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Studies of a Single Vacancy, a Divacancy, and Interstitials in Lead Using Long-Range Oscillatory Pair Potentials

Ryoichi Yamamoto and Masao Doyama

Department of Metallurgy and Materials Science, Faculty of Engineering, University of Tokyo, Bunkyo-Ku, Tokyo 113, Japan

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The long-range oscillatory pair potentials obtained by Johnson, Hutchinson, and March are applied to the calculations of the properties of a vacancy, a divacancy, and interstitials in lead. The formation energies, the migration energies, and the atomic relaxations around the defects have been calculated on the basis of the atomistic model. It has been shown that divacancies are more mobile than single vacancies and a body-centered interstitial is more stable than a ⟨100⟩-split-type interstitial in lead.

I. INTRODUCTION

A number of theoretical calculations based on the atomistic model and the use of interatomic potentials have been published for the study of the properties of lattice defects in metals.[1-4] Computer experiments are always intended to propose a plausible interpretation of experimental results and, in some cases, to give the solution to an experimentally inaccessible problem. The reliability of the predicted values, however, is entirely dependent on the validity of a given interatomic potential and the model used. The selection of a proper potential is very important in these types of calculations for defects. This was one of the main subjects of the Battelle Institute Materials Science Colloquium.[5]

Empirical Morse potentials,[6-8] third-order polynomials,[9,10] and occasionally Born-Mayer potentials[11] have been employed in most of the studies so far published. The short-range nature and the existence of one minimum, except in the case of Born-Mayer potential, are characteristic of these potentials. Rigorously speaking, the validity of these potentials should be verified by experiments. Unfortunately, experimental methods which can directly measure interatomic potentials are not yet available. However, many authors have pointed out from the theoretical point of view that the effect of the conduction electrons on the direct ion-ion interaction should be taken into account and that the potentials in metals are oscillatory at long ranges owing to this effect.[12-14] This theoretical conclusion is partially supported by the indirect experimental evidence of the Knight shift in alloys and the oscillatory force constants obtained from the phonon spectra. The calculations using the potentials with such simple forms as the Morse potential are not satisfactory for this reason, even though these are tractable.

As mentioned above, the direct measurement of an interatomic potential is very difficult. The recent progress of neutron- and x-ray-scattering experiments, however, is encouraging in spite of the inherent problems in the analysis of the data. Johnson, Hutchinson, and March[15] (JHM) have derived pair potentials from neutron scattering data of liquid metals. These show a long-range oscillatory nature (called LRON in the present paper), and in this respect, these are fundamentally different from the potentials used before but consistent with recent experimental and theoretical results.

Different pair potentials in metals can be obtained using pseudopotential theory. These potentials are usually not consistent in both of their amplitudes and phases. Two aspects of this situation should be considered.[16] One is related to the nonunique choice of the bare-ion potential in the pseudopotential method. The concept of a two-body interaction potential itself is correct within the framework of the second-order perturbation theory. If the calculation is carried out only to the second order and the higher-order terms are truncated, then different pseudopotentials may lead to different pair potentials. The other problem is the approximation used to take into account the electron-electron interaction in the dielectric function. Shyu *et al.*[17] and Shaw and Heine[18] have fully investigated this problem. Their results are encouraging and lead us to believe that there exist well-defined pair potentials in metals which can be used to describe the properties of defects.

It is of great interest to apply these LRON potentials to the study of point defects in metals. Harrison[13] made two observations in an intuitive way based on his potential in Al. One is the relaxation of the nearest neighbors to a vacancy and the other is related to the binding energy of a divacancy. Shyu, Brust, and Fumi[19] have calculated the distortions and the relaxation energy around a vacancy in Na, using a LRON potential which was obtained by Cochran from lattice dynamics. Similar calculations in Na have been performed by Torrens and Gerl[20] and Brown *et al.*[21] Particularly, Brown *et al.* used the potentials obtained by

Paskin and Rahman[22] for liquid sodium.

In the present paper, we have treated the energetic problems for these lattice defects in lead with the help of a new technique for relaxation. The JHM potentials were used. The formation energies and the activation energies for the motion of a vacancy and a divacancy have been calculated. The stability of ⟨100⟩-split and body-centered interstitials was also investigated. The justification of using the potential obtained from the liquid state to solve the problems in the solid state is a difficult problem. The most delicate question is whether the LRON part of the pair potential is only the reflection of ion packing in liquid metals, or is the real Friedel oscillation caused by the conduction electrons in metals. Although there are many problems in the approximate theories of liquid metals, it was shown[23–27] at least that the conduction electrons are responsible for the LRON part of a pair potential.

In recent years, some theoretical studies of defect properties using the pseudopotential theory have been published.[28–30] This method is becoming a powerful tool for the study of simple defects such as a vacancy. However, it will be quite difficult to apply this method to more complex lattice defects such as a divacancy, interstitials, and dislocations. Besides the effort required in the calculation, as was discussed in detail by Chang,[31] the results are sensitive to the choice of the pseudopotential even in the case of simple defects. In our opinion, calculations based on the atomistic model and the effective pair potential have not yet lost their usefulness in comparison with a pseudopotential approach. It is premature at this stage to assert that this type of calculation is meaningless.

This paper is divided into five sections. In Secs. II and III, respectively, the method of computation and the interatomic potentials are described. Section IV is devoted to the results and discussions. Concluding remarks are given in Sec. V.

II. METHOD OF COMPUTATION

A. Model

All atoms in a spherical perfect crystal containing about 1000 atoms were initially located on lattice sites. The region of 86 atoms near the center of the crystal is called region I, which contains the lattice defect to be studied. All the atoms around the defect in region I were allowed to relax. The remaining atoms in the crystal, being treated as fixed, are called region II. The size of the crystal was determined as follows: the radius of the spherical region I was taken to be about the cutoff distance of an effective pair potential. The thickness of region II was chosen to be slightly larger than the cutoff distance.

In general, the total crystal energy can be separated into two parts. One is the volume-dependent energy and the other is the structural energy which depends on the detailed atomic configuration. In body-centered-cubic (bcc) alkali metals, the volume-dependent energy is very important and has to be taken into account correctly in the calculation. In face-centered-cubic (fcc) metals including lead, however, the contribution from the volume-dependent energy to the formation energy of a defect may be smaller than that of the structural energy. This is also expected from the fact that in fcc metals the elastic anisotropy, that is, the deviation from the Cauchy relation, is smaller than that for bcc metals. The contribution from the change of the crystal volume owing to relaxation was neglected in this calculation.

As was pointed out by many investigators,[32,33] the problem of the electron redistribution around the defect is very important, particularly for alkali metals. This problem is beyond the framework of the atomistic model or the empirical two-body interaction potential. The change of the crystal energy owing to the redistribution was also ignored. We will only consider the structural energy and hereafter call this the crystal energy.

B. Basic Formulas

The relaxed configuration around the defect is determined so as to minimize the crystal energy of region I. This energy is given by

$$E=\frac{1}{2}\sum_{ij}\phi(r_{ij}) \ , \tag{2.1}$$

where

$$r_{ij}=|\vec{r}_i-\vec{r}_j| \tag{2.2}$$

and $\phi(r_{ij})$ is the interaction potential energy between the ith and jth atom. i and j summations are performed over all the atoms in region I except when $i=j$. $\vec{r}_i$ and $\vec{r}_j$ are the position vectors of the ith and jth atom, respectively. According to Doyama and Cotterill,[4] the formation energy of a cluster of λ point defects can be obtained by the following steps.

(i) λ atoms were removed independently from the crystal at positions sufficiently far from each other and then placed on the surface. The energy required to produce this state is expressed as

$$E_{\lambda V}^{0}-E_P=\lambda E_S \ , \tag{2.3}$$

where $E_{\lambda V}^{0}$ is the energy of the crystal containing λ unrelaxed vacancies and E_P is the energy of the perfect crystal with λ atoms restored to their original lattice points. E_S is defined as the crystal energy of an atom on the surface and is given by

$$E_S = \tfrac{1}{2} E_0 \ , \tag{2.4}$$

$$E_0 = E_j = \sum_i \phi(r_{ij}) \ , \tag{2.5}$$

where the summation over i is taken over all the atoms that interact with the jth atom. In a perfect crystal E_j does not depend on the subscript j and has a unique value noted here as E_0.

(ii) λ unrelaxed vacancies were gathered together and an unrelaxed cluster of order λ was created. The energy required for this step is expressed as

$$E'_{\lambda V} - E^0_{\lambda V} = -E^{B'}_{\lambda V} \ , \tag{2.6}$$

where $E'_{\lambda V}$ is the energy of the unrelaxed λ cluster. $E^{B'}_{\lambda V}$ is expressed as a positive quantity in the present paper. This formula implies that

$$E^{B'}_{1V} = 0 \ . \tag{2.7}$$

(iii) The unrelaxed λ cluster was relaxed and the desired defect was obtained. The final step requires the following energy:

$$E_{\lambda V} - E'_{\lambda V} = -E_{\lambda r} \ , \tag{2.8}$$

where $E_{\lambda V}$ is the minimum energy of the crystal contained the defect and $E_{\lambda r}$ is the relaxation energy. $E_{\lambda r}$ is expressed as the positive quantity as well as $E^{B'}_{\lambda V}$. Finally, the formation energy of a λ cluster can be obtained by adding the contributions of steps i, ii, and iii; then

$$E^F_{\lambda V} = \lambda E_S - E^{B'}_{\lambda V} - E_{\lambda r} \ . \tag{2.9}$$

The binding energy $E^B_{\lambda V}$ of λ clusters is obtained from the above considerations:

$$E^B_{\lambda V} = E^{B}_{\lambda V} + E_{\lambda r} - \lambda E_{1r} \ , \tag{2.10}$$

where E_{1r} is the relaxation energy of a vacancy. Using this formula the formation energy of a vacancy is written

$$E^F_{1V} = E_S - E^{B'}_{1V} - E_{1r} = E_S - E_{1r} \ , \tag{2.11}$$

where $E^B_{1V} = 0$ [see Eq. (2.7)]. $E^F_{\lambda V}$ can be rewritten

$$\begin{aligned} E^F_{\lambda V} &= \lambda E_S - (E^{B'}_{\lambda V} + E_{\lambda r}) && (2.12) \\ &= \lambda E_S - (E^B_{\lambda V} + \lambda E_{1r}) && \text{[from Eq. (2.10)]} \\ &= \lambda (E_S - E_{1r}) - E^B_{\lambda V} \\ &= \lambda E^F_{1V} - E^B_{\lambda V} \ . && \text{[from Eq. (2.11)]} \end{aligned}$$

Thus, we can obtain the binding energy as

$$E^B_{\lambda V} = \lambda E^F_{1V} - E^F_{\lambda V} = -(E^F_{\lambda V} - \lambda E^F_{1V}) \ .$$

Note that the binding energy $E^B_{\lambda V}$ is expressed as a positive quantity.

Finally, we consider the activation energy for motion of a defect. In fcc metals, both the saddle-point configuration of a vacancy and that of a divacancy can be determined simply by considering the symmetry of the lattice. These are shown in Figs. 1 and 2, respectively. As seen from the schematic diagram of Fig. 3 for the motion of a vacancy, the migration energy is calculated from the equation

$$E_m = E_{SP} - E_{DP} \ . \tag{2.13}$$

E_{SP} is the crystal energy with the moving atom at the saddle point and E_{DP} is equal to E_{1V}. Similarly, for the motion of a divacancy, the formula (2.13) is also valid and $E_{DP} = E_{2V}$ in this case.

C. Method of Relaxation

We have relaxed an atom along the direction of the force acting on it in the preliminary calculations. The force on atom i owing to the remaining atoms in the crystal can be calculated as

$$\vec{\mathrm{F}}_i = \frac{1}{2} \sum_j^J \frac{\partial \phi(r_{ij})}{\partial r_{ij}} \cdot \frac{\vec{\mathrm{r}}_{ij}}{r_{ij}} \ , \tag{2.14}$$

where J is the number of truncation. Then atom i was displaced along the direction of the vector $\vec{\mathrm{F}}_i$ and the force on atom i was again calculated at the new position. Each atom in region I was moved in turn in the same manner, until the force on it became zero. Finding the zero-force atomic configuration normally corresponds to finding the minimum-crystal-energy position. In case of an oscillating pair potential, however, this method could not be applied because of the lack of convergence. The difficulty was overcome by using the minimum-total-crystal-energy criterion instead of the zero-force criterion. We have developed a differ-

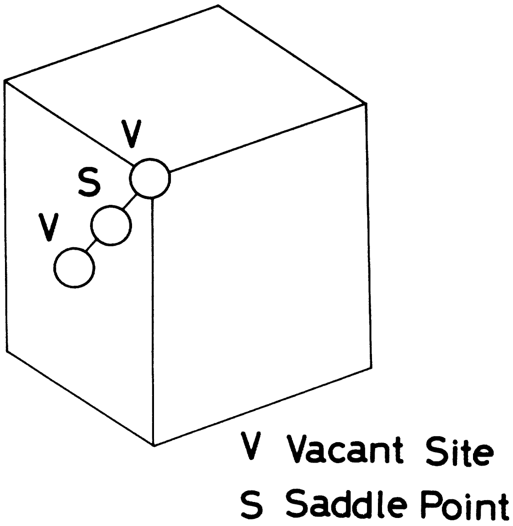

FIG. 1. Saddle point for the vacancy motion in a fcc metal.

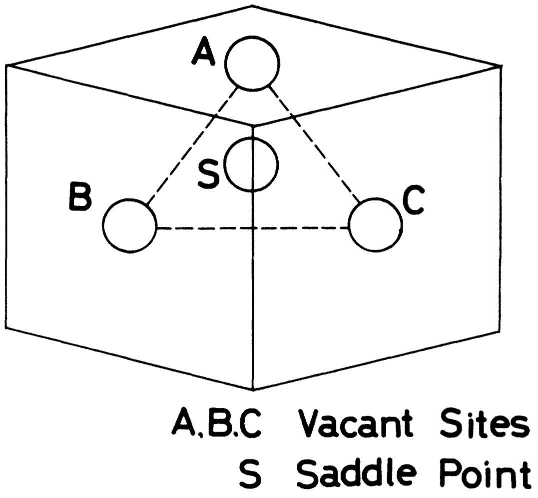

FIG. 2. Saddle point for the motion of a divacancy in a fcc metal.

ent technique for the method of relaxation to obtain the stable configuration. This iterative method has two steps.

As the first step, the atomic shells around the defect were relaxed radially from the center of the defect, one after another. Except for a vacancy, we took into account the anisotropy of atomic displacement in the second step as follows: Let the original position of the relaxed atom be (x, y, z). With the help of the symmetry of the displacement, atoms around the defect were grouped. Atoms in the same group were relaxed at one time followed by the symmetry. The crystal energies at the positions $(x+\Delta x, y, z)$, $(x-\Delta x, y, z)$, $(x, y+\Delta y, z)$, $(x, y-\Delta y, z)$, $(x, y, z+\Delta z)$, $(x, y, z-\Delta z)$, and (x, y, z) were calculated. Δx, Δy, and Δz are the increments of the coordinates x, y, and z, respectively. The relaxed atom was moved to the position corresponding to the minimum energy of the crystal. If the minimum energy in these seven energies corresponds to the original position (x, y, z), Δx, Δy, and Δz were reduced, and the new seven crystal energies were calculated and again compared with each other. In this way the equilibrium positions of relaxing atoms were determined. In most cases, this method which is called here the seven-point criterion has given satisfactory results. The validity of this method was tested in such a way that relaxations around the defect were calculated in two ways using the same truncated Morse potential. One is the method described above and the other is the zero-force criterion, and the two results were compared with each other. The agreement was quite satisfactory. However, the seven-point criterion requires a considerable amount of time to compute the minimum-energy configurations.

III. INTERATOMIC POTENTIAL

LRON potentials obtained by Johnson, Hutchinson, and March[15] were chosen as interatomic potentials in lead. These are shown in Fig. 4. The potential Pb1 was derived from the neutron scatter-

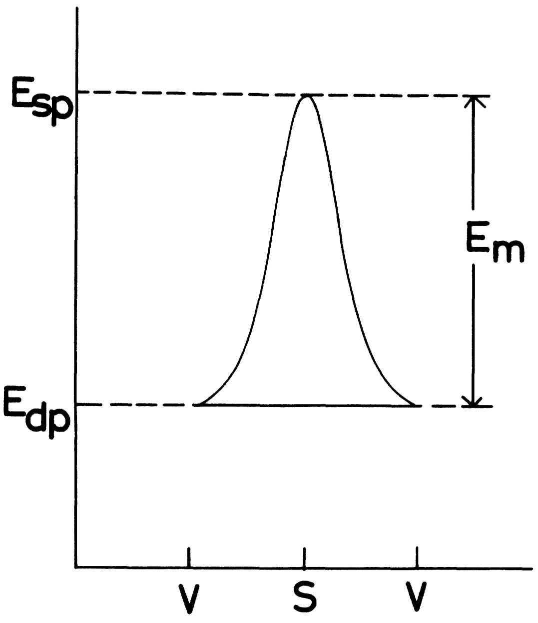

FIG. 3. Schematic energy diagram of atom-vacancy exchange.

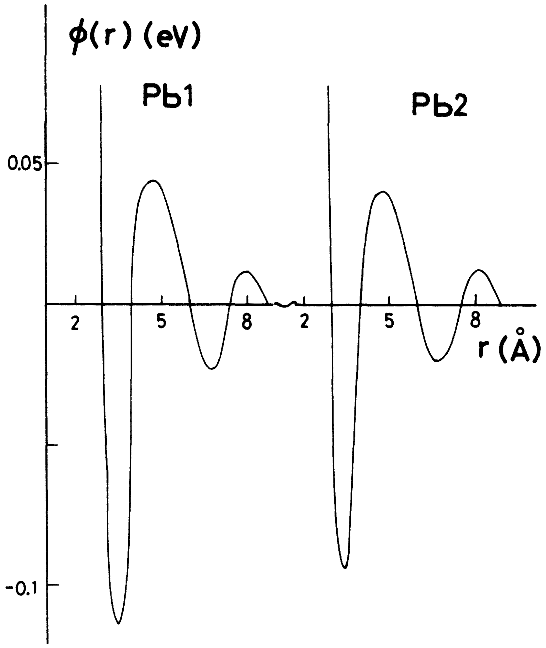

FIG. 4. Johnson, Hutchinson, and March long-range-oscillatory (JHM LRON) pair potentials for lead.

ing data of liquid Pb at 350 °C using the Born-Green's theory. The potential Pb2 was derived from the data at 550 °C in a similar manner. JHM have also given the potentials calculated from the Percus-Yevick theory, but these were not used in this paper because such theory is more suitable for the description of liquid insulators.

In the actual calculation, a truncation of the potential is necessary. The pair potential was truncated at the fifth zero point in a fairly arbitrary manner, but the effect of this truncation on the final results, the relaxation energy and atomic relaxations, was not so large, since only the total-crystal-energy criterion, not the force criterion, was used. The pair potential was further approximated by the third- and the fourth-order polynomials in five ranges of r, r being the distance between two atoms (see Fig. 5). The potential was expressed in regions A and E as

$$\phi(r)=A_1(r-r_1)^3+A_2(r-r_1)^2+A_3(r-r_1)\ , \quad (3.1)$$

and in regions B, C, and D,

$$\phi(r)=A_1(r-r_2)^4+A_2(r-r_2)^3+A_3(r-r_2)^2+A_4(r-r_2)\ . \quad (3.2)$$

All the potential constants were determined so as to fit the experimental curves. These are tabulated in Table I.

The effect of the truncation of the potential on the formation energies of defects has to be carefully examined. From Eq. (2.5), E_S is given by

$$E_S=\tfrac{1}{2}E_0=\frac{1}{2}\sum_j \phi(r_j).$$

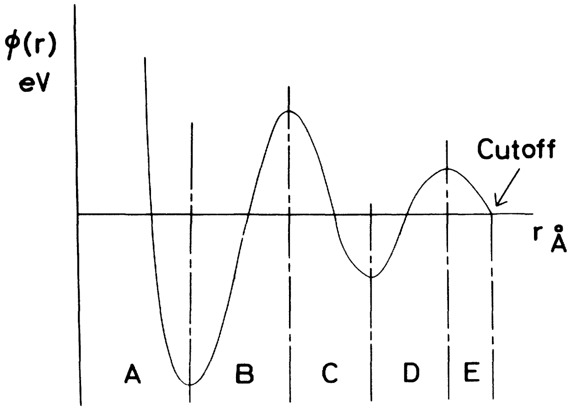

FIG. 5. Fitting of the LRON pair potential by five polynomials.

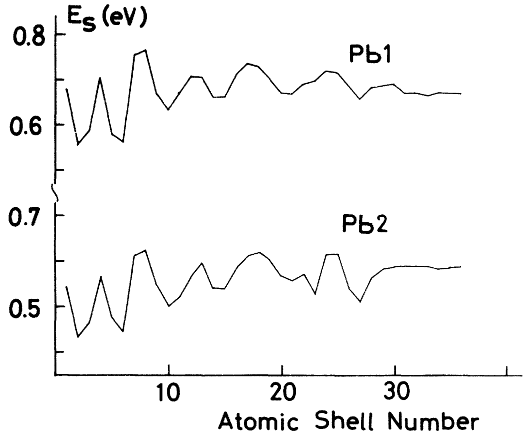

FIG. 6. Crystal energy of an atom on the surface E_S as a function of the atomic shell taken to the summation.

For a vacancy, $E_{1r}/E_S \sim 0.01$ is usual; thus E_S is the dominant part in E^F_{1V}. In contrast to the fact that E_{1r} is the quantity expressing the difference between the unrelaxed and relaxed crystal energies, E_S is the simple summation of the interaction potential between every atom in the crystal. Accordingly, the LRON part of the potential must be taken into account in the calculation of E_S. It is reported[23–25] that the LRON part of a potential can be correctly described by the same form as Friedel oscillation,

$$\phi(r)=A\cos(2Br+C)/r^3. \quad (3.3)$$

A, B, and C are constants, and were determined so as to reproduce the LRON part of a potential. Using this form, E_S was calculated as a function of the crystal size and was plotted against the order of atomic shell in Fig. 6. As the sum approaches about the 36th atomic shell which contains 1198 atoms, E_S nearly converges to the limited value. These are 0.674 eV for Pb1 and 0.597 eV for Pb2, respectively.

Bowley[14] has also given a pair potential in lead by the pseudopotential theory. This potential is very different from JHM potentials in the positions and magnitudes of the maxima and minima. As Bowley himself[34] and Shaw and Heine[18] have stated that the potential obtained by the pseudopotential method has not yet been settled, more detailed study is desirable. Bowley's potential was also applied to the vacancy problem. Preliminary calculation has shown that this potential leads to unreasonable results, so that this potential was not used in the present study.

IV. RESULTS AND DISCUSSIONS

A. Vacancy

The final relaxations of neighbor atoms are given in Table II together with previous results using empirical Morse potentials. The relaxations of atoms are expressed in units of nearest-neighbor distance: a plus sign means that atoms moved

TABLE I. Potential constants of effective pair potentials of lead (r_1 and r_2 are in Å).

Potential	A_1	A_2	A_3	A_4	r_1	r_2
Pb 1 *A*	−0.388611	1.768340			3.03	4.09
B	0.200589	−0.143611	−0.168751	0.182997	4.09	
C	0.004237	0.021834	0.008213	−0.050749	6.00	
D	−0.014632	−0.047859	−0.011369	0.042787	7.50	
E	0.035138	−0.311463			7.50	8.78
Pb 2 *A*	−0.387142	1.685358			3.01	4.06
B	0.145399	−0.117079	−0.126462	0.153276	4.06	
C	0.005077	0.021674	0.006947	−0.047215	6.00	
D	−0.001973	−0.022391	−0.007707	0.033077	7.57	
E	0.009199	−0.104114			7.57	8.86

away from the vacancy and a minus sign means the opposite relaxation. The results in the present calculation are significantly different from those obtained earlier by Girifalco and Weizer[35] and those by Wynblatt and Gjostein.[36] There are two features to be noted

The first point is the direction of displacement of neighboring atoms around the vacancy. So long as we use the Morse potential, we have the same results at least for the first- and second-nearest-neighbor relaxations. The nearest-neighbor atoms move toward the vacancy and the second neighbors move away from it, which can be ascribed to the nature of the Morse potential with one minimum. Using JHM potentials as in the present study, the first and second nearest neighbors move to the opposite direction compared with the case of Morse potential. This situation is quite similar to the case of aluminum which has been discussed earlier by Harrison.[16] These results suggest that in the case of LRON potentials, the effect of distant atoms and the position of the first minimum are important in determining the direction of relaxation of neighboring atoms. Also, each atomic shell around the vacancy does not always relax alternately toward and away from the vacancy even if the empirical Morse potential is chosen. Particularly, the LRON part of JHM potentials complicates the problem.

The second point is the magnitudes of the relaxations of neighboring atoms. The relaxation of the nearest-neighbor atoms is very small and that of the second neighbor atoms is fairly large compared to the previous results.

The relaxation energies and the formation energies are shown in Table II and Table III, respectively. The relaxation energies are significantly small compared to the previous calculations. This may be thought as a common nature of LRON potentials and similar results have been also obtained in Na.[19,20] The LRON part of the potentials must be responsible for these results in a complicated way. Unfortunately, reliable enough experimental data do not exist to conclude whether or not the predicted values are true.

Recently, the neutron scattering and positron-annihilation measurements have been developed. The positron annihilation in metals is particularly sensitive to vacancy-type defects, and in this regard, many studies have been made.[47,48] The results appear promising in providing information on the electron redistribution and the lattice distortions around the defects.

Experimental data are only available for the formation energy of a vacancy in lead. Feder and Nowick[39] have determined the formation energy to be 0.49± 0.10 eV from dilatometric and x-ray experiments. The formation energy can be also obtained from the positron-annihilation measurement in a metal. Recently, McKee *et al.*[40] have used

TABLE II. Atomic relaxations and relaxation energies of a vacancy in lead (in % and eV, respectively).

Atomic relaxations		E_{1r} relaxation energy	Ref.
First nearest neighbor	Second nearest neighbor		
−1.0	0.61	0.162	Girifalco-Weizer (Ref. 35)
−1.0	0.59	0.081	Wynblatt-Gjostein (Ref. 36)
		0.090	Wynblatt (Ref. 37)
0.06	−1.4	0.016	Present work (Pb1)
0.04	−0.85	0.026	Present work (Pb2)

TABLE III. Formation energy (E^F_{1V}) and migration energy (E^M_{1V}) of a vacancy in lead (in eV). Q_1 is the activation energy for self-diffusion.

	E^F_{1V}	$E^M_{1V}=Q_1-E^F_{1V}$	Q_1 1.09	E^F_{1V}/Q_1	Ref. 41–46
Experimental values	0.49 ± 0.10	0.60	···	0.45	Feder-Nowick (Ref. 39)
	0.50 ± 0.03	0.59	···	0.49	McKee *et al.* (Ref. 40)
	0.48	0.61	···	0.44	Pochapsky (Ref. 38)
		$Q_1=E^F_{1V}+E^M_{1V}$			
Calculated values	0.26	0.67	0.93	0.28	DuCharme-Weaver (Ref. 25)
	···	0.76	···	···	Wynblatt (Ref. 37)
	0.66	0.77	1.43	0.46	Present work (Pb1)
	0.57	0.60	1.17	0.49	Present work (Pb2)

this technique and successfully obtained the formation energy in lead to be 0.50 ± 0.03 eV. These experimental values are a little smaller than our results of 0.66 eV for Pb1 and 0.57 eV for Pb2. The discrepancies are mainly due to the large E_S, because, as mentioned above, the relaxation energy is a small quantity compared with E_S. A large E_S is also the direct consequence of a large amplitude of JHM potential. Waseda and Suzuki[29] have shown that a pair potential in Cs has a smaller amplitude than JHM potential. This is probably the case for other alkali and polyvalent metals. Accordingly, the agreement between the calculated and experimental values will be improved by employing a more proper potential in lead. However, it should also be kept in mind that other contributions such as those due to electron redistribution and the volume-dependent part of a crystal energy were not taken into account in the present calculation. The migration energies were calculated to be 0.77 and 0.60 eV for Pb1 and Pb2, respectively. In fcc metals, it is generally accepted that the self-diffusion is conducted by the vacancy mechanism. Therefore, the migration energy can be calculated from the relation

$$Q_1=E^F_{1V}+E^M_{1V} \quad . \tag{4.1}$$

Using $Q_1=1.09$ eV[41–46] and $E^F_{1V}=0.50$ eV as the experimental values, $E^M_{1V}=0.59$ eV is obtained. Although the relaxations of the nearest neighbors are only taken into account in the calculation, the calculated values agree fairly well with the experimental value. If the relaxations of the second- and third-nearest-neighbor atoms were also taken into account, the relaxation energy will increase slightly.

Wynblatt[37] has also given the migration energy to be 0.76 eV using the empirical Morse potential. This result agrees well with our results. These theoretical values and E^F_{1V}/Q_1 are given in Table III. It is quite important to note that different LRON potentials led to the same conclusion that the formation energy of a vacancy is less than the migration energy and E^F_{1V}/Q_1 is about 0.47, which is consistent with experimental results.

As mentioned in Sec. I, DuCharme and Weaver[25] have obtained the activation energies for self-diffusion in metals using a modified point-ion pseudopotential. Their results also show that the formation energy is less than the migration energy. However, since they have completely neglected the lattice distortions, their calculated values can not be compared with our results, because the relaxation energy for the atomic configuration of the motion of a vacancy is not negligible.

B. Divacancy

The relaxation energy, the formation energy, and the binding energy are given in Table IV together with related values. E_d is the potential energy between two atoms separated by the nearest-neighbor distance and equals the binding energy of a divacancy without lattice relaxation. Using notations defined before, $E_d=E^{B'}_{2V}$. The binding energy E^B_{2V} was calculated from

$$E^B_{2V}=E_d+E_{2r}-2E_{1r} \quad . \tag{4.2}$$

E_{2r} is the relaxation energy for divacancy and should not be confused with the relaxation energy E_{1r} in the case of a vacancy. It is unfortunate that experimental values of E_{2r} and E_{1r} are not available.

Comparing with the values of other face-centered-cubic metals, the presented values are reasonable. Doyama and Koehler[49] have given the binding energy of a near-neighbor divacancy for

TABLE IV. Results for a divacancy (in eV). E_s is the energy per atom, E_r the relaxation energy, E_d the binding energy without relaxation, B_v the binding energy, and E^F_{2V} the formation energy.

Potential	E_s	E_{2r}	E_d	E^B_{2V}	E^F_{2V}	E^M_{2V}
Pb1	0.674	0.030	0.113	0.11	1.21	0.36
Pb2	0.597	0.042	0.091	0.08	1.06	0.29

TABLE V. Formation energies of a ⟨100⟩-split interstitial and a body-centered interstitial (in eV).

Potential	⟨100⟩ split	Body
Pb1	2.01	1.76
Pb2	2.21	1.44

Al to be $E_{2V}^{B} = 0.17 \pm 0.05$ eV. On the other hand, by neglecting the lattice relaxation, Harrison[13] has computed $E_{2V}^{B} = E_d$ for Al and obtained $E_{2V}^{B} = 0.05$ eV, which is smaller than the experimental value. He explained this difference as due to the reason that much of the binding comes from elastic relaxation. In our calculation for lead, however, the contribution of elastic relaxation is small and a large part of the binding energy comes from the nearest-neighbor interaction between two vacancies. Therefore, a rough estimate of the binding energy of a divacancy can immediately be made.

The migration energy of a divacancy was calculated to be 0.36 and 0.29 eV for Pb1 and Pb2, respectively. These values are compared with the migration energy of a vacancy, 0.77 and 0.60 eV for Pb1 and Pb2, respectively. Two different LRON potentials, which are determined at two different temperatures, show the same results that the migration energy of a divacancy is less than that of a single vacancy in lead.

C. Interstitials

A ⟨100⟩-split interstitial and a body-centered interstitial are only examined. The formation energies of these interstitials were calculated in order to determine which of these interstitials is more stable in lead. The formation energy for each interstitial was obtained as the difference of two crystal energies, one is the perfect-crystal energy and the other is the energy of a crystal containing an interstitial. These results are given in Table V. A body interstitial is more stable than a ⟨100⟩-split interstitial. This is a very interesting result, because the most stable atomic configuration of interstitials has been normally thought to be a ⟨100⟩-split interstitial type in fcc metals. This has been shown by many theoretical calculations, particularly for Cu. On the other hand, Koehler and Leibfried[50] have suggested that the stable interstitial is a body interstitial in Cu and Ag, and a ⟨100⟩-split interstitial in Au by considering the recovery-peak structures of stage I for these metals. They have also suggested that a ⟨100⟩-split interstitial becomes more stable as the potential is changed from soft to hard, although the repulsive potential of ion core is not well known. According to this suggestion, in case of polyvalent metals including Pb, a body-centered interstitial is thought to be the stable interstitial. This is consistent with our results.

V. SUMMARY

(i) Using the long-range oscillatory pair potentials (Pb1, Pb2) of lead obtained by Johnson, Hutchinson, and March, the formation energies, migration energies, and atomic relaxations around a vacancy and a divacancy were calculated. These values are, respectively, $E_{1V}^{F} = 0.66$ eV, $E_{1V}^{M} = 0.77$ eV, $E_{2V}^{F} = 1.21$ eV, and $E_{2V}^{M} = 0.36$ eV for Pb1 and $E_{1V}^{F} = 057$ eV, $E_{1V}^{M} = 0.60$ eV, $E_{2V}^{F} = 1.06$ eV, and $E_{2V}^{M} = 0.29$ eV for Pb2.

(ii) It has been shown that the formation energy of a vacancy is less than the migration energy and also that divacancies are more mobile than single vacancies.

(iii) The formation energies of a ⟨100⟩-split interstitial and a body-centered interstitial were calculated and compared. In lead, a body-centered interstitial is more stable than a ⟨100⟩-split interstitial.

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