne but cavity formation is not expected in Kr and Xe, because the latter two atoms have positive electron affinity. In the desorption spectra by Feulner *et al.*,[6] very weak or no surface exciton contribution is observed for Kr and Xe. For these reasons Ar is an interesting case to examine. It is the purpose of this calculation to apply the molecular-dynamics method to describe the desorption of excited Ar atoms due to self-trapping of excitons. We report our work as follows: discussion of the potentials used for the calculation, test of cavity size and atomic photoabsorption energy shift, the ejection of an atom from the surface of a perfect crystal and from a damaged crystal.

INTERACTION POTENTIALS

In order to construct average, excited-state, interaction potentials in the solid we begin by using appropriate pair potentials from the gas phase. Gas-phase interaction potentials between an argon atom in the lowest excited state and a ground-state atom are given by a number of authors.[8–10] The potentials we use are based on those given by Castex *et al.*[8] which include the spin-orbit coupling and give good agreement with experiment at reasonably large internuclear separations. The excited atom in a P state can interact with a neighboring atom via a number of states (Σ, Π, g, u, singlet, and triplet in the notation for diatomic molecules). The wave function of the atomic exciton is, in lowest order, some mixture of these states. For describing the static situation of an excited atom in a lattice it is reasonable to construct an average interaction potential with each neighbor which is determined from a mixture of the interactions of an excited atom with a ground state. The $^3P_1$ (or $^1P_1$) atomic state is correlated with the F_{1u} state for an atomic exciton in a crystal with O_h symmetry,[11] where u means antisymmetric with respect to inversion. For the exciton derived from a P state in such a symmetry no g (symmetric) states are formed. For argon, as for neon, this correlation implies that the interaction in the solid between the localized excited species and a neighbor can be approximated by a mixture of dimer states

$$V_1 = F_{1u} = \tfrac{1}{3}\,0_u^+ + \tfrac{2}{3}\,1_u \,, \tag{1}$$

where the 0 and 1 stand for the *total* angular momentum of the state and the (+) reflection symmetry using the notation for diatomic molecules. This relation enables us to calculate an average-pair potential from the molecular potentials of Castex *et al.*[8] The resulting potential is drawn in Fig. 1 for R between $6a_0$ and $24a_0$, where a_0 is the atomic-length unit ($a_0 = 0.529$ Å). A cubic-spline interpolation is used between $6a_0$ and $12a_0$ in order to connect the values obtained from the data in their paper. For R greater than 12 a_0, a C_3/R^3 and C_6/R^6 mixture is used to extrapolate the potential. The coefficients are fit to the function and its derivative at $12a_0$ giving the resulting potential a slowly decaying, long-range part.

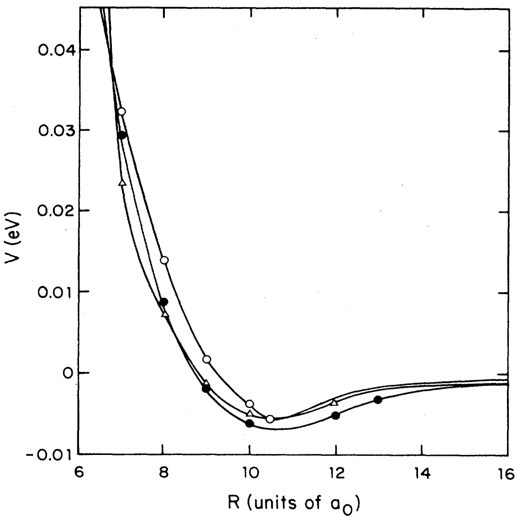

FIG. 1. The interaction potentials between an excited and a ground-state atom as discussed in text. V_1, curve with triangles (long-range part a fit $C_3 = -0.656$ eV cm^3, $C_6 = 52.43$ eV cm^6); V_2, curve with open circles; V_3, curve with filled circles.

For comparison to the above we use a second, average pair potential (V_2) based on the calculated singlet potentials ignoring the spin-orbit coupling. An average of the pair potentials for states Σ and Π having g and u symmetries are calculated at each distance in the range between $6a_0$ and $10.50a_0$. A cubic spline interpolation is also employed between values obtained using Castex *et al.* For R greater than $10.5a_0$, we use

$$V_2(R) = -0.0057(10.5/R)^6, \quad R > 10.5a_0 \,, \tag{2}$$

with V_2 in eV and R in a_0. This is the dominant part of the long-range van der Waals potential and is obtained from the Slater-Kirkwood[12] approximation for the C_6 coefficient

$$C_6 = -\left[\frac{3e^2 a_0^{1/2}}{2}\right] \frac{\alpha_1\alpha_2}{(\alpha_1/N_1)^{1/2} + (\alpha_2/N_2)^{1/2}} \,, \tag{3}$$

where α_1 and α_2 are the polarizabilities of the two interacting atoms, N_1 and N_2 are the number of outer-shell electrons. The polarizability used in the calculation of C_6 is estimated from the standard formula[13]

$$\alpha_i = (e^2\hbar^2/m)\sum_{j\neq i} f_{ij}/(E_i - E_j)^2 \,, \tag{4}$$

but including only the dominant states. Our estimate using tabulated oscillator strengths[14] is $\alpha = 53\times10^{-24}$ cm^3 for $^3P_1$ state, and 55×10^{-24} cm^3 for $^1P_1$ state. Using the experimental value $\alpha = 1.64\times10^{-24}$ cm^3 for the ground state, and taking $\alpha \approx 50\times10^{-24}$ cm^3 for the P states, we are able to estimate C_6 between the first excited state and ground state of argon as 170×10^{-48} eV cm^6.

Finally, we also use a potential (V_3) in the range between $6a_0$ and $13a_0$, which is a full average over all states with appropriate weight, singlet, and triplet Σ and Π states, including both the g and u symmetries. For $R > 13a_0$, an $1/R^6$ form is fitted to the potential value at $R = 13a_0$, which gives

$$V_3(R) = -0.00315(13/R)^6, \quad R > 13a_0 \tag{5}$$

with the same units as Eq. (2), and C_6 is about twice as large. All these potentials are plotted in Fig. 1, and some

TABLE I. Cavity formation. The dash indicates that desorption does not occur.

Potential	Absorption spectra shift (Repulsive contribution) (eV)	Cavity shift (Å)
V_1	0.24 (0.07)	0.17 ± 0.07
V_2	0.41 (0.24)	0.26 ± 0.08
V_3	0.27 (0.10)	0.26 ± 0.06

of the specifics are explained in the figure caption. The *averaged* potentials calculated using Castex *et al.*[9] agree very closely with those obtained using, for example, the potentials of Saxon and Liu.[9]

RESULTS

A molecular-dynamics program described earlier[15] is used with the above potentials to calculate the interaction of the lattice with a self-trapped atomic exciton. The calculated bulk-absorption spectral shifts between the excited-state atom and the ground-state atom are listed in Table I for the three potentials. This shift consists of two contributions: The binding in the ground-state shifts this level down ~0.17 eV (twice the sublimation energy) and the repulsive energy in the excited state shifts this level up by an amount determined by the chosen interaction potentials. As is seen in Table I, the absorption-spectrum energy shift for the V_1 potential is smaller than the experimental values, which are 0.44 eV for $^3P_1$ state and 0.42 eV for $^1P_1$ state. This was the form of the potential that was used successfully to describe Ne.[16] The shift calculated here is also small for the fully averaged potential V_3, but, fortuitously, the averaged singlet potential gives a bulk shift of 0.41 eV, close to the measured shift. The surface absorption-spectrum shifts for each of these potentials are calculated to be about $\frac{2}{3}$ of the corresponding bulk value.

The size of the cavity expansions are also given in Table I. These are calculated by taking the difference between the final average distance of the 12 nearest neighbors from the excited atom in the center and the corresponding initial average distance. In our calculation, every atom is initially located at its equilibrium crystal site, one atom is then "excited" to the atomic exciton state, and the interaction becomes that between an atomic exciton and ground-state atoms. We find that, upon excitation of the central atom, neighbors move away so that the cavity quickly expands to a maximum size. It then contracts and expands in an oscillatory manner and eventually reaches an equilibrium size. The equilibrium sizes are listed in Table I. The calculated expansions are smaller than predicted by Fugal[7] (≈0.7 Å) from a simple Hooke's-law calculation. However, Fugal's Hooke's-law calculation for neon also differs by about a factor of 2 from the calculation of Kunsch and Coletti[16] for Ne. These sizes depend on the long-range attractive interaction of the excited species with neighbors as well as on the cavity repulsion energy.

A fraction of the cavity energy (roughly two-thirds of the repulsive contribution in Table I) is available for ejection at the surface. If the lattice is rigid then the kinetic energy of ejection is equal to this energy. The energies of the ejected atoms calculated here for each potential are listed in Table II for the (100) face and for the (111) face. The "dots" entered in the table means that desorption does not occur. Those ejected from the (100) face are calculated with and without the 0.01-eV zero-point energy (ZPE). The atom ejected is found always to be the one that was initially excited. The kinetic energies of ejection are seen to be smaller than the maximum indicating that the lattice absorbs some of the energy and it is seen, by comparing V_1 and V_3, that the nature of the long-range

TABLE II. Ejected atom energies. ZPE is the zero-point energy; E_V is the calculated ejection energy for each potential; ellipses denote no ejection.

	E_{V_1} (eV)		E_{V_2} (eV)		E_{V_3} (eV)
No. of neighbors	ZPE=0.0	ZPE=0.01	ZPE=0.0	ZPE=0.01	ZPE=0.0
		(100) face			
4	0.024	0.033	0.087	0.107	. . .
3	. . .	0.021	0.074	0.087	
2		. . .	0.052	0.060	
1			0.033	0.049	
0			0.019	0.028	
		(111) face			
6	0.055		0.130		0.045
5	0.039		0.109		. . .
4	0.023		0.091		
3	. . .		0.070		
2			0.059		
1			. . .		

attractive force is important.

Because sputtering experiments are not performed on perfect crystals calculations are also made in which neighbors are removed. The energy of the ejected atom is seen to be dependent on the number of neighbors. The first-nearest neighbors contribute most of the repulsive energy of the excited atom. As the number of the nearest neighbors decreases, the repulsive potential energy becomes lower and finally ejection ceases. We also find that the kinetic energies of the ejected atoms for the (111) face are slightly higher than for atoms ejected from the (100) face. This is because there are a maximum 6 nearest neighbors on the surface and a total of 9, including the bulk, for the (111) face while there are only 4 on the surface and a total of 8 for the (100) face. The effect of the zero-point energy is to slightly enhance the kinetic energy. Since the time for ejection is $\approx 10^{-11}$ s, the excited atom will have desorbed before it decays radiatively ($\approx 10^{-9}$ s). Therefore an atomic line spectra will contribute to the luminescence spectrum as is found experimentally.

It is interesting to compare our three-dimensional calculation with an early result by Rashba and Sherman.[17] Using a one-dimensional model, they predicted that a self-trapped atomic exciton close enough to the end of the one-dimensional atomic chain can cause the ejection of the ground-state atom at the end of the chain. To test its applicability to the three-dimensional case we performed a calculation with the atomic exciton trapped in the second layer, and found no ejection for all the potentials used. Based on this, it can be concluded that a *ground-state* atom cannot be ejected by trapping of an isolated *atomic exciton* in solid Ar.

CONCLUSION

Based on the constructed potentials, a cavity (or bubble) is found to form around the atomic exciton as predicted by many authors. However, the radial expansion of the cavity is not as large as anticipated and the argon cavity expansion is much smaller than that for neon. Our calculation shows that in the process of self-trapping, the atomic exciton can cause desorption as predicted by Coletti *et al.*[3] but only when it is on the surface, and only the excited atom itself is ejected. The probability of desorption of the excited atom and the size of its final kinetic energy are found to be very sensitive to the assumed potential both at long range and short range. Compared to the measured kinetic energy spectra of ejected Ar atoms desorbed following electronic excitation of the solid,[18,19] our calculated kinetic energies are in all cases much smaller than the high-energy peak (≈ 0.4 eV for Ar). O'Shaughnessy *et al.*[18] identify this peak as arising from a surface process. This implies that *atomic* exciton trapping and decay do not contribute to this feature, but could contribute to the lower-energy ejecta in the measured kinetic energy spectra.

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