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Electronic structure in the Al-Mn alloy crystalline analog of quasicrystals

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Electronic structure in crystalline α-($Al_{114}Mn_{24}$) is calculated by the linear muffin-tin orbital–atomic-sphere approximation method with the local-density-functional theory. The density of states consists of a set of spiky peaks. The electronic structure is discussed for quasicrystalline Al-Mn alloy from the viewpoint of the stability and the role of the vacant center of the Mackay icosahedron. The stability is actually owing to the pseudogap of the Mn 3*d* band and the deep *s,p*-bonding bands of the Al glue atoms.

Since the discovery of the quasicrystals, theoretical considerations have focused on their structures and structural defects.[1] However, only a few papers have been devoted to theoretical studies on the electronic structures. The tight-binding models of the one-dimensional quasicrystal (Fibonacci lattice) and the two-dimensional quasicrystal (Penrose lattice) have been studied intensively from the viewpoint of the singular behavior of energy spectra and the localization of wave functions.[2,3]

The electronic structure in three-dimensional Penrose lattice was analyzed in a very simple tight-binding model, and we observed the existence of infinitely degenerate states confined strictly in a finite range of the real space.[4] The electronic structure of realistic quasicrystals is a completely open problem except for a small-cluster calculation[5] and a phenomenological attempt at the energetics of icosahedral stability.[6] Transport properties were also discussed on the basis of the weak scattering and the perturbation treatment.[7] Knowledge of the electronic structure in three-dimensional quasicrystals is quite important not only for understanding the electronic properties but also for understanding the stability and interatomic potentials. Recently, it has been proved that the incorporation of both attractive and repulsive interactions is essential for the observed equilibrium shapes of icosahedral quasicrystals.[8]

The purpose of this paper is to present the electronic band structure of a cubic $Al_{114}Mn_{24}$ alloy crystal analogous to quasicrystals and to discuss the cohesive properties, the stability of the so-called 54-atom Mackay icosahedron as a constituent unit, and several interatomic interactions.

We calculated the electronic structure of the idealized α-(Al-Mn-Si) alloy (the Elser-Henley model[9]), which is the three-dimensional (1/1)-periodic Penrose lattice with a uniquely decorated unit, i.e., rhombic dodecahedron. The periodic Penrose lattice can be generated by introducing phase defects (equivalent to the minimal rational approximation to the golden mean) and is a commensurate structure of the original quasiperiodic lattice.[3,9] We will not distinguish Si atoms from Al atoms because the preferred positions of Si atoms have not been experimentally determined. We then call it α-(Al-Mn) rather than α-(Al-Mn-Si).

In the idealized α-(Al-Mn-Si) structure, there are six classes of atomic sites: one Mn atomic site and five Al or Si atomic sites [α, $\beta(1)$, $\beta(2)$, γ, and δ]. The large holes are at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, forming a perfect bcc lattice, which is of two interpenetrating simple-cubic (sc) sublattices. Six δ sites are occupied in one sc sublattice by Al or Si but the other six δ sites in the other sc sublattice remain unoccupied. Therefore, α-(Al-Mn-Si) is not a bcc but rather a simple-cubic crystal and its space-group symmetry is $Pm3$. The unit cell is a packing of six rhombic dodecahedra (RD) and eight prolate rhombohedra (PR), where the atomic decoration is only for a RD and a PR has no interior atoms. The faces of a PR are shared with RD's. Two vertices of one RD connected by the longest body diagonal are positions of the already mentioned large holes. Around this hole (a MI center), 12 Al(α), 12 Mn, 24 Al($\beta(1)$), and 6 Al($\beta(2)$) form a so-called 54-atom Mackay icosahedron (MI).

The innermost shell of a MI consists of 12 Al(α) atoms, and 12 Mn atoms are on the vertices of a MI. An Al(α) atom sits at the midpoint of an edge joining the MI center to a Mn atom. Atoms Al($\beta(1)$) and Al($\beta(2)$) locate nearly on the edges of a MI midway between two Mn atoms. Two adjacent MI's share a distorted Mn octahedron. (See Fig. 1 of Guyot and Audier.[9] These six Mn atoms on vertices of the octahedron and two centers of adjacent MI's form a PR.) The center of this distorted octahedron is a small vacant site (a PR center). An Al($\beta(1)$) is on the face of PR and, therefore, shared by a MI and a distorted octahedron. The Al icosahedra [Al(α)'s on the inner shells of MI's] are themselves interconnected through chains of three octahedra of Al atoms [Al(α) and Al($\beta(1)$)]. An Al($\beta(2)$) sits on one of the other six edges of a MI, whose nearest-neighbor sites are a δ. Sites γ and δ are for glue Al and Si atoms. In α-(Al-Mn-Si), all γ sites and half of the δ sites are occupied by Al or Si atoms but the other half of the δ sites (six sites) are unoccupied. Hereafter, the sc sublattice with vacant atomic δ sites is labeled by subscript "2" and the other sc sublattice with Al atoms on the δ sites labeled by subscript "1", whenever necessary. It is widely believed that the MI is the stable unit, so that MI's are packed randomly and some glue atoms fill the remaining vacant

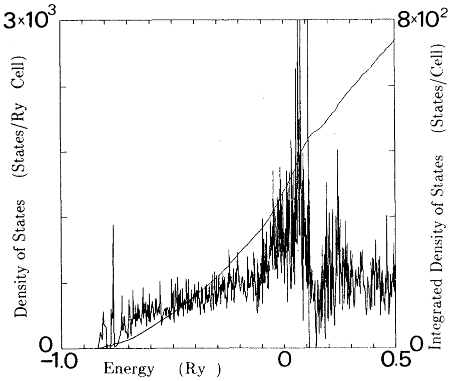

FIG. 1. Total density of states and integrated density of states in a unit cell. The Fermi energy is 0.115 Ry, shown by the vertical line.

space in quasicrystals.

The electronic structure of the idealized α-(Al-Mn) was calculated self-consistently by the linear muffin-tin orbital (LMTO) method[10] with use of the von Barth–Hedin exchange-correlation potential.[11] The LMTO method is sufficiently precise and one of the more transparent among several band-structure calculation methods, related to the energy linearization of the Korringa-Kohn-Rostoker (KKR) method, and is quite efficient in computations for solids with large unit cells. The whole space is divided into overlapping atomic spheres (atomic-sphere approximation), which are 114 Al, 24 Mn and 16 atomic-site vacancies (empty atoms), totaling 154 atoms and vacancies, in a simple-cubic unit cell. The atomic positions have been shifted slightly from the observed values in α-(Al-Mn-Si) to the idealized values and summarized in Table I together with the values of atomic-sphere radii. The position of δ sites is shifted slightly further from the idealized position on the body diagonal of the internal PR of the RD, because the atomic-sphere radius on the idealized position would be too small for an Al atom. Self-consistency was achieved with use of 20 **k** points in an irreducible wedge of the sc first Brillouin zone.

The total density of states (DOS) and integrated density of states (IDOS) are shown in Fig. 1. The DOS consists of a set of spiky peaks and each band is highly dispersionless, as may be seen in Fig. 2. The Fermi energy E_F is 0.115 Ry; the main peak at $E \simeq -0.1-0.3$ Ry comes mainly from the Mn $3d$ states and the deep tail of the DOS mainly from the Al $3s$ state with hybridization of Mn $4s$. The Al $3p$ states are strongly mixed with Mn $3d$ states. These can be seen in the local DOS's projected according to s, p, and d symmetries. This very narrow ($\simeq 0.07$ Ry) and high peak of the Mn $3d$ DOS in α-(Al-Mn) is simply due to disfavor of Mn-Mn neighbor pairs. The antiresonance pseudogap locates at the middle of the Mn $3d$ band, which is clearly seen at $E \simeq 0.14$ Ry in both the DOS and E-**k** structure. This pseudogap is one of origins stabilizing the locally icosahedral symmetry. The small-cluster calculation[5] shows that an isolated icosahedral symmetry always gives rise to a high peak of the DOS at E_F and the relative instability of a MI.

The overall feature of the DOS is rather similar to that of τ-(Mn-Al) (Ref. 12) (the ordered CuAu-I structure) ex-

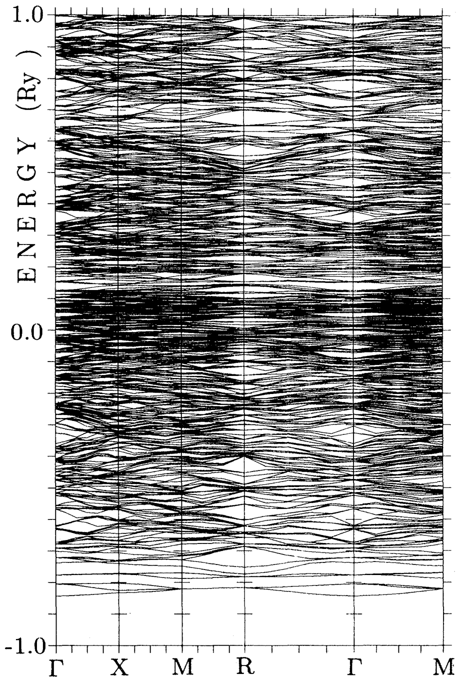

FIG. 2. Energy band along high-symmetry lines.

TABLE I. Coordinates and radii of atomic spheres. $u = D/2(D+d)$ and $v = d/2(D+d)$ [$\tau = (\sqrt{5}+1)/2$, $D = \sqrt{2}(1+1/\sqrt{5})$ $d = \sqrt{2}(1-1/\sqrt{5})$] in the unit of the sc lattice constant $a = 12.68$ Å. The space-group symmetry is $Pm3$. The independent positions in one sc sublattice are given. Another set of independent positions in the other sc sublattice is generated by the translation $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. All sites can be generated by the symmetry operations of $Pm3$.

Site	Number in a unit cell	Coordinate	Atomic-sphere radius (Å)
Mn	24	$(u,v,0)$	1.4560
α	24	$(u/2,v/2,0)$	1.4560
$\beta(1)$	48	$(u,-v/\tau,v)$	1.5126
$\beta(2)$	12	$(2v,0,0)$	1.6002
γ	24	$(u+v,v,u/3)$	1.4457
δ	12	$(u+v,0,v-0.03)$	1.4457
MI center	2	$(0,0,0)$	1.4561
PR center	8	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})$	1.0115

cept for the Mn $3d$ band splitting. The paramagnetic DOS of τ-(Mn-Al) has a very high and narrow peak of Mn $3d$ at E_F without splitting and, resultingly, gives rise to a strong ferromagnetism with a saturation moment $2.31\mu_B$/Mn-atom. In the present α-(Al-Mn) case, on the other hand, the high peak of the Mn $3d$ band is split at its middle near E_F and the crystalline α-(Al-Mn-Si) should have the paramagnetic ground state. Even so, the Fermi energy E_F locates at the tail of the very high DOS peak and some fluctuation of local environment might cause the formation of the local magnetic moment, which may explain the spin-glass-like magnetic behavior in the icosahedral Al-Mn-Si.[13]

The local DOS's and IDOS's are shown in Figs. 3 (a)–3(j). Those in sublattice (2) are quite similar to corresponding ones in sublattice (1) except for $[\mathrm{Al}(\beta(2))]_{(2)}$ and the vacancy $\delta_{(2)}$. Below E_F in both Mn and Al atoms, the main contribution of the s DOS is in a lower-energy region and that of the p DOS in a higher-energy region.

The deviation of E_F from the high DOS peak is mainly due to the antiresonance pseudogap at $E\simeq0.14$ Ry, which is related to the resonance peak at $E\simeq0.1$–0.13 Ry in Mn d, Al(α) p and $[\mathrm{Al}(\beta(2))]_{(2)}$ p. In the sc sublattice (1), an $[\mathrm{Al}(\beta(2))]_{(1)}$ atom has neighboring $[\mathrm{Al}(\delta)]_{(1)}$ atoms, the electron wave function extends outside the MI through $[\mathrm{Al}(\delta)]_{(1)}$ atoms, and the resonance peak cannot be seen at $E\simeq0.1$–0.13 Ry in $[\mathrm{Al}(\beta(2))]_{(1)}$. In other words, the resonance peak at $E\simeq0.1$–0.13 Ry is mainly confined within atoms forming the MI. The Mn $3d$ DOS has a very sharp resonance peak at $E\simeq0.05$ Ry and an abrupt drop at the pseudogap just above it. The related peaks are also seen ($E\simeq0.05$ Ry) in DOS's of Al(γ) p and $[\mathrm{Al}(\delta)]_{(1)}$ p but not in that of the vacancy δ. Another binding peak of the DOS can be also observed at $E\simeq-0.05$ Ry in the local projected DOS of Mn d, Al(α) p, and Al($\beta(2)$) p which can also claim the stability of the MI.

Table II shows the valence-electron density parameter r_s ($=r_{\mathrm{AS}}/n_{\mathrm{VE}}^{1/3}$ where r_{AS} is the atomic-sphere radius and n_{VE} is the valence-electron number.) The value of the atomic-sphere radius in a pure Al is 2.99 a.u. and $r_s=2.07$ a.u. The r_s in Al($\beta(2)$) is increased but is partly due to the large atomic-sphere radius. The valence-electron densities are enhanced in Al(α), Al(γ), and $[\mathrm{Al}(\delta)]_{(1)}$. In $[\mathrm{Al}(\delta)]_{(1)}$, this may be due to the formation of the bonding Al s states with $[\mathrm{Al}(\gamma)]_{(1)}$ and $[\mathrm{Al}(\beta(2))]_{(1)}$ at $E\simeq-0.8$ Ry. The pseudopotential theory can tell that the repulsive core largely expands in the pure Al crystal and covers the first minimum (approximately equal to the nearest-neighbor distance) of the interatomic potential.[14] Therefore, the first-neighbor interaction is repulsive in pure Al and this may be expected also here in Al-Al pairs. The nearest-neighbor interactions through Al atoms, especially $[\mathrm{Al}(\delta)]_{(1)}$, may be repulsive and distant-neighbor interaction should be attractive. These complicated interactions might stabilize the exotic structure of quasicrystals and its equilibrium shape. The bonding state at $E\simeq-0.8$ Ry shows the importance of glue atoms. It should be noticed that

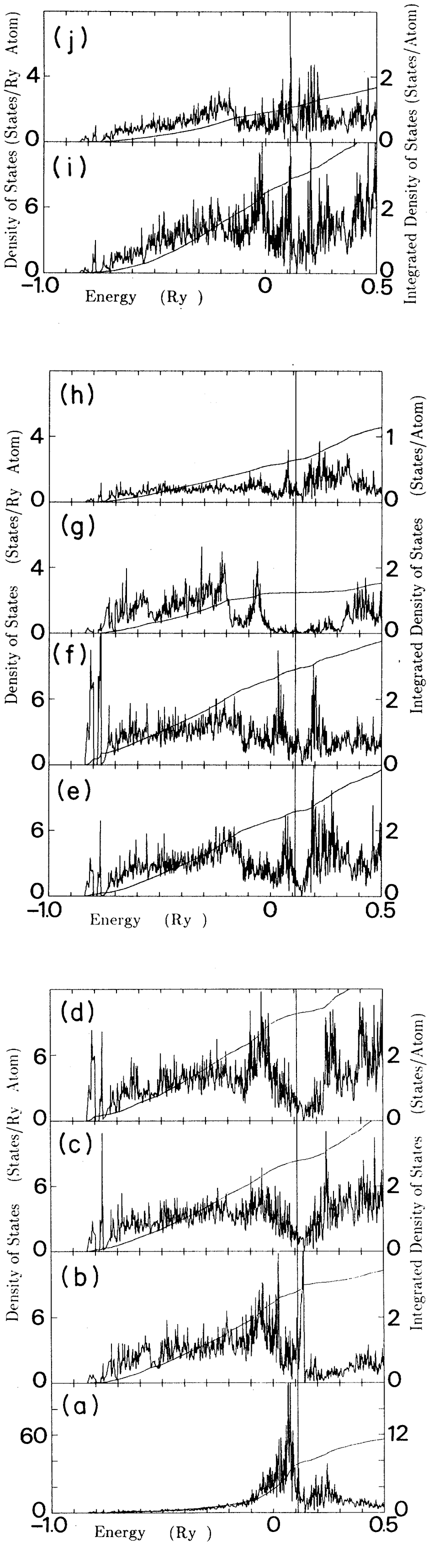

FIG. 3. Local density of states and integrated density of states in atoms in the sc sublattice (1) and in $[\mathrm{Al}(\beta(2))]_{(2)}$ and the vacancy $\delta_{(2)}$. (a) $\mathrm{Mn}_{(1)}$, (b) $[\mathrm{Al}(\alpha)]_{(1)}$, (c) $[\mathrm{Al}(\beta(1))]_{(1)}$, (d) $[\mathrm{Al}(\beta(2))]_{(1)}$, (e) $[\mathrm{Al}(\gamma)]_{(1)}$, (f) $[\mathrm{Al}(\delta)]_{(1)}$, (g) $(\text{MI center})_{(1)}$, (h) $(\text{PR center})_{(1)}$, (i) $[\mathrm{Al}(\beta(2))]_{(2)}$, and (j) vacancy $\delta_{(2)}$.

TABLE II. Charge density of Al atomic spheres (r_s in atomic units).

Site [sublattice (1)]	r_s	Site [sublattice (2)]	r_s
$[\mathrm{Al}(\alpha)]_{(1)}$	1.95	$[\mathrm{Al}(\alpha)]_{(2)}$	1.94
$[\mathrm{Al}(\beta(1))]_{(1)}$	2.03	$[\mathrm{Al}(\beta(1))]_{(2)}$	2.04
$[\mathrm{Al}(\beta(2))]_{(1)}$	2.20	$[\mathrm{Al}(\beta(2))]_{(2)}$	2.12
$[\mathrm{Al}(\gamma)]_{(1)}$	1.99	$[\mathrm{Al}(\gamma)]_{(2)}$	1.97
$[\mathrm{Al}(\delta)]_{(1)}$	1.91	vacancy $\delta_{(2)}$	2.66
MI center	2.55	MI center	2.56
PR center	2.20	PR center	2.20

$[\mathrm{Al}(\beta(2))]_{(1)}$ has a peak at $E \simeq -0.8$ Ry but not $E \simeq 0.1$ Ry and $[\mathrm{Al}(\beta(2)]_{(2)}$ has at $E \simeq 0.1$ Ry but not $E \simeq -0.8$ Ry.

The local DOS's at a MI center, a PR center, and a vacant δ site are quite different from each other. Those at the PR center and the vacant δ site do not have any characteristic structure and are broad, flat, and low bands, which means that the tails of neighboring wave functions extend uniformly inside the PR center and the vacant δ site. On the other hand, that at a MI center shows specific s- and p-type character in lower-energy region but near the Fermi energy no DOS is seen. We then conclude that the tail of the neighboring wave functions extends inside the MI center in the deep energy range but not at E_F.

To understand the stability of the MI, we see a role of glue atoms Al(γ) and Al(δ). After determining all potential parameters[10] by the self-consistent calculations, we changed the values of the unhybridized band centers of Al(γ) and Al(δ) atoms by an amount of 0.5 Ry to the higher-energy side and kept other potential parameters unchanged. This may give an approximate situation where Al(γ) and Al(δ) atoms would be replaced by vacant atoms. The total valence charge on each atom does not change much but the local DOS in the region $E \leq -0.5$ Ry is highly reduced, which causes a large reduction of cohesive energy. Furthermore, several narrow peaks appear in the whole energy range, which corresponds to the almost localized states within each MI. These facts suggest that the large amount of electrons extends outside MI through the glue atoms and forms Al s, p-bonding bands at $E \leq -0.5$ Ry and deep bonding Al s states at $E \simeq -0.8$ Ry.

The center of a MI has enough space for an Al atom but actually it remains vacant. This must be understood from the viewpoint of stability. For doing this, we calculated the self-consistent electronic structure again in a system with Al atoms occupying the MI centers. Overall features have not been altered except the following: The p DOS on Al (MI center) is enhanced at $E \simeq -0.6$ to -0.8 Ry and the s DOS on Al (MI center) at $E \simeq -0.8$ Ry with resonating s DOS in the same energy range on Al(α), $[\mathrm{Al}(\beta(1))]$, and $[\mathrm{Al}(\beta(2))]_{(1)}$. The local DOS on Al (MI center) vanishes in the Fermi energy region with a width of about 0.3 Ry as the original vacant MI center. The total valence charge on an Al atom at the MI center is reduced to about $2.4e$/atom ($r_s = 2.06$ a.u.). The remaining excess valence charge is distributed on the surrounding neighbors (reducing their r_s) at around the Fermi energy and we do not find a gain in the cohesive energy. Therefore, the MI center could be a stabilization center for group-I or -II atom but not for Al, and is left vacant.

The spiky DOS should be a common feature in crystalline and quasicrystalline Al-Mn. The spiky peaks are due to the densely distributed dispersionless bands shown in Fig. 2, which are not localized states. We might imagine that this is the case also in amorphous systems. In amorphous systems, the randomness can actually achieve the self-averaging and the DOS should be smooth and of well-defined quantity. In the present case and quasicrystalline systems, if there would be no randomly distributed defects, the spiky peaks survive and affect some characteristics in physical properties, for instance, nonlinear electric conductivity.

Finally, we can try to explain the role of Si atoms in α-(Al-Mn-Si) and quasicrystal (Al-Mn-Si). With 14 Al atoms substituted by Si atoms ($\mathrm{Al}_{100}\mathrm{Mn}_{24}\mathrm{Si}_{14}$)=$\alpha$-(Al-Mn-Si), the Fermi energy climbs towards the antiresonance gap (an energy shift $\Delta E \simeq 0.02$ Ry), and the stability of the compound would be much enhanced.

We have calculated electronic structures in crystalline α-(Al-Mn). In order to understand the role of glue atoms and vacancies at MI centers, we have done several calculations. The antiresonance pseudogap stabilizes the linked MI's, which was not seen in an isolated one. Glue atoms are essential for forming bonding s,p bands at $E \leq -0.5$ Ry and deep bonding Al s states at $E \simeq -0.8$ Ry, and stabilize the dense-packed system of Mackay icosahedra, periodic or aperiodic. From the electronic point of niew, the MI's should be densely packed, adjusting their sites and allowing enough space for glue atoms. This point might be taken into account while constructing structural models of icosahedral glasses, for example, favorable content and geometry of glue atoms might be important parameters of the structural models.

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[1] D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984); D. Levine and P. J. Steinhardt, *ibid.* **53**, 2477 (1984); *The Physics of Quasicrystals,* edited by P. J. Steinhardt and S. Ostlund (World Scientific, Singapore, 1987).

[2] M. Kohmoto, B. Sutherland, and C. Tang, Phys. Rev. B **35**, 1020 (1987); P. A. Kalugin, A. Yu. Kitaev, and L. S. Levitov, Zh. Eksp. Teor. Fiz. **91**, 692 (1986) [Sov. Phys.—JETP **64**, 410 (1986)].

[3] H. Tsunetsugu, T. Fujiwara, K. Ueda, and T. Tokihiro, J. Phys. Soc. Jpn. **55**, 1420 (1986).

[4] M. Krajci and T. Fujiwara, Phys. Rev. B **38**, 12 903 (1988).

[5] M. E. McHenry, M. E. Eberhart, R. C. O'Handley, and K. H. Johnson, Phys. Rev. Lett. **56**, 81 (1986).

[6] A. C. Redfield and A. Zangwill, Phys. Rev. Lett. **58**, 2322 (1987).

[7] J. B. Sokoloff, Phys. Rev. B **36**, 6361 (1987).

[8] K. Ingersent and P. J. Steinhardt, Phys. Rev. B **39**, 980 (1989).

[9] V. Elser and C. L. Henley, Phys. Rev. Lett. **55**, 2883 (1985); P. Guyot and M. Audier, Philos. Mag. B **51**, L15 (1985).

[10] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[11] V. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[12] T. Fujiwara (unpublished).

[13] K. Fukamichi, T. Goto, T. Masumoto, T. Sakakibara, M. Oguchi, and S. Todo, J. Phys. F **17**, 743 (1987).

[14] J. Hafner and V. Heine, J. Phys. F **13**, 2479 (1983).