

Localized electronic structure of boron-impurity–vacancy complexes in Ni

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The localized electronic structure of boron-impurity–vacancy (B-*V*-B) complexes in Ni was calculated for four models with different configurations by use of the multiple-scattering $X\alpha$ method. Results are presented for the total energy, density of states, and local charge transfer. Comparisons are made among the four models. The related physical response was discussed in terms of the physical quantities introduced, such as the binding tendency between the boron atom and the vacancy, the hybrid-bond energy, and the energy for charge redistribution. The calculations indicate a strong binding between the boron atom and the vacancy. The B-*V*-B complex has a tendency to be formed spontaneously in boron-containing alloys with two different configurations. Boron-containing alloys with a B-*V*-B complex show a strong potential for charge redistribution, and therefore can have good ductility. The results are consistent with the experiments on the segregation of boron in defect areas and indicate the effect of boron on the alloy.

I. INTRODUCTION

Boron-containing alloys have been widely used in modern aeronautical and astronautical technology, as well as modern nautical engineering. A large amount of experiments have shown that a small amount of boron impurities greatly improves some physical properties, such as brittleness, rupture strength, and creep, in superalloys, austenitic stainless steel, heat-strength steel, and metals. The optimal concentration of B is only of the order of 10^{-5} . The great effect of the trace element B on alloys has stimulated intensive research^{1–11} in the past several decades. For example, Aust *et al.*² and Karlsson *et al.*¹¹ have carefully studied the segregation behavior of boron.

The key effect of B impurity on alloys must have its origin in the electronic structure of materials. We study, therefore, the action of boron from first-principles calculations. We believe that a combination of theoretical studies of the electronic structure of solids with materials science can provide a basis for developing and designing materials with specific, desired properties.

In recent years there have been many first-principles calculations on the relation between the electronic structure and the mechanical properties of materials.^{12–23} In that research, the influence of impurities and defects on the electronic structure and the mechanical properties of materials has been studied using calculations of models of the local environment of materials. Some concepts such as bond directionality, charge polarizability,¹⁷ *s*-orbital electron-negativity,¹⁸ and effective neighbors²¹ have been

introduced and proved to be useful in the analysis of mechanical properties.

In this paper, based on our proposed model of a double-impurity –single-vacancy (B-*V*-B) complex,^{21–23} using the multiple-scattering $X\alpha$ method,²⁴ we calculated the electronic structure of four possible local configurations of the B-*V*-B complex in Ni. We obtained the total energy, density of states as well as local charge transfer corresponding to different configurations of the B-*V*-B complex. The results were compared with those of Ni₁₂B cluster, in which a B atom occupies a central site. For the purpose of quantitatively expressing the binding tendency between B and the vacancy, charge-redistribution ability, and orbital-hybridization ability, we introduced related physical quantities and defined these in terms of energy change. It was found that the quantities are very sensitive to local environmental modification and they provide an understanding of the properties of boron steel.

II. STRUCTURAL MODEL AND CALCULATION PARAMETERS

During the cooling process of a solid alloy annealed at high temperature, supersaturated vacancies diffuse toward the defect area, which acts as a sink.¹¹ Mobile complexes of impurity and vacancy can then be formed due to the interaction between the impurity and the vacancy. The supersaturated vacancies will be annihilated in defect areas, such as the grain boundary and interface. As a result, B-*V*-B complexes can be produced with the

segregation of B atoms.² However, the configuration of the B-V-B complex is indefinite. In order to study the electronic states of the B-V-B complex and the action of B, we take account of the size effect,²⁵ chemical-bond theory^{22,26} as well as related experiments,^{4,11} and thereby present four models (shown in Fig. 1) of the B-V-B complex corresponding to four different configurations.

The size factor δ of each configuration is given in Table I. The electronic configurations for Ni and B atoms are chosen to be $3d^8 4s^2$ and $2s^2 2p^1$, respectively. The crystal constant is taken as 3.5238 \AA .

III. RESULTS AND DISCUSSION

In this section we present the results calculated for the four models of the B-V-B complex and the Ni_{12}B cluster. The related physical quantities are introduced and their numerical values are given as a measure of the binding tendency between the B impurity and the vacancy, the charge-redistribution ability, and the orbital-hybridization ability. The results are compared among the five clusters and discussed in relation to the mechanical properties of boron steel.

A. $X\alpha$ statistical total energy

The total energy of a system can be written as

$$\langle E_{X\alpha} \rangle = \langle T \rangle + \langle V_{e-e} \rangle + \langle V_{e-N} \rangle + \langle V_{N-N} \rangle + \langle V_{X\alpha} \rangle, \quad (1)$$

where $\langle E_{X\alpha} \rangle$ is the $X\alpha$ statistical total energy, $\langle T \rangle$ is the total kinetic energy, $\langle V_{e-e} \rangle$, $\langle V_{e-N} \rangle$, $\langle V_{N-N} \rangle$ are the electron-electron, electron-nucleus, nucleus-nucleus Coulomb energy, respectively, and $\langle V_{X\alpha} \rangle$ is the exchange-correlation potential energy.

In Table I we list the calculated results of $\langle E_{X\alpha} \rangle$, $\langle V_{e-e} \rangle$, and $\langle V_{e-N} \rangle$. It can be seen that the total energy of a cluster has a close relation to the symmetry and the size factor of the system. The model with a higher symmetry and a smaller size factor has a lower energy and thereby has a greater probability to exist in the solid phase. However, considering the energy fluctuation on atomic scales due to the inhomogeneity in real materials as well as the restriction of size factor, we think that the

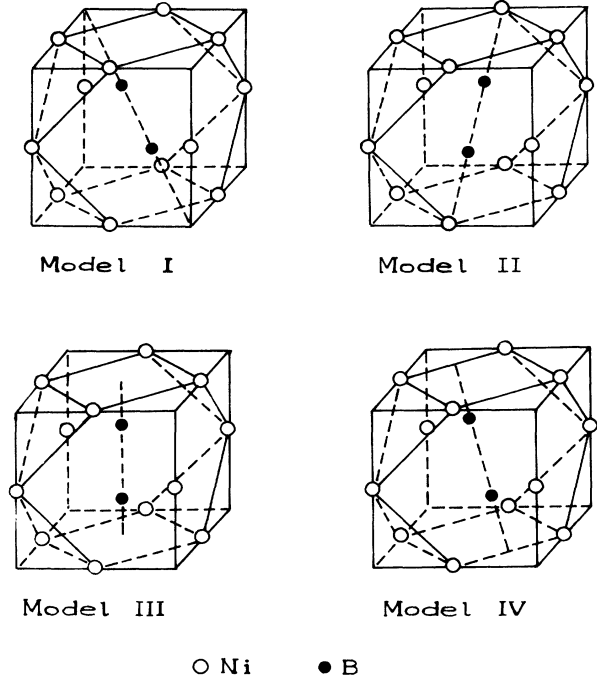


FIG. 1. Model clusters of a B-V-B complex.

B-V-B complex may appear in the alloy with different configurations and that models I, III, and IV have greater probabilities of existence compared with model II. In addition, it can also be seen that there are marked differences in the electron-nucleus Coulomb energy and the electron-electron Coulomb energy among the five clusters, which means that the configuration of B atoms have a direct and sensitive effect on the details of electronic structure associated with the distribution of the electron clouds of the orbitals.

B. Binding between boron and vacancy

From experimental and theoretical studies it can be concluded that the key effect of B on an alloy is caused by a mobile B-V-B complex, which is formed by the annihilation of supersaturated vacancies and the segregation of B atoms, as well as by the interaction between a B atom

TABLE I. The symmetry, size factor δ , $X\alpha$ total energy $\langle E_{X\alpha} \rangle$, electron-electron Coulomb energy $\langle V_{e-e} \rangle$, electron-nucleus Coulomb energy $\langle V_{e-N} \rangle$, binding tendency S_{B-V-B} between the boron impurity and the vacancy, hybrid-bond energy E_{hyb} , and the energy E_{red} for charge redistribution in four models of the B-V-B complex and the Ni_{12}B cluster.

	Model I	Model II	Model III	Model IV	Ni_{12}B
Symmetry	D_{3d}	C_{2h}	D_{4h}	C_{2h}	O_h
δ (%)	7.5	28	Very small	17.8	Very small
$\langle E_{X\alpha} \rangle$ (10^4 Ry)	-3.6258	-3.6157	-3.6266	-3.6245	-3.6216
$\langle V_{e-e} \rangle$ (10^4 Ry)	3.3098	3.2176	3.3590	3.3279	3.3226
$\langle V_{e-N} \rangle$ (10^5 Ry)	-1.2172	-1.2067	-1.2253	-1.2220	-1.2174
S_{B-V-B} (Ry)	-0.3327	-2.010	-0.1391	-1.757	
E_{hyb} (Ry)	-1.353	-2.445	-0.9429	-1.624	-0.0912
E_{red} (Ry)	-1.548	-3.423	-0.4670	-1.499	-0.3977

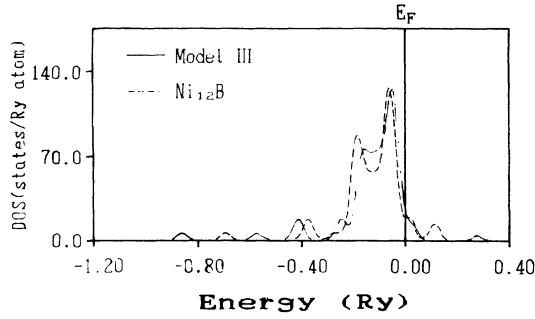


FIG. 2. Total density of states for model III and Ni_{12}B cluster.

and a vacancy. In our previous work²² the electronic structure of impurity B-vacancy complex in Fe was studied by use of the recursion method. According to the properties of truncated Green's function²⁷ and the calculated result of the discrete eigenvalues outside continuous energy spectrum due to impurities,²² it may be thought that the main action of impurity B localizes upon the first nearest neighbors, which is subject to short-range effect. In order to investigate the local effect of the combination of B and vacancy, we introduce a quantity $S_{\text{B-V-B}}$ to express the binding tendency between B and a vacancy:

$$S_{\text{B-V-B}} \equiv E_{\text{B}}^{\text{B-V-B}} - E_{\text{B}}^0 = \sum_k \rho_{k_{\text{B}}} E_{k_{\text{B}}} - \sum_k \rho_{k_{\text{B}}}^0 E_{k_{\text{B}}}^0, \quad (2)$$

where $\rho_{k_{\text{B}}}$ and $E_{k_{\text{B}}}$ are, respectively, the orbital occupation number and the orbital eigenenergy of a B atom in the model cluster, and $\rho_{k_{\text{B}}}^0$ and $E_{k_{\text{B}}}^0$ are the corresponding quantities of a free atom of B.

The numerical results of $S_{\text{B-V-B}}$ for four models of the B-V-B complex are given in Table I. The distinct feature is that the binding tendency between boron and a vacancy is dependent on the configuration of B atoms as well as the size factor, which expresses the compactness between

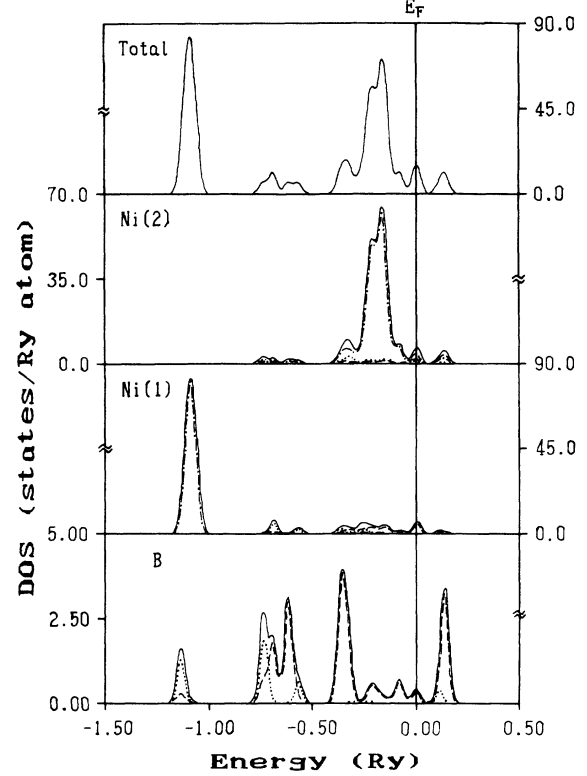


FIG. 3. Total density of state, local density of states (LDOS), and partial-wave local density of states (PLDOS) for model I of the B-V-B complex. Solid line, LDOS for atoms; dashed-dotted line, PLDOS for d orbitals; dashed line, PLDOS for p orbitals; dotted line, PLDOS for s orbitals. The Fermi energy E_F is chosen to be zero.

the boron atom and the vacancy. It may be regarded that in boron-containing alloys, the boron atom and the vacancy combine spontaneously, which, from the point of view of the electronic structure, explains the formation of the mobile B-V-B complex.

TABLE II. The major components of total density of states in each energy region for four models of the B-V-B complex.

	Antibonding region	The Fermi level	Nonbonding region	Bonding region
Model I	$\text{Ni}(1)_p\text{-B}_p\text{-Ni}(2)_{pd}$	$\text{Ni}(1)_p\text{-B}_p\text{-Ni}(2)_{pd}$	$\text{Ni}(1)_{sp}\text{-B}_p\text{-Ni}(2)_{sd}$	$\text{Ni}(1)_d\text{-B}_{sp}$
Model II	$\text{Ni}(1)_d\text{-Ni}(2)_{dp}\text{-B}_p\text{-Ni}(3)_p\text{-Ni}(4)_d$	$\text{Ni}(1)_{dp}\text{-Ni}(2)_{dp}\text{-B}_p\text{-Ni}(3)_p\text{-Ni}(4)_d$	$\text{Ni}(1)_p\text{-Ni}(2)_{pd}\text{-B}_p\text{-Ni}(3)_{sp}\text{-Ni}(4)_{pd}$	$\text{Ni}(1)_s\text{-Ni}(2)_{sp}\text{-B}_{sp}\text{-Ni}(3)_d\text{-Ni}(4)_s$
Model III	$\text{Ni}(1)_{pd}\text{-Ni}(2)_{spd}\text{-B}_p\text{-Ni}(3)_{pd}\text{-Ni}(4)_p$	$\text{Ni}(1)_{pd}\text{-Ni}(2)_{pd}\text{-B}_p\text{-Ni}(3)_{pd}\text{-Ni}(4)_p$	$\text{Ni}(1)_p\text{-Ni}(2)_d\text{-B}_{sp}\text{-Ni}(3)_d\text{-Ni}(4)_{sp}$	$\text{Ni}(1)_s\text{-B}_{sp}\text{-Ni}(4)_d$
Model IV	$\text{Ni}(1)_{pd}\text{-Ni}(2)_{spd}\text{-B}_p\text{-Ni}(3)_{pd}\text{-Ni}(4)_p$	$\text{Ni}(1)_{pd}\text{-Ni}(2)_{pd}\text{-B}_p\text{-Ni}(3)_{pd}\text{-Ni}(4)_p$	$\text{Ni}(1)_p\text{-Ni}(2)_d\text{-B}_{sp}\text{-Ni}(3)_d\text{-Ni}(4)_{sp}$	$\text{Ni}(1)_s\text{-B}_{sp}\text{-Ni}(4)_d$

C. Density of states and hybrid-bond energy

We obtain a continuous density of states (DOS) by broadening the discrete eigenvalue spectrum with a set of Gaussian functions. The Gaussian-broadened DOS for model III and Ni₁₂B cluster are shown in Fig. 2. Particular attention should be paid to the similarity of DOS profiles for model III to those for Ni₁₂B and Ni₁₃ (Ref. 28) clusters, which suggests that the B-V-B complex in model III has little effect on the electronic structure. The total density of states (TDOS), the local density of states, and the partial-wave local density of states are shown in Figs. 3–7, respectively, for four models of the B-V-B complex and the Ni₁₂B cluster. We find two common features, which are (1) the low value of TDOS passing through the Fermi level and (2) the dispersed states con-

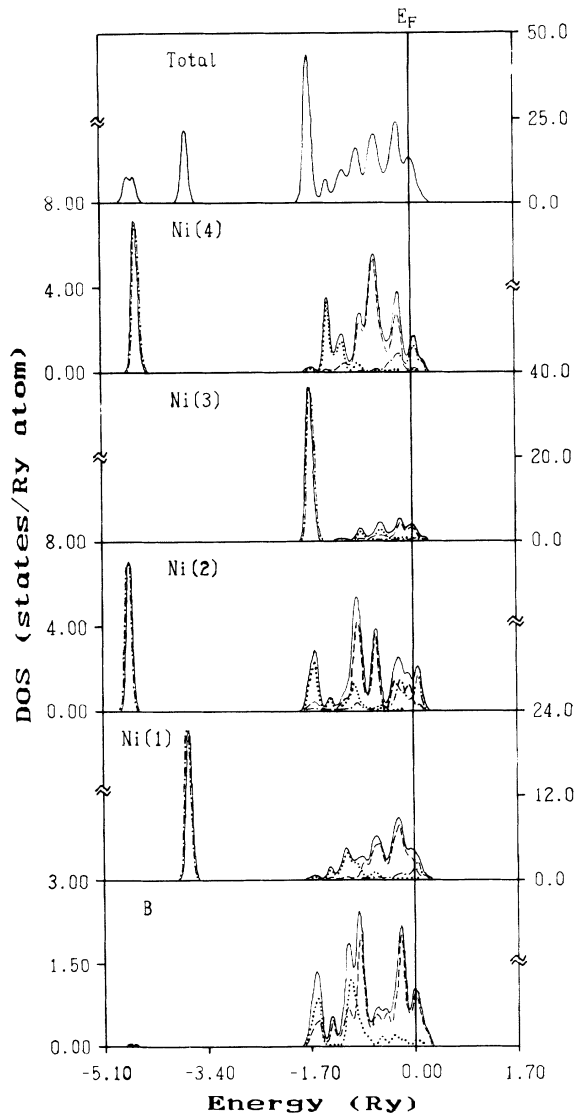


FIG. 4. Total density of state, local density of states (LDOS), and partial-wave local density of states (PLDOS) for model II of the B-V-B complex. Solid line, LDOS for atoms; dashed-dotted line, PLDOS for *d* orbitals; dashed line, PLDOS for *p* orbitals; dotted line, PLDOS for *s* orbitals. The Fermi energy E_F is chosen to be zero.

tributed by B atoms. If we list the major components of TDOS in each energy region in Table II, the third common feature of DOS stands out immediately; this is the bridge role of the *p* orbitals of B atoms causing the hybridization of Ni-B-Ni orbitals.

To assess quantitatively the degree of orbital hybridization, we introduce the hybrid-bond energy E_{hyb} . It can be given that

$$E_{\text{hyb}} = \left[\sum_i \sum_{\alpha} \sum_k \rho_{k_i}^{\alpha} E_k - \sum_i \sum_{\alpha} \sum_k \rho_{k_i}^{\alpha} E_k^{\text{nonhyb}} \right] / N_b, \quad (3)$$

where the first term corresponds to the summation of one-electron energy, and the second term corresponds to the summation of diagonal element of Hamiltonian in the tight-binding-bond representation. E_k^{nonhyb} is the eigenenergy of the nonhybrid state and N_b is the number of hybrid bonds. α, i, k , respectively, label the partial-wave orbital, the atom and the eigenstate. From the numerical result of E_{hyb} given in Table I it can be seen that E_{hyb} is also sensitive to the configuration of B atoms. The cluster with a higher total energy and a stronger binding strength between B and a vacancy has a larger hybridization of orbitals.

We can now assess the probability of occurrence and

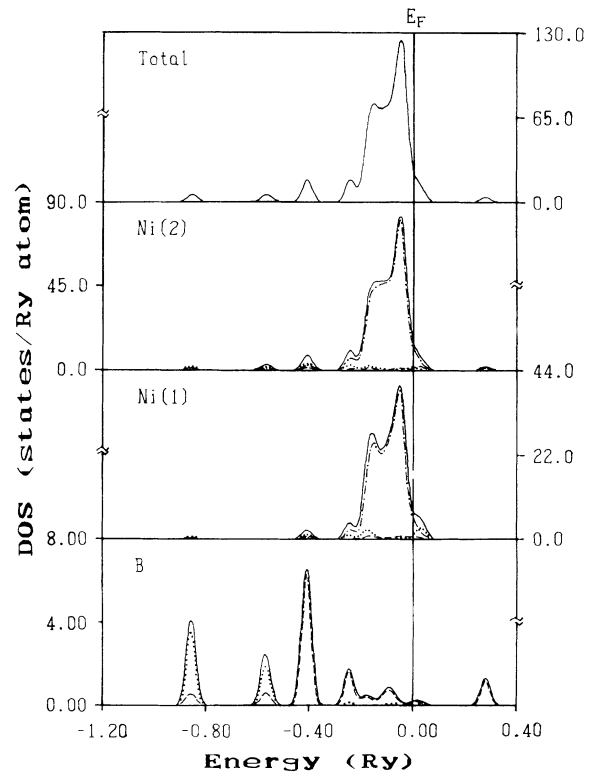


FIG. 5. Total density of state, local density of states (LDOS), and partial-wave local density of states (PLDOS) for model III of the B-V-B complex. Solid line, LDOS for atoms; dashed-dotted line, PLDOS for *d* orbitals; dashed line, PLDOS for *p* orbitals; dotted line, PLDOS for *s* orbitals. The Fermi energy E_F is chosen to be zero.

the significance of each model cluster. From the point of view of the size effect, the B-V-B complex in model II is overcompacted, which corresponds to a higher-energy condition. On the other hand, in model III the B-V-B complex is so loosely coupled with such a large separation between B and Ni atoms that it has little effect on the electronic structure. In terms of total energy, model II is the least probable and model III is the most probable. However, model III is insignificant because of the weak interaction and the small effect that the B-V-B complex has on the electronic structure, and model II is impossible because of the higher total energy. These comprehensive analyses show that models I and IV are the most likely and may have the most practical significance.

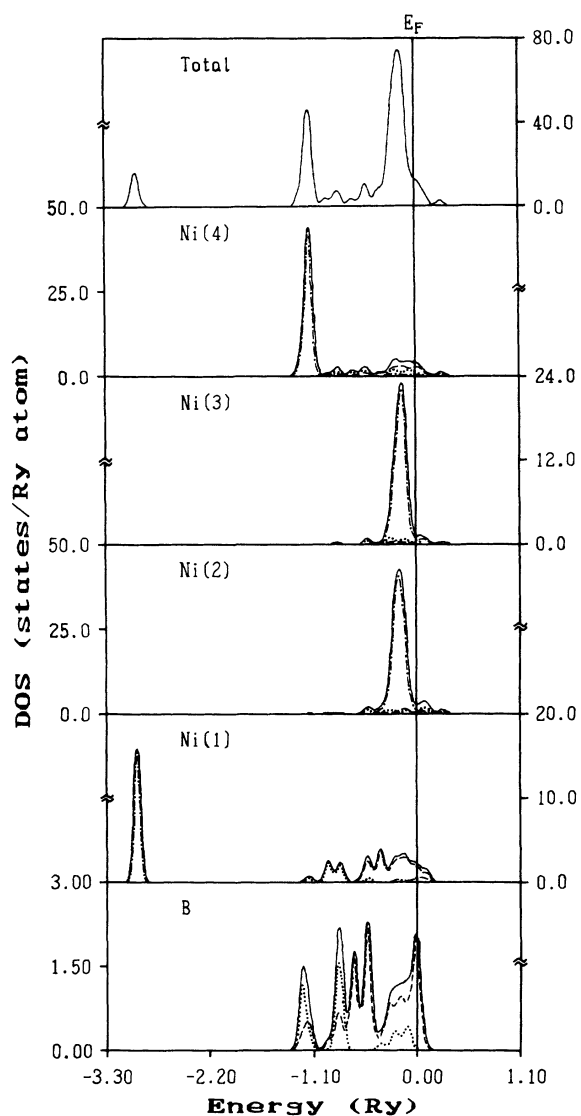


FIG. 6. Total density of state, local density of states (LDOS), and partial-wave local density of states (PLDOS) for model IV of the B-V-B complex. Solid line, LDOS for atoms; dashed-dotted line, PLDOS for d orbitals; dashed line, PLDOS for p orbitals; dotted line, PLDOS for s orbitals. The Fermi energy E_F is chosen to be zero.

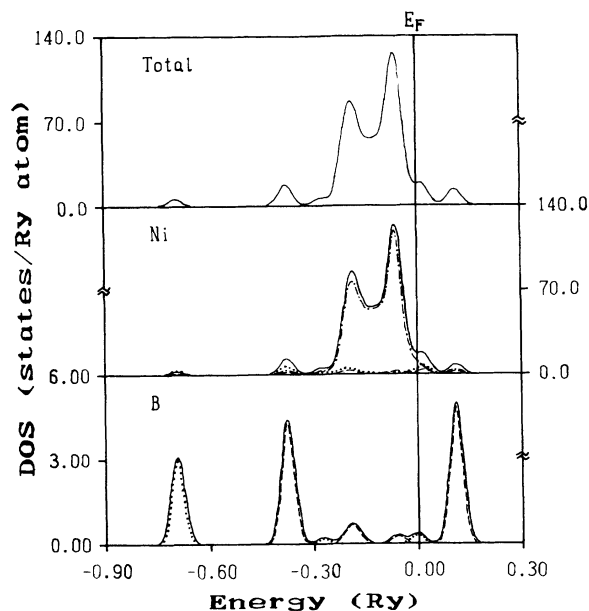


FIG. 7. Total density of state, local density of states (LDOS), and partial-wave local density of states (PLDOS) for the $Ni_{12}B$ cluster. Solid line, LDOS for atoms; dashed-dotted line, PLDOS for d orbitals; dashed line, PLDOS for p orbitals; dotted line, PLDOS for s orbitals. The Fermi energy E_F is chosen to be zero.

D. Charge transfer and the energy for charge redistribution

For studying the effect of B-V-B complex on charge distribution, we calculated the charge transfer and found it closely related to the orbital interaction among atoms. The calculated charge transfer on a B atom and its partial-wave orbitals are listed in Table III. The important feature of the charge transfer for the system containing B is that the electronic configuration of a B atom has been approximately changed into a $2s^1 2p^2$ state from a $2s^2 2p^1$ state of a free atom of B, that is, an s -orbital electron hole is produced on a B atom. The electron hole on the extended state may be regarded as an expression of the potential for charge redistribution. The displacement of atoms is related to the charge redistribution, and so we think that the improvement of the ductility of alloys caused by B impurities is related to the s -orbital electron holes on B atoms.

In order to quantify the energy closely related to the formation of the electron hole, we define the energy E_{red}^i for charge redistribution as follows:

$$E_{red}^i = \sum_{\alpha} \Delta n_i^{\alpha} \sum_k E_k \rho_{k_i}^{\alpha}, \quad (4)$$

TABLE III. Charge transfers on a B atom and its partial-wave orbitals in four models of the B-V-B complex and the $Ni_{12}B$ cluster.

	Model I	Model II	Model III	Model IV	$Ni_{12}B$
s	0.73	1.13	1.02	0.97	1.30
p	2.40	2.76	1.95	2.38	1.95
Total	5.13	5.89	4.97	5.35	5.25

where Δn_i^α is the variation of the electron occupation number on the α partial-wave orbital of the i th atom with respect to the free atom, E_k is the eigenvalue of the orbital, and ρ_k^α is the charge on the k th eigenstate contributed by α partial-wave orbital of the i th atom. The calculated result of E_{red}^i for the charge redistribution on a B atom is also given in Table I. The result indicates that besides model II, which has a low probability of occurring, models I and IV have also shown great potential for charge redistribution. Thus we may think that boron-containing alloys with a B-V-B complex can have good ductility.

IV. CONCLUSIONS

In this paper we have performed detailed calculations on the electronic structure of the B-V-B complex in Ni. The related physical response has been discussed in terms of physical quantities such as the binding tendency between the boron impurity and the vacancy, hybrid-bond energy, and the energy for charge redistribution. The major results and conclusions are as follows.

(1) The calculated results of the total energy and the binding tendency between the boron impurity and the vacancy indicate a strong binding between them, which is related to the mobility and the annihilation of supersaturated vacancies in a defect region. It may be expected that the B-V-B complex has a tendency to be formed spontaneously in a boron-containing alloy. The results are consistent with the experiments¹¹ on the segregation of boron in defect regions.

(2) From the density of states and the result of hybrid-bond energy it can be seen that, while model II with the highest total energy has the least probability, model III with the lowest total energy is also insignificant because of the weak interaction among atoms and the small effect of the B-V-B complex on the electronic structure. The results provide an understanding of the formation of a B-V-B complex. Although a B-V-B complex has a tendency to be formed spontaneously in a boron-containing alloy, it will eventually take one of the two configurations that are most probable, and will have a great effect on physical properties of the alloy.

(3) Information about the s -orbital electron hole has been obtained from the calculations of charge transfer. The relevant result of the energy for charge redistribution means that boron-containing alloys with a B-V-B complex are likely to have charge redistribution and thereby can have good ductility.

The quantities introduced in this paper for developing a quantitative understanding of some physical properties on the basis of electronic-structure calculations may be useful in studying various kinds of alloy system containing an impurity-defect complex, and can be regarded as a theoretical means to predict physical properties of materials.

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¹W. J. Pennington, *Met. Prog.* **73**, 82 (1958).

²A. T. Aust *et al.*, *Acta Metall.* **16**, 291 (1968).

³W. F. Jandeska, Jr. *et al.*, *Metall. Trans.* **3**, 2933 (1972).

⁴T. M. Williams, A. M. Stoneham, and D. R. Harries, *Met. Sci.* **10**, 14 (1976).

⁵*Boron in Steel*, edited by S. K. Banerji and J. E. Morral, in *Proceedings of the International Symposium on Boron Steels* (AIME, Warrendale, PA, 1980).

⁶N. Mori *et al.* (unpublished).

⁷E. Davis *et al.*, *Met. Constr.* **15**, 338 (1983).

⁸Y. Ogino and T. Yamasaki, *Metall. Trans. A* **15**, 519 (1984).

⁹B. Paintendre *et al.*, in *High Temperature Alloys for Gas Turbines and Other Applications*, edited by W. Betz *et al.* (Reidel, Dordrecht, 1986), Pt. 2, p. 877.

¹⁰T. J. Garossen, *Metall. Trans. A* **18**, 69 (1987).

¹¹L. Karlsson *et al.*, *Acta Metall.* **36**, 1 (1988); **36**, 13 (1988); **36**, 25 (1988).

¹²R. Haydock, *J. Phys. C* **14**, 3807 (1981).

¹³C. L. Braint and R. P. Messmer, *Acta Metall.* **30**, 457 (1982).

¹⁴R. P. Messmer and C. L. Braint, *Acta Metall.* **30**, 1811 (1982).

¹⁵M. Hashimoto *et al.*, *Acta Metall.* **32**, 13 (1984).

¹⁶M. E. Eberhart, K. H. Johnson, and R. M. Latanision, *Acta Metall.* **32**, 955 (1984).

¹⁷M. E. Eberhart, R. M. Latanision, and K. H. Johnson, *Acta*

Metall. **33**, 1769 (1985).

¹⁸M. E. Eberhart and D. D. Vvedensky, *Phys. Rev. Lett.* **58**, 61 (1987).

¹⁹G. S. Painter and F. W. Averill, *Phys. Rev. Lett.* **58**, 234 (1987).

²⁰M. E. Eberhart and D. D. Vvedensky, *Phys. Rev. B* **37**, 8488 (1988).

²¹Chen Ying, Wang Chongyu, and Fu-sui Liu, *Phys. Rev. B* **37**, 10510 (1988).

²²Wang Chongyu *et al.*, *Phys. Rev. B* **38**, 3905 (1988).

²³Wang Chongyu *et al.*, *J. Appl. Phys.* **71**, 239 (1992).

²⁴K. H. Johnson and F. C. Smith, Jr., *Phys. Rev. B* **5**, 831 (1972); J. C. Slater and K. H. Johnson, *ibid.* **5**, 844 (1972).

²⁵R. I. Jaffee, *Progress in Metals Physics* (Pergamon, New York, 1958), Vol. 7, p. 65.

²⁶M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry* (McGraw-Hill, New York, 1969), p. 134.

²⁷V. Heine, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35, p. 1.

²⁸Li Keng *et al.*, *Acta Scientiarum Naturalium Universitatis Pekinensis* **27**, 146 (1991); R. P. Messmer *et al.*, *Phys. Rev. B* **13**, 1396 (1976).