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The possibility of ferromagnetic BCC ruthenium

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Abstract. Band-structure calculations based on the augmented-plane-wave method and the rigid-band model are used to investigate the ferromagnetic 4d transition metals in the constrained crystal structure. The densities of states of 4d transition metals at the Fermi energy are estimated from those calculated for BCC and FCC Rh in paramagnetism. The results show that BCC Ru seems to be ferromagnetic using the Stoner criterion because of the high density of states. The band structure of Ru is studied in detail using the first-principles total-energy-band calculation by the Korringa–Kohn–Rostoker method based on the local-density approximation, whether ferromagnetic BCC Ru exists or not. It is concluded that BCC Ru has a magnetic moment of about $1\mu_B$ at 5% expanded lattice constant.

1. Introduction

It is expected that changes in the crystal structure and lattice constant cause a transition in magnetism. The volume and structure dependence of the ground-state magnetic properties of FCC Fe predicted by electron band-structure calculations have stimulated new theoretical and experimental activities. Kübler [1] has made calculations for BCC and FCC Fe using the augmented-spherical-wave method based on the spin-density-functional approximation. It was predicted that FCC Fe is antiferromagnetic. This prediction has been confirmed by Macedo and Keune [2] experimentally. Thin epitaxial layers of FCC Fe have been stabilized on FCC Cu substrates and proved to be antiferromagnetic.

It is very useful to make calculations and to predict properties for the assumed crystal structure and lattice constant. Epitaxial growth technology has recently made remarkable progress. This technology can be directly applied to the material design for industrial use and is one of the most attractive techniques. Now it is possible to obtain materials with the desired crystal structure and lattice constant to some extent.

The magnetic properties of 3d transition metals which exist naturally have been studied in detail using band calculations [3]. The effect of impurities of the 3d and 4d transition metals in Fe has been calculated [4] and it has been shown that the results were in good agreement with the experimental results. In a non-equilibrium phase the magnetic dependences on the crystal structure and volume of ferromagnetic (FM) Fe, Co, Ni [5] all 3d transition metals [6], FCC Rh, Pd [7], BCC Mn, FCC Mn, BCC Nb, FCC Rh [8] and FCC Pd [9] and of all AFM 3d [10] and 4d [11] elements have been calculated over the past decade. It is found that the susceptibility of the transition metals increases with increasing volume and may lead to a paramagnetic–ferromagnetic or paramagnetic–antiferromagnetic phase transition. The magnetic structure of alternative cubic phases of transition metals was

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investigated [12] using the Stoner theory and Janak's procedure. However, the magnetic dependence on the crystal structure and volume of 4d transition metals have not been studied in detail. The 4d transition metals are not ferromagnetic normally, although the electronic structures are similar to the 3d transition metals which include ferromagnetic Fe, Co or Ni.

In this paper, we investigate systematically the possibility of ferromagnetic 4d transition metals assuming that they have the BCC and FCC structure using a band calculation. In particular, we study the assumed BCC Ru in detail which has the possibility of being ferromagnetic using the first-principles total-energy-band calculation.

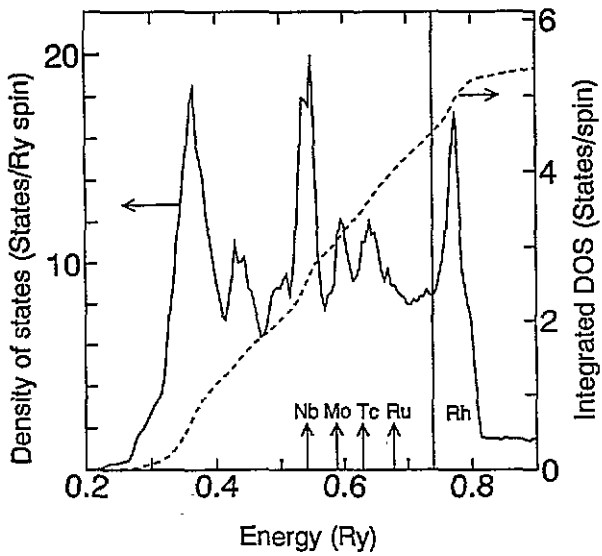

Figure 1. DOS of paramagnetic FCC Rh calculated by the APW method. The Fermi energy of the other 4d transition metals estimated by applying the rigid-band model are also shown with arrows.

2. Calculation method

First of all, the band structures of paramagnetic Rh are calculated as a representation of 4d transition metals using the augmented-plane-wave (APW) method [13] based on the local-density approximation. The rigid-band model has been used to study the possibility of ferromagnetism for 4d transition metals. Rh is a FCC structure in the ground state. The calculation is made at a lattice constant a_{FCC} of 7.186 au, which is obtained experimentally. The lattice constant a_{BCC} of BCC Rh is assumed to be the muffin-tin radius of BCC Rh which agrees with that of FCC Rh. It follows that the lattice constant of BCC Rh is 5.868 au. The relations between the muffin-tin radius r_i and the lattice constant are as follows: $r_i = \sqrt{3}/4a_{BCC}$; $r_i = \sqrt{2}/4a_{FCC}$. Applying the rigid-band model to the calculated density of states (DOS) of BCC and FCC Rh, the Fermi energy and DOS at the Fermi energy of the other 4d transition metals (Nb, Mo, Tc, Ru and Rh) are estimated.

It is well known that, if the Fermi energy is on the peak of the paramagnetic DOS, the elements have the tendency to become ferromagnetic [14]. Some elements are candidates

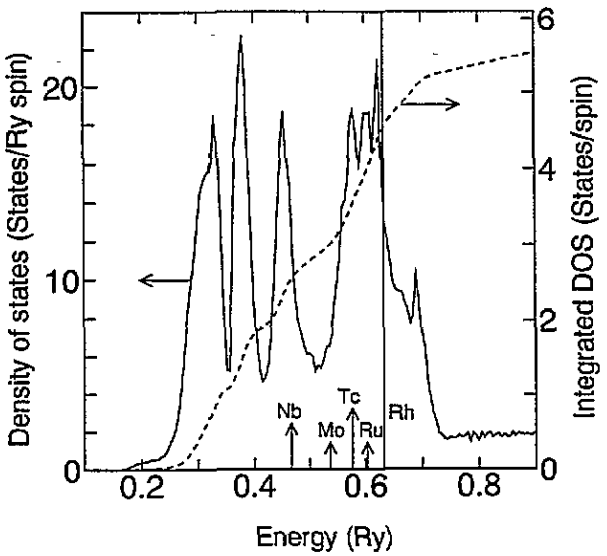

Figure 2. DOS of paramagnetic BCC Rh calculated by the APW method. The Fermi energies of the other 4d transition metals estimated by applying the rigid-band model are also shown with arrows.

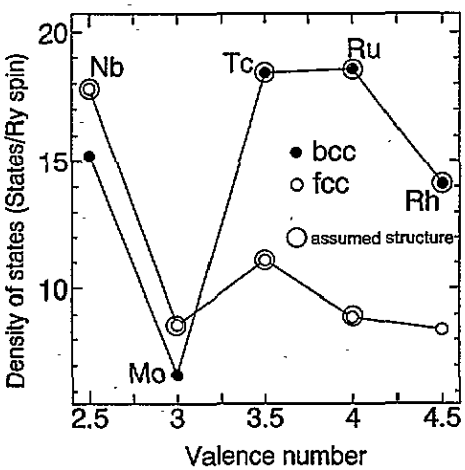

Figure 3. DOSS at the Fermi energy of 4d transition metals versus valence number: ○, FCC Ru; ●, BCC Ru.

for ferromagnetic elements using this criterion. It is found that BCC Ru is one of the most promising elements. So, the electronic structure and magnetism of BCC Ru have been calculated as functions of the volume using the Korringa–Kohn–Rostoker (KKR) Green function method [15, 16] based on the local-spin-density functional theory. The first-principles KKR method shows good agreement with the experimental results in electronic structure [17]. The Perdew–Zunger [18] formula for the exchange–correlation potential is adopted. The basis set contains s, p and d orbitals. The k-integral is calculated with the prism method [19, 20]. The number of k-points within the one-fortyeighth irreducible wedge of

the Brillouin zone is 1920 [17]. The total energy converges to less than 10^{-2} mRyd atom^{-1}. The moment and energy of FCC Ru are also calculated to estimate the energy difference between the ground state and the BCC structure.

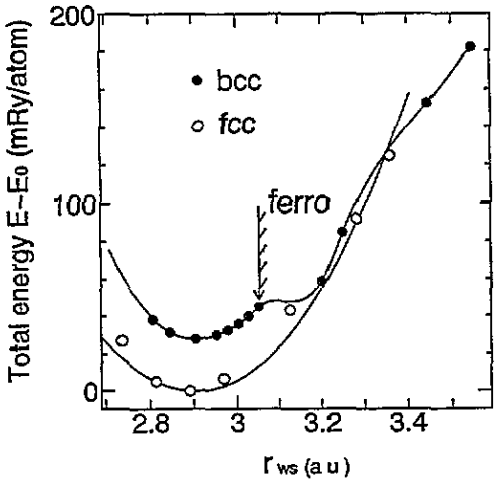

Figure 4. Total energy versus r_{WS} for BCC and FCC Ru: ●, total energy of BCC Ru; ○, total energy of FCC Ru. The reference energy E_0 is the energy minimum for the FCC Ru.

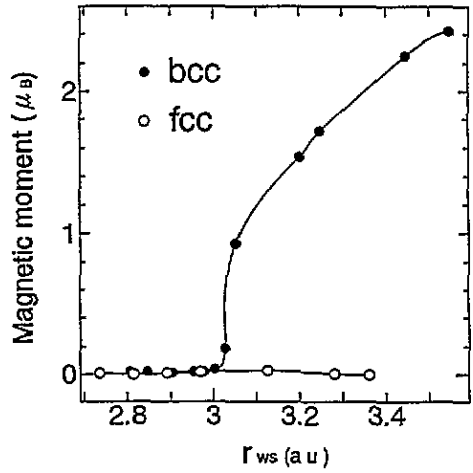

Figure 5. Magnetic moment versus r_{WS} for BCC and FCC Ru: ●, magnetic moment of BCC Ru; ○, magnetic moment of FCC Ru.

3. Results and discussion

The DOSs of FCC and BCC Rh calculated in paramagnetism are shown in figure 1 and figure 2, respectively. The Fermi energies of the 4d transition metals estimated from the rigid-band model are also shown with arrows in the figures. The Fermi energies of FCC Nb, BCC Tc and BCC Ru are near the peak of the DOS. Figure 3 shows the DOS at the Fermi energy of each element. BCC Ru has the largest value at the Fermi energy. Asano and Yamaguchi [21] show that 3d transition metals become ferromagnetic when the DOS at the Fermi energy in a paramagnetic state is larger than 17–20 states Ryd^{-1} spin. The BCC Ru is expected to become ferromagnetic. The fact that BCC Fe (isoelectronic to Ru) is ferromagnetic with a moment of $2.2\mu_B$ also encourages such an expectation. Here BCC Ru is found to be a candidate for a new ferromagnetic element.

The total energy and magnetic moment per atom of Ru as functions of the Wigner–Seitz radius r_{WS} (or equivalently, as functions of the volume V per atom given by $V = (4\pi/3)r_{WS}^3$) are shown in figures 4 and 5, respectively. The reference energy E_0 is the energy minimum for FCC Ru. The full circles show the energies for the BCC structure and the open circles show the energies for the FCC structure. FCC Ru does not have a magnetic moment within the range of calculated volumes and the total energy of FCC Ru varies in a quadratic manner as functions of the Wigner–Seitz radius. On the other hand, BCC Ru has a magnetic moment while the Wigner–Seitz radius is larger than 3.05 au. BCC Ru is metastable when the Wigner–Seitz radius is 2.91 au. The total energy of FCC Ru is lower than that of BCC Ru, relatively. The total energy of BCC Ru is quadratic as a function of the Wigner–Seitz radius near the

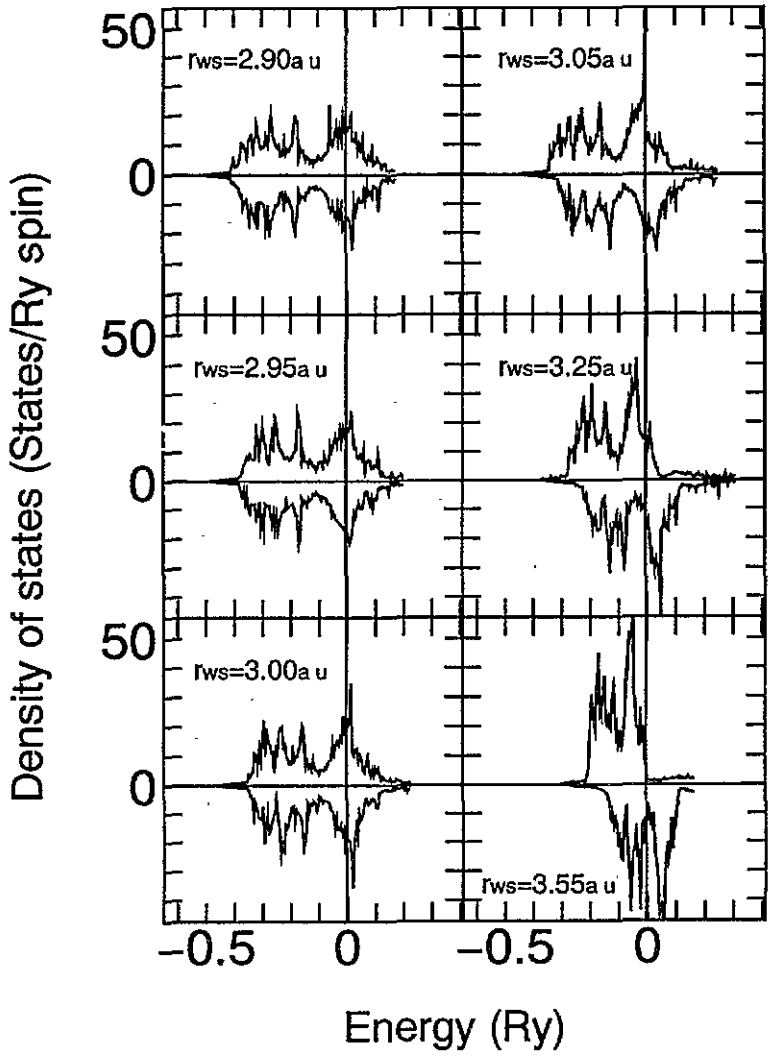

Figure 6. DOS of BCC Ru at various Wigner–Seitz radii.

minimum point but the ferromagnetic transition causes a decrease in the energy. The point of inflection appears because the spin polarization of BCC Ru profits in the exchange energy and increase its energy compared with FCC Ru; so the difference between the total energy of BCC and that of FCC Ru becomes smaller when the volume is larger.

Figure 6 shows the DOS of BCC Ru when the Wigner–Seitz radii are 2.90, 2.95, 3.00, 3.05, 3.25 and 3.55 au. The Fermi energy is on the peak of the DOS when BCC Ru is paramagnetic. The band width becomes narrow and the DOS at the Fermi energy becomes large as the Wigner–Seitz radius increases.

The d-band width of BCC Ru is shown in figure 7. Figure 7(*a*) gives the relation between the d-band width and the Wigner–Seitz radius. The d-band width becomes narrow as r_{WS} increases. Figure 7(*b*) shows the relation between the d-band width and r_{WS}^{-5}. Hein's [22] r^{-5} dependence for d-band width is confirmed by the linear relations. The majority d band

is lower in energy than the minority d band and they merge into one where the system becomes paramagnetic.

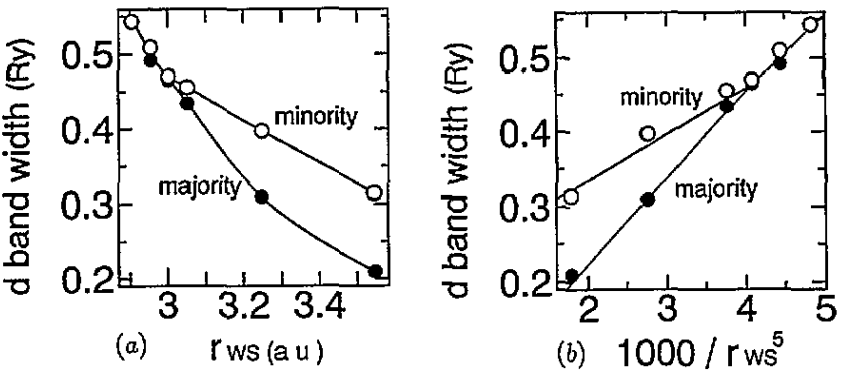

Figure 7. (*a*) The d-band width versus r_{WS} and (*b*) the d-band width versus r_{WS}^{-5} for BCC Ru.

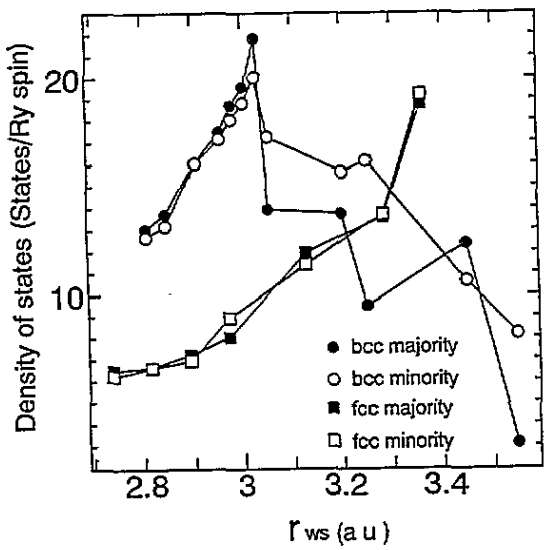

Figure 8. DOS at the Fermi energy of BCC Ru versus r_{WS}: ●, majority spin of BCC Ru; ○, minority spin of BCC Ru; ■, majority spin of FCC Ru; □, minority spin of FCC Ru.

The DOSs at the Fermi energy for up and down spins as functions of the Wigner–Seitz radius are shown in figure 8. The increase in volume causes an enhancement in the DOS at the Fermi energy for both the BCC and the FCC structure. This is attributed to narrowing of the d band width which is caused by the expanded volume. The DOS at the Fermi energy of BCC Ru is relatively larger than that of FCC Ru at the same r_{WS}. The DOS for both spins at the Fermi energy is nearly proportional to the volume when it is smaller than a critical value. When the DOS is larger than the critical value, i.e. the DOS exceeds the Stoner criterion, spin polarization occurs and the DOS at the Fermi energy decreases. The largest

DOS at the Fermi energy is about 43 states Ryd^{-1} adding the majority- and minority-spin values. Using the Stoner criterion $n(E_F)J_{eff} > 1$, the effective exchange integration J_{eff} of Ru is determined to be about 0.023 Ryd. Janak [23] has calculated J_{eff} systematically and he showed that the J_{eff} of Ru is 0.022 Ryd. Our result is in good agreement with Janak's value. By simple extrapolation of the DOS at the Fermi energy of the FCC phase, the value of r_{WS} which exceeds the Stoner criterion is predicted to be 3.45 au. This value is about 22% larger than that of the stable state of FCC Ru; so it is difficult for Ru to become ferromagnetic.

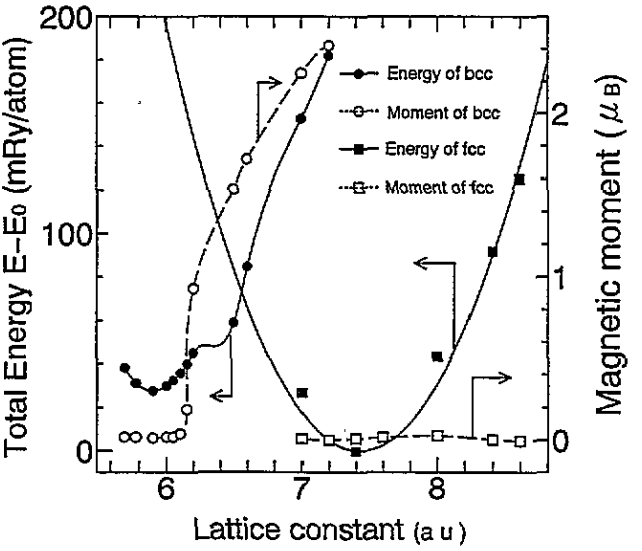

Figure 9. Total energy and magnetic moment of BCC and FCC Ru versus r_{WS}: ●, energy of BCC Ru; ○, magnetic moment of BCC Ru; ■, energy of FCC Ru; □, magnetic moment of FCC Ru.

Figure 9 shows the total energy and magnetic moment as functions of the lattice constant. BCC Ru has a magnetic moment when the lattice constant is larger than 6.20 au. The energy of BCC Ru is smaller than that of FCC Ru when the lattice constant is smaller than 6.55 au. The ferromagnetic phase appears at 5% expanded lattice constant from the metastable state of BCC Ru. Yamada and co-workers [24] have formed Al films by ion cluster beam deposition and Ag films by molecular beam epitaxy deposition on Si(111) substrates. Both the Al and the Ag films have been found to be epitaxial despite their large lattice mismatch to Si substrates (both are close to 25%). The lattice expansion of 5% is not so large compared with the mismatch of Al and Ag films. Therefore, there is a large possibility of realizing ferromagnetic BCC Ru by depositing Ru at a lattice constant within the range from 6.20 to 6.55 au.

The addition of Ru to BCC-like ferromagnetic alloys does not decrease the magnetic moment very much, compared with the other non-magnetic elements [25, 26]. It seems to be due the ferromagnetic nature of BCC Ru. Ru has a local moment in such alloys [27, 28] and improves anti-corrosion, wear resistivity and thermal stability [26]. So, Ru is one of the most valuable ferromagnetic elements in 4d transition metals.

4. Conclusion

The first-principle KKR calculation shows that the total energy of BCC Ru is larger than that of FCC Ru. However, the energy difference between BCC Ru and FCC Ru is about 30 mRyd atom, which is not very large. The difference decreases as the unit volume becomes large. A magnetic moment appears when the lattice constant is 5% larger than that of the metastable state of the BCC phase. Epitaxial growth may produce BCC Ru. When Ru is deposited on materials which have a lattice constant larger than 6.20 au, BCC Ru is thought to be ferromagnetic.

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