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THE CONFIGURATION AND ENERGY OF DEFECTS ON THE (100) SURFACE OF A MOLECULAR CRYSTAL

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ABSTRACT

Using a Lennard-Jones 6-12 potential function to represent the interactions of the atoms, the binding energies of neon, argon, and krypton atoms in and above the (100) surface of argon are computed. Relaxations of the defects are considered and are found to be small; however relaxation appreciably affects the energies of the defects. The binding energies of neon, argon, and krypton atoms above the (100) argon surface are 687 cal, 1367 cal, and 1682 cal, respectively. The binding energies of neon, argon, and krypton atoms in the (100) argon surface are 1290 cal, 2603 cal, and 3160 cal, respectively. Relaxation appreciably affects the binding energies.

The free energy of formation of a mole of vacancies on the (100) surface of argon is found to be

$$\Delta F = 1236 - 3.58\ T \text{ cal}$$

This implies that at the melting point of argon there is one vacancy per three hundred (100) surface sites on 2×10^{12} per cm^2 of surface.

INTRODUCTION

A number of investigators have calculated the energy of formation of surface vacancies and the binding energies of excess atoms above the surface for ionic crystals.[1,2] Computations for ionic crystals encounter a number of problems which are due to the nature of the forces between the ions. The correct mathematical representation of the potential function is a matter of some question primarily because of the representation of the polarization effects. The calculation of the surface energies for ionic crystals is a very difficult problem;[3] thus one can not expect much exact information from surface defect calculations on ionic crystals.

It would be desirable to do extensive calculations on the surface properties of a material whose mathematical representation is simple in the hope that the results obtained would give some insight into the surface properties of other materials. Potential functions for adsorption of excess atoms onto the surface and for the removal of atoms (both host and impurity) from the perfect surface and information on the configuration of the surface, both perfect and defective, would be useful.

Argon is most suited for the calculation of defect properties. It is well known that argon is reasonably well represented by a Lennard-Jones 6-12 potential[4] which yields adequate energy values by the direct summation of the two body potential function. Accordingly, we have chosen to examine certain surface properties of argon. It is hoped that information gained from this simple solid will be of value in understanding the surface properties of more complex materials.

Previously, the distortion of the perfect (100) surface of argon has been calculated.[5,6] It has also been shown that the configuration of the perfect surface layer is probably identical with that of the bulk except for the displacement of the surface layers away from the bulk.[7] A number of authors have made a theoretical investigation of the configuration and energy of internal defects in argon.[8,9]

We have calculated the binding energies of argon and impurity atoms (neon and krypton) above and in the (100) surface plane of argon. We consider only the potential energy; therefore the results are reasonably valid only at 0°K. We also neglect all many-body forces. Using the high temperature Einstein approximation to calculate the entropy, we estimate the concentration of vacancies in the equilibrium (100) surface of argon at its melting point assuming that the vacancies obey Boltzmann statistics. Though use of our data at the melting point is not justified by our assumptions, it is felt that the results obtained in this way are at least a rough estimate of the surface vacancy concentration at the melting point.

We find, as expected, that the binding energy to the argon surface decreases in the series krypton, argon and neon. We also find, in accord with expectations, that the binding energy of neon and krypton above the perfect surface is less than that in the surface plane. We find that though the relaxations are usually numerically small, they appreciably affect the energy.

CALCULATIONS

The model adopted for the semi-infinite argon crystal is: (1), all quantum effects may be neglected; (2), only the potential energy need be considered; (3), the total potential is pair-wise additive; (4), the

atoms interact with a Lennard-Jones 6-12 potential of the form

$$V(r) = \frac{\beta}{r^{12}} - \frac{\alpha}{r^{6}}$$

where r is the distance between the atoms; and (5), the (100) surface of argon exhibits the displacements (Fig. 1) calculated by Alder, Vaisnys and Jura[6] which are given in Table 1. It is also assumed that the concentration of defects is sufficiently small that defect-defect interactions are neglectable.

Of these assumptions, the one most open to question is that of pair-wise additivity of the potential function. For a perfect lattice this assumption is not seriously in error. Bullough, Clyde and Venables,[10] considering stacking faults in argon, have concluded that many-body forces contribute no more than .4% of the total binding energy. However, Sparnaay[11] has estimated that an error of as much as 10-30% might be made if van der Wal's forces are treated as pair-wise additive; Jansen[12] has shown that three body forces can explain the observed stability of the face-centered cubic form of argon over the hexagonal close-packed form. Rossi and Danon[13] have indicated that the inclusion of three-body forces introduce a large error in the predicted energy of vaporization and attribute this error to either four-body forces or a poor potential function.

We have also used a Lennard-Jones 6-12 potential function to represent the interactions of neon and krypton atoms with argon atoms. The argon-impurity potentials were obtained from the 6-12 potentials of Ar,[4] Ne,[4] and Kr[14] in the following way. If r_{A-A} represents the gas equilibrium distance of atoms of type A and U_{A-A} is the depth of the well in the gas

$$r_{A-B} = \frac{r_{A-A} + r_{B-B}}{2}$$

$$U_{A-B} = (U_{A-A}\, U_{B-B})^{1/2}$$

Subject to these assumptions, one may write an expression for the total energy of the system as a function of the positions of all the atoms. One may then minimize the total potential energy of the system as a function of these positions and arrive at the energy and configuration of the relaxed defect. In practice this is not feasible, and we assume that atoms not close to the defect are not displaced from their normal positions. Only displacements of atoms close to the defective site are considered; we further assume that the distortions around the defect preserve the symmetry of the lattice, as much as is possible. This last assumption was found to be warranted in the case of an internal vacancy[9] and we have not checked it for the surface problems. These assumptions reduce the problem to a reasonable number of variables. We have not computed the interactions of the relaxing atoms with the entire semi-infinite lattice but rather only with the atoms through the twelfth nearest neighbors to the relaxing atom. Previous work indicates that the relaxations and energies are insensitive to distant neighbors.[9,15]

The energy of formation of a vacancy at (0,0,0) in a (100) surface plane without allowing for relaxation is

$$E_o = \sum_{\substack{i+j+k=\text{even} \\ k \geq 0}}{}' V(i,j,k)$$

where the prime (') indicates that the point (0,0,0) is not included in the summation and V(i,j,k) is the potential energy between an atom at

(i,j,k) and an atom at (0,0,0). The summation over only lattice points with (i+j+k) = even is the convention adopted by Alder et al.[6] and makes the edge of the unit equal to 2. Allowing the lattice to assume the distortions, δ_k, (Table 1) determined by Alder et al. and allowing the atoms at (1,1,0) and equivalent atoms {(-1,1,0), (1,-1,0) and (-1,-1,0)} to relax to (1-D, 1-D, 0), etc., the energy of formation of the defect may be written as

$$E = \sum_{\substack{i+j+k = \text{ even} \\ k \geq 0}}' V\left(k, j, k + \sum_{l=0}^{k} \delta_l\right)$$

$$+ 4\sum_{\substack{i+j+k = \text{ even} \\ k \geq 0}}' V\left(i+D,\ j+D,\ k + \sum_{l=0}^{k} \delta_l\right)$$

$$- 4\sum_{\substack{i+j+k = \text{ even} \\ k \geq 0}}' V\left(i, j, k + \sum_{l=0}^{k} \delta_l\right)$$

$$+ 4V(2-2D,\ 0,\ 0) + 2V(2-2D,\ 2-2D,\ 0)$$
$$+ 4V(2,0,0) - 8V(D,\ 2-D,\ 0)$$
$$+ 2V(2,2,0) - V(2-D,\ 2-D,\ 0)$$

This expression for E was minimized with respect to the relaxation D of atom (1,1,0) by a half interval technique on a CDC 6600 computer. More complicated expressions must be minimized when more relaxations are allowed. Similar expressions may be developed for other types of defects.

RESULTS

The binding energy, E, and relaxations of argon, neon and krypton atoms above the argon surface are given in Table 2, as are the binding energies without consideration of relaxation, E_o. The defect is located initially at the point (0,0,0) above a semi-infinite argon crystal with lattice points (i,j,k) subject to $k \geq 1$ and $(i+j+k)$ an even number. An atom at the lattice point (i,j,k) relaxes to the new position $(i - \delta i, j - \delta j, k - \delta k)$. δi, δj, δk are tabulated.

Configuration and energy of surface vacancies and surface substitutional impurities are tabulated in Table 3. Here again the defect is located initially at (0,0,0); the bulk atoms now are at points (i,j,k) subject to $k \geq 0$, $(i+j+k)$ even. The atom at (i,j,k) relaxes to $(i - \delta i, j - \delta j, k - \delta k)$ and $(\delta i, \delta j, \delta k)$ is tabulated. The binding energy of substitutional impurities is relaxative to the impurity atom infinitely removed from a surface with a vacancy.

In all cases many relaxations were calculated to assure convergence of the energy of the defect to .05%.

The relaxations of the lattice around an extra argon atom above the surface are illustrated in Fig. 2 (top view) and Fig. 3 (side view). The nearest neighbors to the extra atom relax towards the bulk .6% from their normal surface positions and outwards tangentially to the surface .3%. The distance between the extra surface atom and its nearest neighbors was found to be roughly equal to the distance between first and second layer atoms in the perfect relaxed surface. The second nearest atoms to the extra atom (in the second layer of the lattice) relax upwards. The second nearest neighbors (in the surface layer) to the extra atom relax in such a way as to decrease their distance to the defective site but

increase their separation from the relaxed nearest neighbors. This behavior is similar to that noted previously for the relaxation of the atoms around an internal defect.[9]

With a neon atom above the surface the relaxations of the nearest neighbors are smaller (.2% downwards and .2% outwards) while for krypton they are larger (.8% downwards and .4% outwards).

It is interesting to note that in the fully relaxed situation, an extra neon atom lies closer to the bulk than an extra argon which, in turn, lies closer than an extra krypton atom.

With a vacancy in the surface, the nearest neighbors to the defect are displaced towards the center of the vacancy (Fig. 4). Krypton substituted in the surface plane (Fig. 5) displaces its nearest neighbors away from the defect; the krypton atom is displaced 6% up from the normal argon location in the crystal surface. A neon substituent in the plane affects its nearest neighbors like the vacancy but the neon atom is displaced 18% towards the bulk of the crystal from the normal argon site.

The direction and magnitude of the displacements are attributable to the sizes of the impurity atoms; argon is larger than neon and smaller than krypton.

With the computed binding energies it is possible to caculate the energy of formation of a vacancy in an argon surface. This was done by assuming that the relevant process involves the removal of a surface atom to a position above the surface and isolated from any other defects. Using the high temperature Einstein approximation to compute the entropy, we have calculated the free energy of formation of a mole of vacancies to be

$$\Delta F = 1236 - 3.58\ T \text{ cal}$$

when relaxations are considered and

$$\Delta F = 1272 - 3.58\ T \text{ cal}$$

without relaxation. This implies that at the melting point of argon there is one vacancy for each three hundred sites on the ideal flat (100) surface or 2×10^{12} per cm^2 of surface.

With slight modification of the programs developed for calculation of the energy of surface defects, we were able to calculate the potential curves for binding of an atom to the lattice, both at a point above the surface and at a normal surface position.

Figure 6 shows the potential curves for binding of a neon atom in a normal lattice position in the surface both with and without relaxation. The unrelaxed position is in the argon plane (0 Å above). Relaxation increases the binding energy by 15%.

Figure 7 shows the potential curves for binding of neon atoms above and in the surface with relaxation allowed. The in plane curve is deeper and wider than the above plane potential curve.

Figures 8 and 9 show the potential curves for binding of neon, argon, and krypton atoms in the surface plane and above it. As expected, the krypton potential curves have the deepest wells and are the widest.

CONCLUSIONS

The distortion of the crystal surface around a defect is small in most cases but appreciably alters the energy of the defect and is not neglectable in the calculation of surface properties.

Distance of excess atoms above the surfaces increases in the series neon, argon, and krypton. A neon atom substituted in the argon surface is displaced towards the bulk from the normal position while a

krypton atom is displaced away from the bulk.

The binding energies of atoms in the surface plane are greater than those of atoms in normal lattice sites above the surface plane.

It was found that the free energy of formation of a mole of vacancies in an argon surface is

$$\Delta F = 1236 - 3.58\ T \text{ cal}$$

which implies that at the melting point of argon there is one vacancy for each three hundred sites on the ideal (100) crystal surface or 2×10^{12} vacancies per cm^2 of surface.

ACKNOWLEDGMENTS

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TABLE I

Relaxations, δ, of the (100) surface of solid argon from Alder et al.[6]

δ_1	δ_2	δ_3	δ_4	δ_5
.025782	.005892	.001981	.000849	.000420

TABLE II

The relaxations of the (100) surface of argon with an extra atom above the surface at (0,0,0). The lattice points have coordinates (i,j,k), $k \geq 1$, and are grouped into sets of equivalent points

$$(0,0,0)$$
$$(1,0,1) \equiv (-1,0,1) \equiv (0,1,1) \equiv (0,-1,1)$$
$$(0,0,2)$$
$$(2,1,1) \equiv (2,-1,1) \equiv (-2,1,1) \equiv (-2,-1,1)$$
$$\equiv (1,2,1) \equiv (-1,2,1) \equiv (1,-2,1) \equiv (-1,-2,1)$$

The point (i,j,k) relaxes to $(i-\delta i, j-\delta j, k-\delta k)$ and $\begin{pmatrix}\delta i\\ \delta j\\ \delta k\end{pmatrix}$ is tabulated for one point of each set of equivalent points.

The binding energy of the extra atom is tabulated without and with relaxation, E_o and E respectively.

	Extra Atom		
	Ar	Ne	Kr
E_o	1355 cal/mole	592 cal/mole	1578 cal/mole
E	1367 cal/mole	687 cal/mole	1682 cal/mole
Points			
$\begin{pmatrix}0\\0\\0\end{pmatrix}$	0 0 .01831	0 0 -.16982	0 0 .06647
$\begin{pmatrix}1\\0\\1\end{pmatrix}$	-.00319 0 -.00558	-.00196 0 -.00167	-.00378 0 -.00752
$\begin{pmatrix}0\\0\\2\end{pmatrix}$	0 0 .00255	0 0 .00249	0 0 .00252
$\begin{pmatrix}2\\1\\1\end{pmatrix}$	.00035 -.00017 .00188	-.00001 -.00028 .00117	.00054 -.00010 .00226

TABLE III

The relaxations of the (100) surface of argon with a defect (vacancy or substituent) in the surface at (0,0,0). The lattice points have coordinate (i,j,k), $k \geq 0$, and are grouped into sets of equivalent points

(0,0,0)
(1,1,0) ≡ (1,-1,0) ≡ (-1,1,0) ≡ (-1,-1,0)
(0,1,1) ≡ (0,-1,1) ≡ (1,0,1) ≡ (-1,0,1)
(2,0,0) ≡ (-2,0,0) ≡ (0,2,0) ≡ (0,-2,0)
(0,0,2)

The point (i,j,k) relaxes to (i-δi,j-δj,k-δk) and $\begin{pmatrix}\delta i\\ \delta j\\ \delta k\end{pmatrix}$ is tabulated for one point of each set of equivalent points.

The binding energy of the substituent atom (or surface binding energy of argon in the case of the vacancy) is tabulated without and with relaxation, E_o and E respectively.

	Defect		
	Vacancy	Ne	Kr
E_o	2627 cal/mole	1134 cal/mole	3081 cal/mole
E	2603 cal/mole	1290 cal/mole	3160 cal/mole
Points			
$\begin{pmatrix}0\\0\\0\end{pmatrix}$	* * *	0 0 -.18131	0 0 .06060
$\begin{pmatrix}1\\1\\0\end{pmatrix}$	.01589 .01589 .00299	.02682 .02682 -.00009	-.013061 -.013061 .00218
$\begin{pmatrix}0\\1\\1\end{pmatrix}$	0 .00265 .00110	0 .00181 -.00453	0 -.00004 .00479

TABLE III (Cont.)

	Defect		
	Vacancy	Ne	Kr
E_o	2627 cal/mole	1134 cal/mole	3081 cal/mole
E	2603 cal/mole	1290 cal/mole	3160 cal/mole
Points			
2	-.00468	-.00249	.00131
0	0	0	0
0	.000625	-.00103	.00250
0	0	0	0
0	0	0	0
2	-.00317	-.00411	.00317

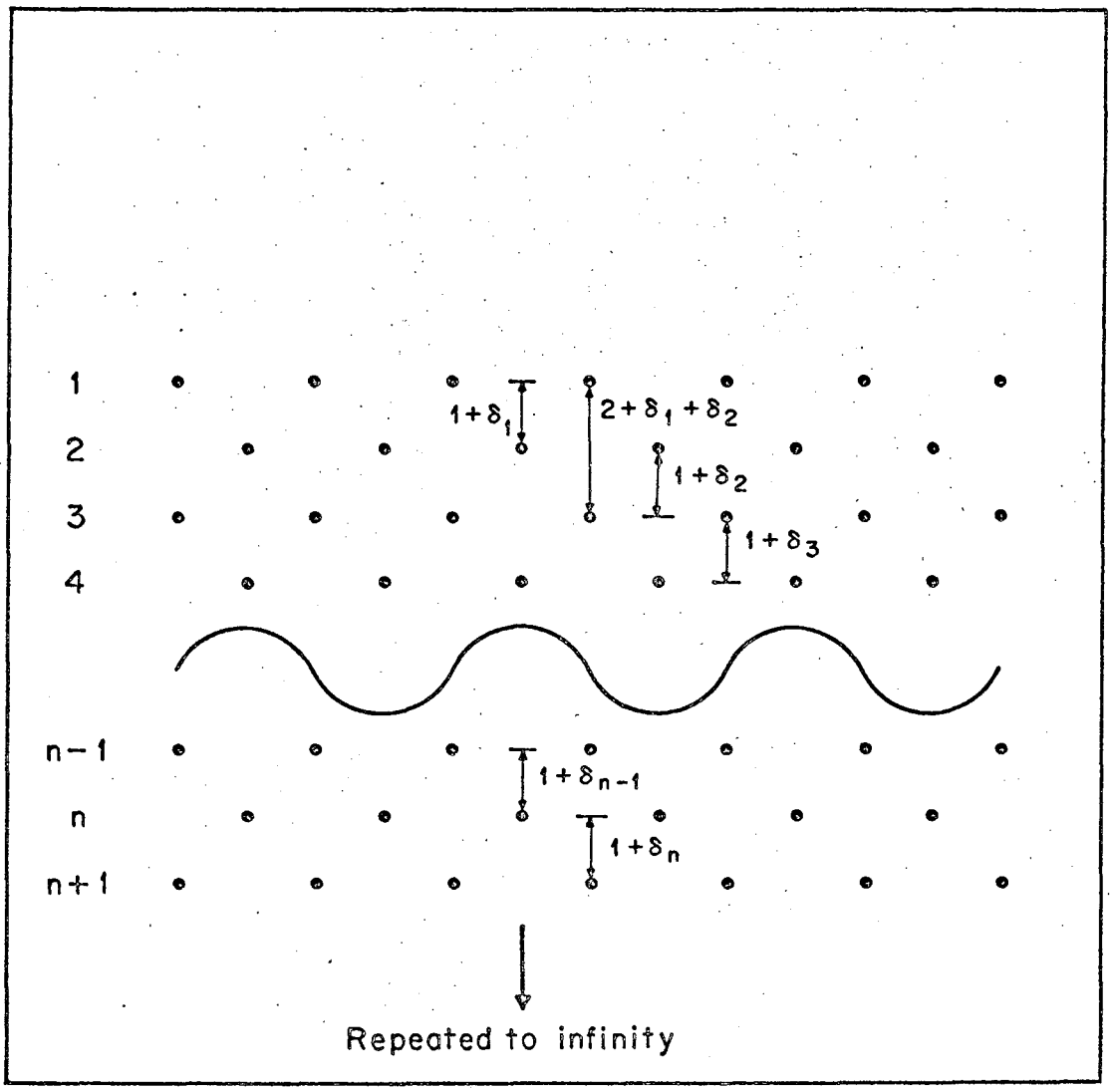

Fig. 1 Schematic diagram of a semi-infinite crystal with displacements indicated.

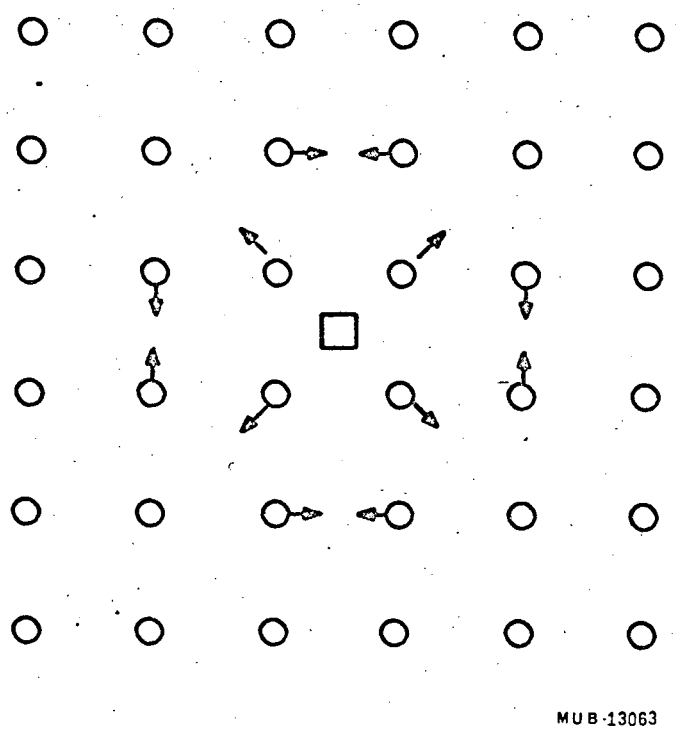

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Fig. 2 Top view of the relaxations of the surface layer with an excess argon atom above it. Arrows indicate the directions of the displacements from the normal positions. The excess atom is represented by a square (□).

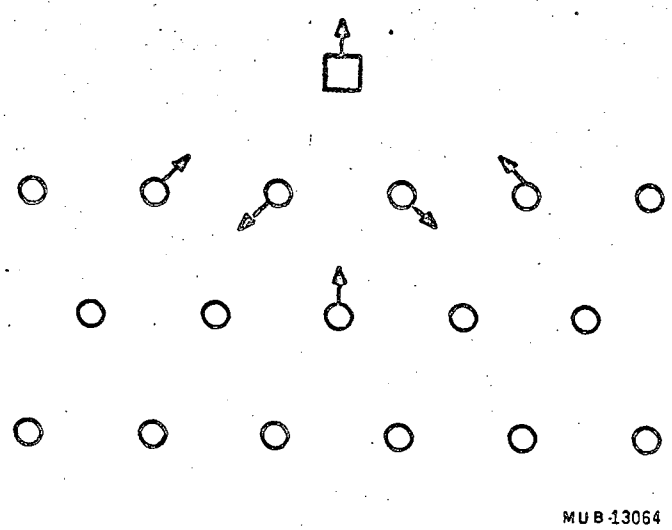

Fig. 3 Side view of the relaxations of the surface layer with an excess argon atom above it. Arrows indicate the directions of the displacements from the normal positions. The excess atom is represented by a square (□).

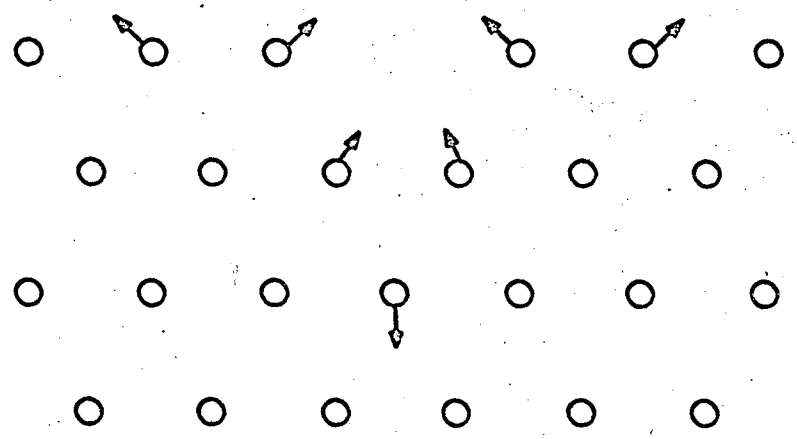

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Fig. 4 Side view of the relaxations of the surface layer with a vacancy in the surface. Arrows indicate the directions of the displacements.

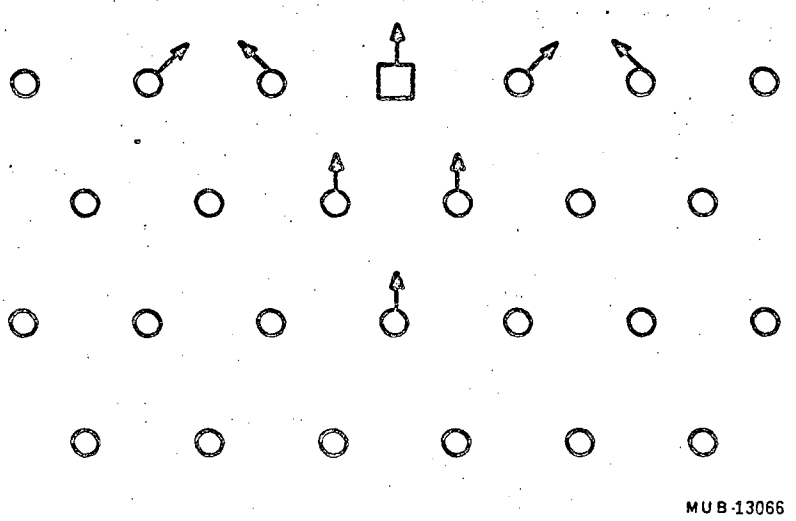

Fig. 5. Side view of the relaxations of the surface layer with a krypton atom substituted in the surface plane. Arrows indicate the directions of the displacements from the normal positions. The krypton atom is represented by a square (□).

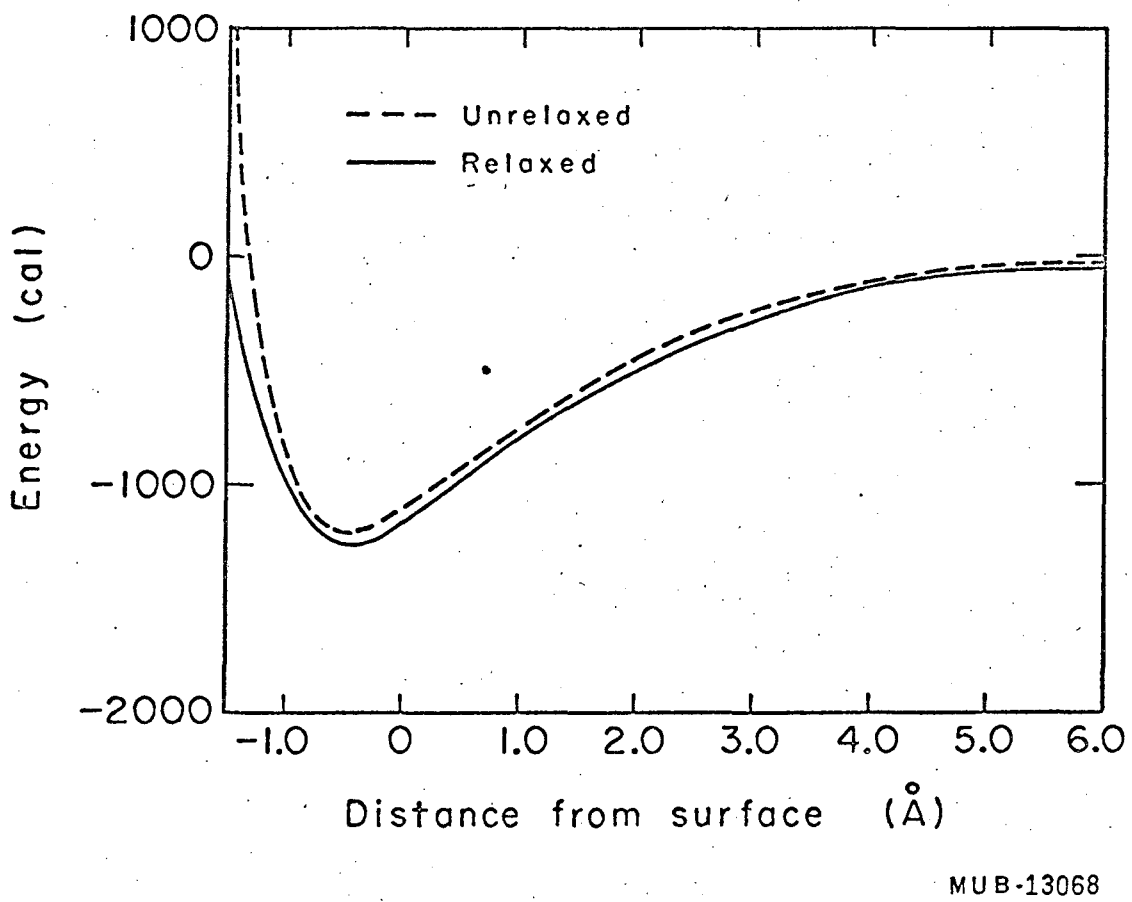

Fig. 6 Potential curve for binding of a neon atom in the surface plane with and without relaxations.

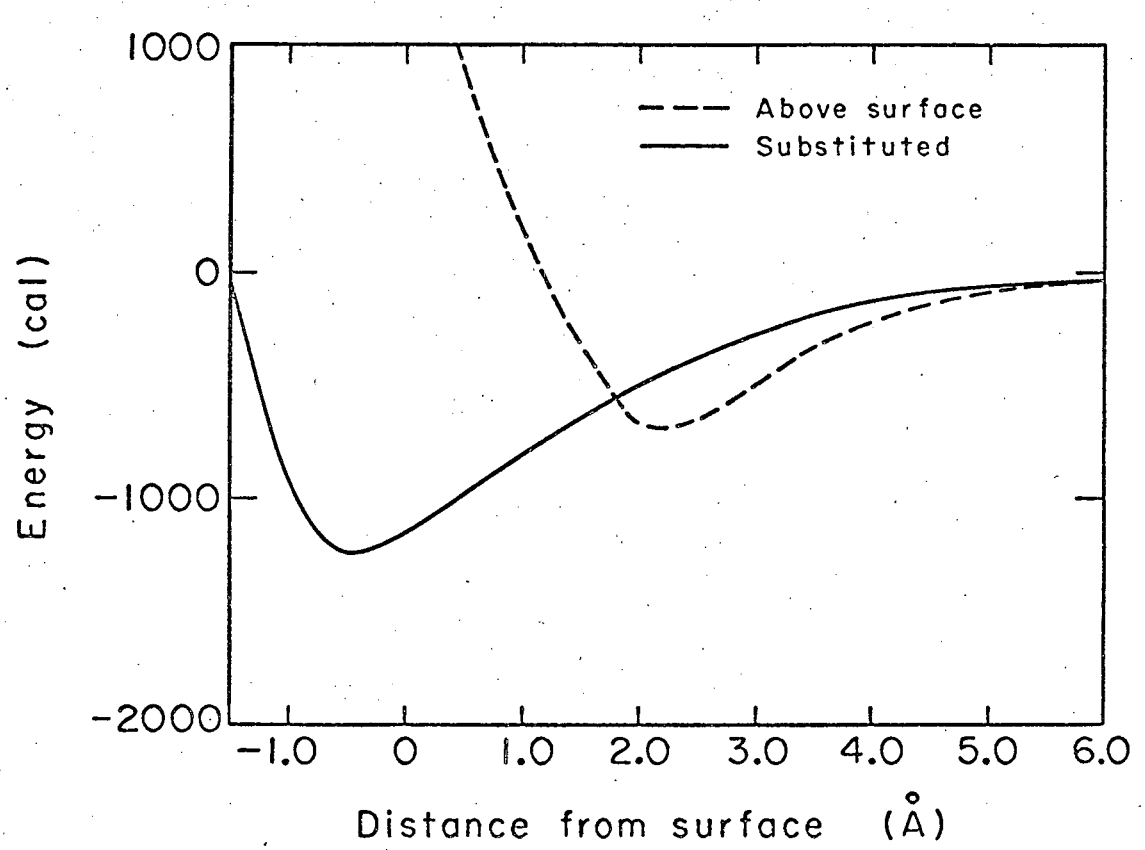

Fig. 7 The potential curves for binding of neon atoms above and in the surface with relaxation allowed.

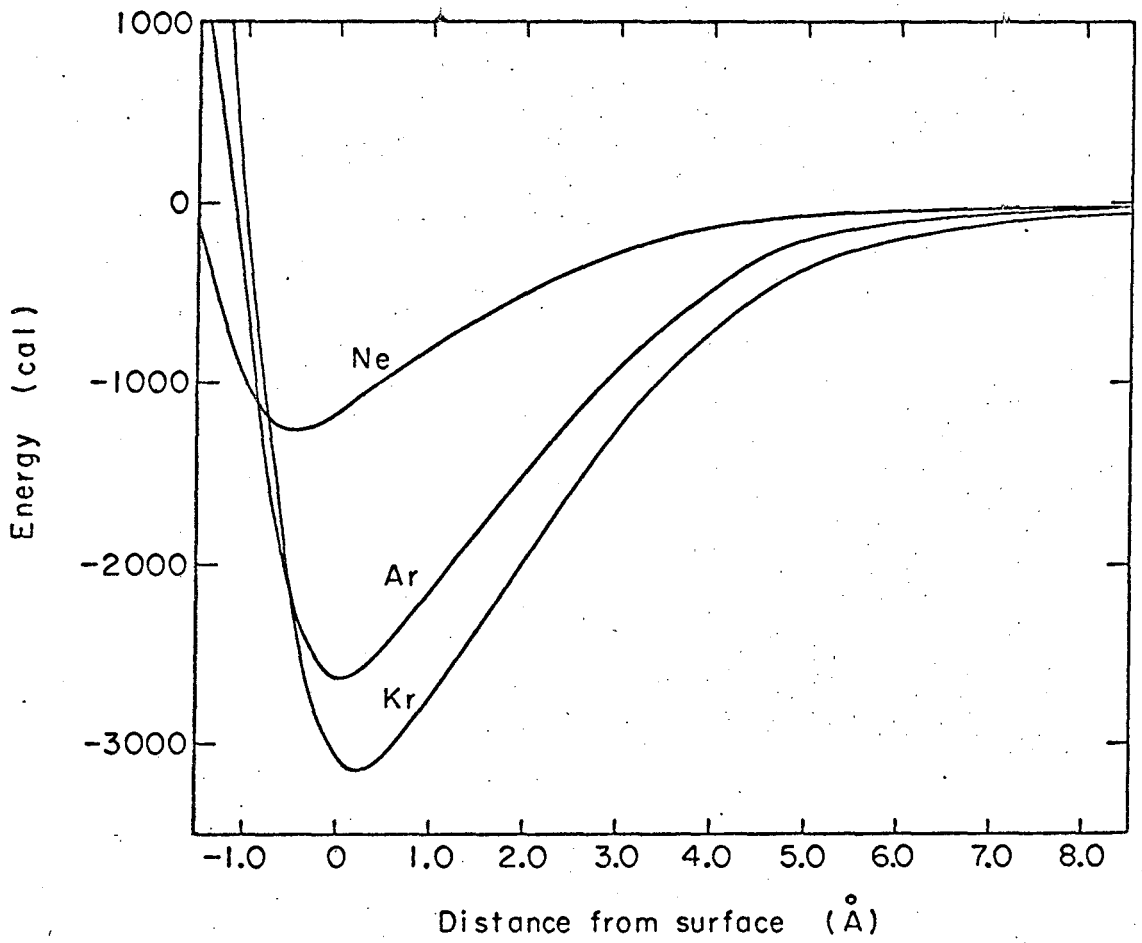

Fig. 8 The potential curves for binding of neon, argon, and krypton atoms above the (100) surface of argon with relaxation allowed.

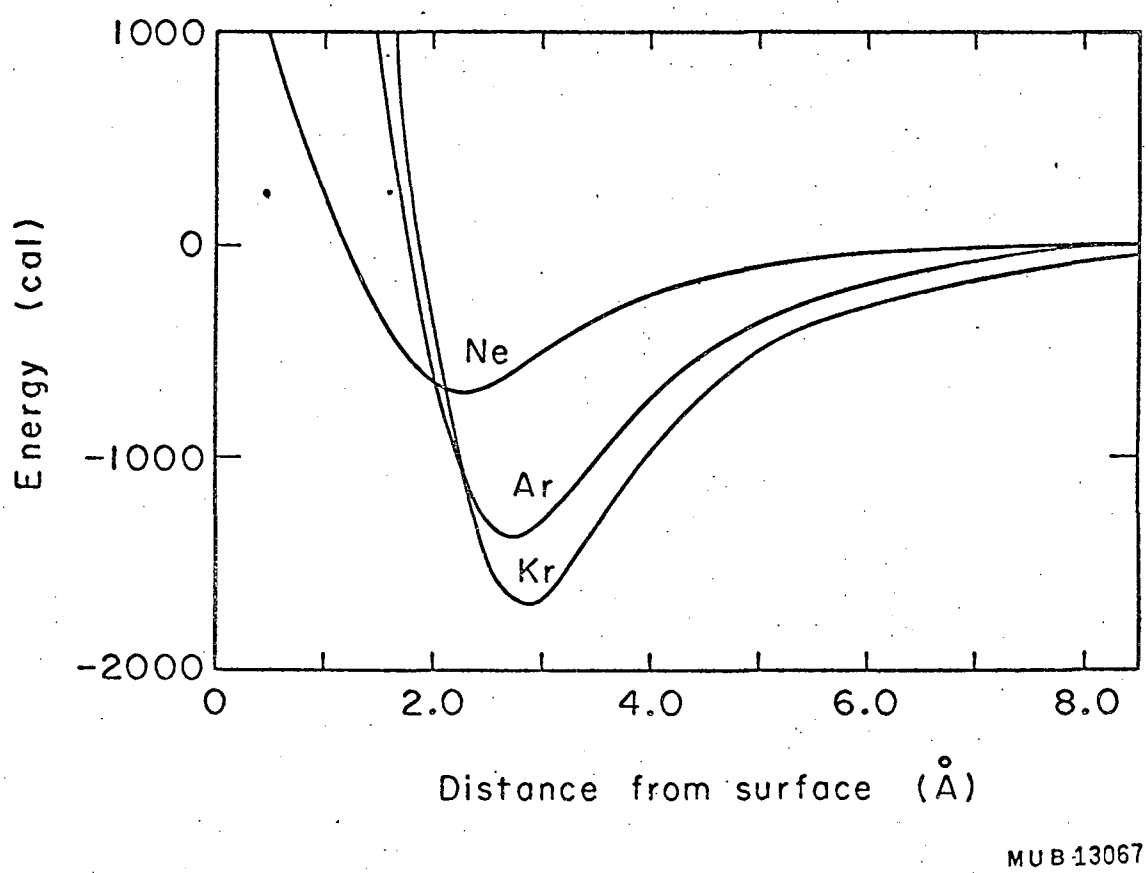

Fig. 9 The potential curves for binding of neon, argon, and krypton atoms in the (100) surface of argon with relaxation allowed.