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Interatomic potential for copper

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An interatomic potential for copper is constructed, using the best available intermediate- and low-energy experimental information. It reproduces satisfactorily the threshold energies for atomic displacements as well as the phonon spectrum of the metal. This potential is also extrapolated to include higher-energy data. An analytical expression is proposed, of which every constituent is physically well understood. It is emphasized that such a potential may be quite useful for lattice-defect studies in which short-range as well as long-range effects are involved.

I. INTRODUCTION

The atomic interaction energies in general range from 10^5 to ~1 eV for radiation-damage studies. One may also look for even lower energies if the information on the configuration and potential energy of the final defects is desired. Acceptable theories exist only for the extreme cases of high and low energies. In the high-energy domain (~10^3 eV), the interaction potential is well described by the so-called Thomas-Fermi-Dirac (TFD) model,[1] which, being statistical in nature, is expected to become less and less reliable as the density of electrons in the region of overlap decreases. Also, the conduction-electron screening, which is outside the scope of the TFD theory, begins to become important below ~100 eV. In the low-energy domain (~1 eV), the situation is already less favorable. The lattice-dynamical studies, through coherent inelastic scattering of neutron experiments, afford a quite reliable basis to the theory, while theoretical techniques such as pseudopotentials are available to treat the problem. In fact, although some interesting results have been obtained, the screened pseudopotentials give only semiquantitative agreement with experiment. A better agreement is usually obtained if the parametrized pseudopotential is used.[2] In the intermediate region (~1 to ~100 eV), the most important in the dynamical studies of atomic displacements, no reliable theory exists and one has to use the semiempirical or purely empirical potentials, the parameters of which are adjusted to the property one is looking for. Evidently, such a potential can be valid only in a restricted energy domain.

As a consequence, to study the formation and the properties of point defects in metals, an approach from first principles is presently not feasible; one introduces the suitable parameters at one stage or the other. In this work, we try to construct a composite interatomic potential by interpolation through the vast energy domain in point, the number of parameters being kept to a minimum by staying as close to the theory—when reliable—as possible.

In a metallic system, the interatomic potential may be divided into two parts: (i) The long-range part which includes the bare Coulomb interaction and the screening due to conduction electrons; (ii) the short-range part which arises from the polarizability of ion cores, and from the Pauli exclusion principle.

The first contribution is oscillatory, which is well established through the study of phonon spectra and Kohn anomalies.[3] Physically, the source of this oscillatory behavior is the screening by conduction electrons which is cut off sharply at the Fermi wave number. In general, then, the screening has the effect of eliminating the long-range Coulomb potential and replacing it by a more rapidly decaying oscillatory term. It hardly affects the interaction at very short distances. This contribution is fairly understood by pseudopotential theory for simple metals but the puzzle is still unresolved for transition and rare-earth metals.[4]

The short-range interactions are little understood through the theory. Rahr *et al.*[5] have calculated recently the Van der Waals interactions for noble metals using a simplified picture of a metallic system in which the ions are regarded as nonoverlapping and immersed in a uniform background of conduction electrons. Though far from a real situation for a d-band metal, these authors estimated its contribution to the cohesive energy from 6 to 17% in the noble metals. As concerns the exchange-overlap interaction, Benedek[6] has recently made an attempt to calculate it in a number of metals by the Heitler-London method. This method seems unsound, however, for d-band metals where the separation between

core and conduction electrons is unclear and the hybridization between s and d bands is dominating. There have also been numerous empirical and semiempirical calculations of exchange-overlap potential using various experimental information.[7] However, many uncertainties still exist as to the nature and magnitude of short-range potentials.

Therefore, in our composite potential, we will tie together a long-range oscillatory part as it is given by the pseudopotential theory with a purely empirical short-range part. In order to adjust the latter's parameters, we will use the well-established physical data obtained through low- and intermediate-energy-range experiments, i.e., (a) The potential should reproduce as well as possible the phonon spectrum; (b) it should allow to estimate correctly the threshold energies for atomic displacements; (c) at still higher interaction energies, it should join smoothly the TFD potential.

The metal copper has been chosen because a number of experimental data are available and the generalized pseudopotential analysis has also been done satisfactorily. The plan of this paper is as follows: (a) Section II is devoted to the use of the threshold energies for atomic displacements to calculate short-range repulsive potentials, which are then compared with others; (b) in Sec. III these potentials, in conjunction with the screened Coulomb potential deduced from pseudopotential treatment, are used to calculate the phonon frequencies and parametric adjustments for improving the agreement with experiment are examined; (c) in Sec. IV a composite interpolated potential is constructed and discussed.

II. COMPARISON OF SHORT-RANGE INTERATOMIC POTENTIALS

For several decades, the parameter calculations of empirical or semiempirical so-called short-range potentials have been done with the help of data such as compressibility—or more generally elastic properties, cohesive energy, etc., which correspond to interaction distances close to atomic distances a_0 in the perfect crystal. These potentials explain some properties but fail to explain others or, to say it differently, the parameter values differ following the property used to adjust them. The main reason for it is probably that the form of the potential used (usually exponential) is hardly physically justified for all the distances.

Keeping in view that the TFD potential is valid for distances $\leq \frac{1}{10} a_0$ and knowing for sure that the oscillatory nature of the composite potential should occur in the vicinity of a_0, we see that data corresponding to interaction distances $\sim \frac{1}{2} a_0$ should be best suited for an intermediate landmark. This is just the case of atomic displacements in metals near threshold energies. Actually, from threshold-energy values, parametric potentials may be derived either through the classical many-body calculations of Gibson *et al.*[8] or through a simple geometrical model of Lucasson *et al.*[9-11] Gibson *et al.*'s calculations already exist for copper with a Born-Mayer type potential. Although it is a self-consistent calculation, the deduced threshold energy is 25 eV while the experimental value is 19 eV.[12] It is worthwhile to explore the best possible parametric potential for copper through the geometrical model of Lucasson *et al.*, as the method is attractive because of its simplicity. As it is rather different from the so-called barrier model, with which it has sometimes been confused,[13] we recall here its main features; for more details, the reader may refer to Ref. 10.

In order to result in the formation of a Frenkel pair, a knocked-on atom A—projected with a kinetic energy T_0, in a direction close to $\langle 100 \rangle$, $\langle 110 \rangle$, or $\langle 111 \rangle$—has to cross a potential barrier, also called "lense," to get into a neighboring atomic polyhedron and forms momentarily with the atom B inside it, a compressed configuration before transferring to it part of its remaining kinetic energy T. The process has to be repeated a number of times, so increasing the distance between the compressed site (or interstitial) and the vacancy left behind until a recombination is precluded. The approximations done to estimate the energy loss $(T_0 - T)$ in each lense passage are the following:

(i) The transverse impulses given by the mobile atom to the atoms of the lense may be neglected in first approximation because their effect is to decrease the height of the potential barrier. (This mutual compensation is the physical basis of the so called barrier model).

(ii) The longitudinal impulse given to the atom B is evaluated through Lehman and Leibfried's approximation,[14] taking into account the kinetic energy gained by A going down the lense barrier.

(iii) If the height of the potential barrier of the lense is comparable to the threshold energy (in a ratio of $\sim \frac{1}{2}$ for instance), as in the [100] or [111] events, one has to consider two cases: in the ultimate passage, the mobile atom A stops in the close vicinity of the lense saddle point so that a longitudinal impulse is given not only to B but also to the lense atoms. It is easily evaluated classically. In penultimate passages, A crosses the lense, coming closer to B so that

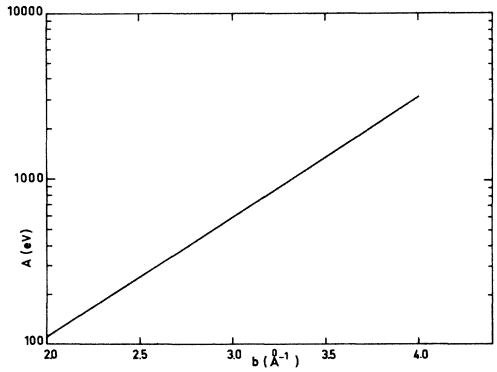

FIG. 1. Semilogarthimic linearity of Born-Mayer potential parameters.

the impulse given to the lense atoms while climbing the barrier is partly cancelled by taking it back while going down the barrier and the resultant impulse is small enough to be neglected.

(iv) If the height of the barrier is small compared to the threshold energy, as in the case in [110] events, A stops in positions close to the saddle point for several passages because the energy loss per passage is small (the main contribution to the threshold energy is due to the building up of a compressive energy between A and B). In that case only, the longitudinal impulse to the lense atoms must be evaluated. Therefore the number of passages necessary for the stability of Frenkel pair is larger than in the previous case (five or six instead of two along ⟨100⟩). As the energy loss per passage is small, the error introduced in the number of passages is of the order of 1%.

In copper, we know that the absolute threshold energy for atomic displacement is 19 eV and should correspond to both [100] and/or [110] events. For displacements along [111] directions, the threshold is 2.5–3 times higher.[9,12] We have first considered the [100] direction case: assuming that the stable Frankel pair is formed after two passages,[8] the geometrical model yields a set of parameters A and b of the Born-Meyer potential

$$\phi(r) = Ae^{-br}, \tag{1}$$

which reproduces the same threshold energy. Under these conditions when the interaction energy and the distance are fix these parameters show a semilogarithmic linear dependence[1] as is evident from Fig. 1. We have used several couples of this set of parameters to calculate threshold energies for displacements along [110] with five or six successive knock-ons and along [111] with two passages through the corresponding double triangular lenses.[9] The results are shown in Table I. The best fit to experimental data is obtained with either $A = 558$ eV, $b = 3.0$ Å^{-1} or $A = 1309$ eV, $b = 3.5$ Å^{-1}. In what follows, the corresponding potentials will be noted P_1 and P_2 respectively. The fact that a choice is possible when displacements in several directions are considered stems from the differences in geometry and in dynamical processes. Larger values of A (with correspondingly larger values of b) would give too low [110] and too high [111] thresholds compared to [100].

In Fig. 2 we have plotted P_1 and P_2 in an interaction distance domain extending from the vicinity

TABLE I. Threshold energies for displacement in different directions for a varying number of lense passages with several sets of potential constants (eV).

b (Å^{-1})		2.0	2.5	3.0	3.5	4.0
A (eV)		113	245	558	1309	3122
Passages						
(1)		6.92	8.31	9.09	9.57	9.86
(2)	⟨100⟩	19.02	19.01	18.99	19.00	19.00
(3)		31.18	29.69	28.85	28.37	28.04
(4)		43.13	40.25	38.63	37.69	37.07
(1)		1.62	3.96	5.82	7.68	9.82
(2)		7.02	7.83	8.73	9.94	11.61
(3)	⟨110⟩	12.42	11.70	11.64	12.20	13.40
(4)		17.82	15.57	14.55	14.46	15.19
(5)		23.22	19.44	17.46	16.72	16.98
(6)		28.60	23.31	20.37	18.98	18.77
(1)		13.61	17.50	21.19	25.13	29.55
(2)	⟨111⟩	31.81	37.66	45.59	56.44	71.03
(3)		50.74	59.31	72.20	90.47	115.22

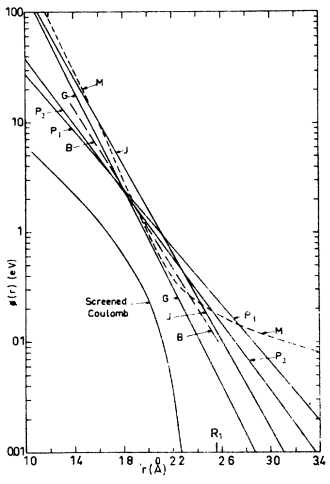

FIG. 2. Comparison of various short-range potentials. G: Gibson *et al.* (Ref. 8), J: Jaswal and Girifalco (Ref. 15), B: Benedek (Ref. 6), M: Moriarty (Ref. 4), P_1, P_2: Present calculations. R_1 denote the position of the nearest neighbors.

of core radius (0.95 Å) to the vicinity of second neighbors (3.61 Å) on a semilog scale. We have also chosen some potentials representative of the empirical or of the theoretical category and have plotted them—for intercomparison purposes—on the same graph. G and J represent the empirical potentials, respectively, obtained by Gibson *et al.*[8] and by Jaswal and Girifalco.[15] J is obtained using cohesive energy, lattice parameter and compressibility data. Both are represented as

$$\phi(r) = Ae^{-b(r/a_0-1)}. \tag{2}$$

The parameters (A, b) for these potentials used in the present calculations are (0.051, 13.0) and (0.0958, 13.64). A is in eV and b is dimensionless. The first one (G) is harder than P_1 and P_2 at distances less than 1.8 Å and softer beyond it. This agrees with the high threshold energy it gives. The second one (J) is even harder than (G) but it is softer than P_1 and P_2 for $r > 2.3$ Å.

The curves (M) and (B) represent the potentials calculated theoretically by Moriarty[4] and by Benedek,[6] through the analysis of overlapping of d-wave functions. Moriarty potential appears in the framework of a pseudopotential analysis while Benedek has used the Heitler-London method. Visibly, the potentials are found in close agreement among themselves and with the empirical potentials for intermediate values of r (from ~1.7 to ~2.2 Å) but diverge for smaller and for larger values of r.

We have finally to wonder what may be the contribution of the screened Coulomb part in this interaction distance domain. There have been many calculations of screened Coulomb potential for copper[16] but only Moriarty's evaluation is free from adjustable parameters, therefore we have shown his results in curve "screened Coulomb" of Fig. 2. It is evident that this contribution is always much smaller than the exchange-overlap part and can be neglected in the calculation of threshold energies which involves distances from 1.55 to 2.55 Å. However, in the calculation of the point defects produced, it may play a dominant role as it is long range and oscillatory at distances where the overlap potential almost vanishes.

III. INTERMEDIATE- AND LONG-RANGE INTERATOMIC POTENTIALS

The test of validity of the potential functions in this section will be the correct prediction of the phonon spectrum. Moriarty calculated the phonon frequencies of copper using the generalized transition metal pseudopotential approach of Harrison.[2] His results are shown in curves M of Fig. 3. He finds strong anomalies in the transverse branches in the [100] and [110] directions and in the longitudinal branch in the [111] direction which are associated with s-d hybridization. His results are up to 20% lower than the experimental values.[17] As the contribution of the first neighbors is a major one in the calculation of phonon frequencies, the empirical potentials discussed in Sec. II include certainly reliable informations in the vicinity of $\sim a_0$ while a theoretically evaluated potential may have some uncertainties because of difficulties involved in multicentral integrals and nonavailabilty of crystal wave functions. Therefore, we will tentatively add to Moriarty screened Coulomb potential the short-range potentials discussed in Sec. II.

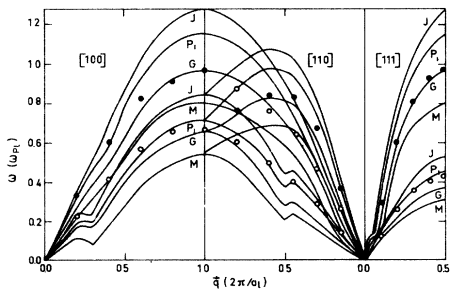

FIG. 3. Phonon frequencies of copper. The description is the same as that of Fig. 2. The solid and open circles represent the observed values. ω_{pl} is the plasma frequency.

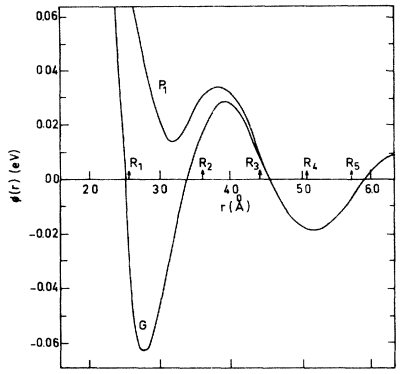

FIG. 4. Oscillatory pair potential for copper. The description is the same as that of Fig. 2.

The consequences on calculated phonon spectrum appear in Fig. 3, where the computed phonon frequencies for three principal symmetry directions [100], [110], [111] along with the experimental values are drawn. In any case, the frequencies increase and this leads to a better agreement with the experimental values. The curves (J) show that Jaswal and Girifalco's function overestimates the frequencies. The most reasonable agreement is obtained by the potentials derived from the threshold-energy data. With P_1, for the longitudinal branches, there is good agreement for lower values of wave vectors while the frequencies for higher values of wave vectors are overestimated. Surprisingly good agreement is obtained for the transverse branch in the [111] direction. Gibson *et al.* potential yields phonon frequencies which are lower than the experimental values for lower values of phonon wave vector except for the longitudinal branch in the [111] direction and the T_2 branch in the [110] direction (curves G). For higher values of wave vectors, a close agreement is obtained with experiment. The calculated phonon frequencies using potential P_2 are found to be similar to those obtained with P_1 and therefore, they are not shown in the figure. We had no explicit form of Benedek potential and so we did not carry out the calculations for this potential. It is possibly not justified to represent this potential by an exponential function near $r = a_0$. The positions and magnitudes of the anomalies found by Moriarty were left almost unaltered and therefore, it appears that the overlap potentials do not contribute to the anomalous behavior.

We conclude that Gibson *et al.* and P_1 potentials in conjunction with screened Coulomb potential reproduce reasonably the phonon spectrum of copper. At the same time these short-range potentials also reproduce fairly the threshold energies (in which the contribution of screened Coulomb interaction to the threshold energies is very small and may be neglected). Therefore, we construct the composite interatomic potential by adding the two segments. This addition eliminates all the uncertainties involved in the extrapolation of two segments. Such a potential explains well the intermediate- and low-energy-range experiments. These potentials are shown in the Fig. 4 for $r \geq 1.55$ Å. Both have positive derivatives at the first-nearest-neighbor distance. The first minimum is between the first- and second-nearest neighbor, which might, correspond to some resonance states or bound states for P_1 and G, respectively, as far as the nature is in view.[18] As concerns the position of the absolute minimum, it is not required in the vicinity of first neighbor.[19]

Finally we represent these potentials with unified expressions:

$$\phi_1(r) = \begin{cases} 0.0568 \exp[-13.0(r/a_0 - 1)] - (1.75/r^3)\cos(2.36r - 0.1) & \text{for } 0.4 < r \leq 4.6 \text{ Å}, \\ -(2.9/r^3)\cos(2.36r - 0.1) & \text{for } r > 4.6 \text{ Å} \end{cases} \tag{3}$$

and

$$\phi_2(r) = \begin{cases} 0.2921 \exp[-7.67(r/a_0 - 1)] - (1.81/r^3)\cos(2.33r - 0.1) & \text{for } 0.4 < r \leq 4.6 \text{ Å}, \\ -(3.02/r^3)\cos(2.33r - 0.1) & \text{for } r > 4.6 \text{ Å}. \end{cases} \tag{4}$$

ϕ_1 and ϕ_2 represent the potentials when Gibson *et al.* and P_1 potentials are added to Moriarty screened Coulomb potential, respectively. These potentials are in units of eV. The parameters of ϕ_1 and ϕ_2 are obtained by fitting the numerical values of the potential within the deviation of (5–10)%. The most important point is that every contribution of this expression is physically well understood while this is not true for other parametrized potentials.[20] The potentials are combinations of exponential repulsive and screened Coulomb attractive parts. For larger values of r these reduce exactly to the asymptotic form.

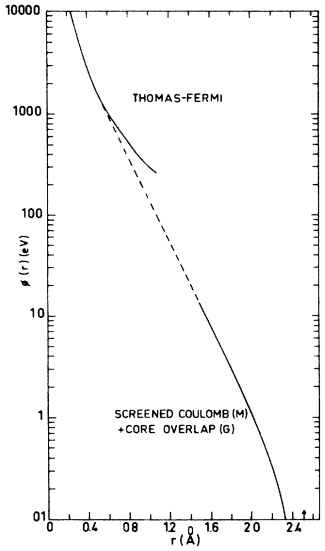

FIG. 5. Composite interatomic potential for copper.

IV. COMPOSITE INTERATOMIC POTENTIAL

In this section we obtain the composite interatomic potential with the help of potential calculated in Sec. III, and TFD potential. We calculate TFD potential by the formula obtained by Firsov[21]:

$$\phi(r) = (Z^2e^2/r)\chi[(2\sqrt{Z})^{2/3}(r/0.885a_B)] , \qquad (5)$$

where Z is the atomic number, e is the electronic charge, and a_B is Bohr radius. The tabulated values of Thomas-Fermi screening function χ are used in the calculation. This is the high-energy segment of the potential. The intermediate- and low-energy segments consist of the sum of overlap and screened Coulomb potentials. Two segments are joined graphically. Such an interpolation is shown in Fig. 5. The Thomas-Fermi potential deviates considerably from the linear relation on a semilog scale beyond 0.7 Å. We joined the high-energy segment of $r < 0.7$ Å to low-energy segment which continues to long-range oscillatory pair potential shown in Fig. 4. Linear interpolation on semilog scale is justified because in the vicinity of core radius (~1 Å) Born-Mayer potential should be a good representative. At these small distances the cores get deformed, and exchange and correlation interactions between core and conduction electrons may become important. White[22] has shown that the latter contribution amounts to only 6% of the ion–ion Coulomb interaction and it can easily be neglected. However no estimation exists for the deformation of the ion core.

V. CONCLUSION

We have constructed the composite interatomic potential for copper using the best available experimental and theoretical information. In principle, the band-structure effects, which may give rise to three-body interaction because of partial localization of d electrons, should also be included. Such an analysis would be extremely complicated and we can only say that the corresponding information is included in our potential through parametrization. This potential describes the low- and intermediate-energy-range experiments satisfactorily and it may be evaluated easily. We think that it might be quite useful for the study of the properties of metals where short-range as well as long-range effects are involved.

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[1]I. M. Torrens, *Interatomic Potentials* (Academic, New York, 1972); R. A. Johnson, J. Phys. F 3, 295 (1973), and references therein.

[2]W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966).

[3]W. Kohn, Phys. Rev. Lett. 2, 393 (1959).

[4]W. A. Harrison, Phys. Rev. 181, 1036 (1969); N. Singh, J. Singh, and S. Prakash, Phys. Rev. B 12, 1076 (1975); J. A. Moriarty, *ibid.* 6, 1239 (1972); A. O. E. Animalu, *ibid.* 8, 3542 (1973).

[5]J. J. Rehr, E. Zaremba, and W. Kohn, Phys. Rev. B 12, 2062 (1975).

[6]R. Benedek, International Conference of Fundamental Aspects of Radiation Damage in Metals, Gatlinburg, Tenn., 1975 (unpublished).

[7]*Vacancies and Interstitials in Metals*, edited by A. Seeger, D. Schumacher, W. Schilling, and J. Diehl (North-Holland, Amsterdam, 1970); *Interatomic Potentials and Simulation of Lattice Defects*, edited by P. C. Gehlen, J. R. Beeler, and R. I. Jaffee (Plenum, New York, 1972).

[8]J. B. Gibson, A. N. Goland, M. Milgram, and G. H. Vineyard, Phys. Rev. 120, 1229 (1960).

[9]P. Lucasson and A. Lucasson, J. Phys. (Paris) 24, 503 (1963).

[10]F. Maury, P. Vajda, A. Lucasson, and P. Lucasson, Phys. Rev. B 8, 5506 (1973).

[11]F. Maury, P. Vajda, M. Biget, A. Lucasson, and P. Lucasson, Radiat. Eff. 25, 175 (1975).

[12]P. Lucasson, International Conference of Fundamental Aspects of Radiation Damage in Metals, Gatlinburg, Tenn., 1975 (unpublished).

[13]P. Jung and W. Schilling, Phys. Rev. B 5, 2046 (1972).
[14]C. Lehman and G. Leibfried, Z. Phys. 162, 203 (1961).
[15]S. S. Jaswal and L. A. Girifalco, J. Phys. Chem. Solids 28, 457 (1967).
[16]S. K. Sinha, Phys. Rev. 143, 422 (1966); S. Prakash and N. Singh, Phys. Rev. B 8, 5532 (1973); T. Toya, Prog. Theor. Phys. 20, 974 (1958).
[17]R. M. Nucklow, G. Gilat, H. G. Smith, L. J. Raubenheimer, and M. K. Wilkinson, Phys. Rev. 164, 922 (1967).
[18]C. P. Flynn, *Point Defects and Diffusion* (Clarendon, Oxford, 1972), p. 753.
[19]W. A. Harrison, in *Interatomic Potentials and Simulation of Point Defects*, edited by P. C. Gehlen, J. R. Beeler, and R. I. Jaffee (Plenum, New York, 1972), p. 69.
[20]R. A. Johnson, J. Phys. F 3, 295 (1973).
[21]O. B. Firsov, Zh. Eksp. Teor. Fiz. 33, 696 (1957) [Sov. Phys.-JETP 6, 534 (1958)], and Ref. 1.
[22]H. C. White, Phys. Rev. 112, 1092 (1958).