

Magnetic properties of Co and Co-Ag alloys in equilibrium/nonequilibrium structures studied by *ab initio* calculations

L. T. Kong, R. F. Zhang, Z. C. Li, and B. X. Liu*

*Advanced Materials Laboratory, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China
and Laboratory of Solid-State Microstructure, Nanjing University, Nanjing 210093, China*

(Received 14 May 2003; published 24 October 2003)

Ab initio calculations predict that the magnetic moments of the metastable fcc and bcc Co are 1.63 and $1.69\mu_B$, respectively, which are greater than the $1.57\mu_B$ value of the equilibrium hcp Co. For the Co-Ag system, *ab initio* calculations reveal that the CoAg_3 , Co_3Ag , and CoAg alloys are energetically favored to be in $D0_{19}$, $D0_{19}$, and $B2$ structures, respectively, and all prefer to be ferromagnetic rather than paramagnetic. Moreover, the magnetic moments of Co atom are enhanced to 1.62 and $1.76\mu_B$ in $D0_{19}$ Co_3Ag and $B2$ CoAg alloys, respectively, while reduced to $1.43\mu_B$ in the $D0_{19}$ CoAg_3 alloy. The results seem to suggest that an expansion of average atomic volume would enhance the magnetic moment of Co, which, however, would be reduced by nonmagnetic element alloying. Interestingly, the predictions agree reasonably well with those obtained from experimental as well as theoretical studies.

DOI: 10.1103/PhysRevB.68.134446

PACS number(s): 75.30.Cr, 03.67.Lx, 61.66.Dk, 75.50.Cc

I. INTRODUCTION

Magnetism of solid/condensed matter has long been one of the most important scientific issues for the global physical society and a clear understanding of the magnetic property of the ferromagnetic elements as well as their alloys is of vital importance for both scientific and technical concerns. In theoretical pursuits, since the mid 1980's, first-principles calculations have been employed to study the magnetic properties of the ferromagnetic elements.¹⁻⁴ Meanwhile, a number of nonequilibrium materials processing techniques have been developed and employed to obtain various nonequilibrium alloys containing ferromagnetic metals of Fe, Co, and Ni. Generally, the obtained nonequilibrium alloys crystallized in one of three simplest structures, i.e., hcp, bcc, and fcc, yet not in those complicated structures corresponding to the equilibrium compounds.⁵ In addition, some of the newly obtained nonequilibrium alloys showed interesting magnetic properties, which required further theoretical studies for a better understanding of the depth of electronic structures of solids. In recent decades, the theoretical calculation methods have also been developed/modified to improve the precision of the calculated results. All these developments led the authors' group to initiate, very recently, a systematic study concerning the structural dependence of the magnetism of the ferromagnetic elements (Fe, Co, and Ni) as well as their equilibrium/nonequilibrium alloys by *ab initio* calculations based on the newly developed projector augmented wave (PAW) pseudopotentials.⁶ In the present work, we concentrated on calculating the magnetic moments of metal Co and the metastable Co-Ag alloys. Choosing Co and the equilibrium immiscible Co-Ag system are based on the following considerations. First, Co is a strong ferromagnetic element and keeps its ferromagnetic characteristics well in very thin films, which are frequently used in fabricating magnetic sensors and experimental studies. Second, the recent discovery of the giant magnetoresistance (GMR) in granular materials^{7,8} has generated a great interest in studying those

alloy systems featuring a GMR effect with special attention devoted to the Co grains embedded in the Ag medium. Third, it has also been found that though the Co-Ag system is essentially immiscible, an effective intermixing did take place at the Co-Ag interface under some specific circumstances⁹⁻¹¹ which are expected to considerably affect the alloying behavior between Co and Ag as well as the associated magnetic property of the Co atom in the alloys. We present, in this paper, the *ab initio* calculation results concerning the magnetic moment (MM) of Co in pure metal and the metastability of the Co-Ag system at three representative alloy compositions of CoAg_3 , Co_3Ag , and CoAg, as well as the associated magnetic property of the Co-Ag alloys. In addition, the present calculation results are compared with those obtained from previous experimental/theoretical studies.

The Vienna *ab initio* simulation package (VASP)¹²⁻¹⁴ was employed to conduct the calculations based on the projector augmented wave (PAW) pseudopotentials, which have been constructed by considering the all-electrons effect, thus improving the precision and computation.⁶ Concerning other detailed procedure of the VASP calculation, the readers are referred to some of our previous publications.¹⁵⁻¹⁷

II. RESULTS AND DISCUSSION

A. Structural stability of Co and metastable Co-Ag alloys

We first examine the structural stability of pure Co metal with different structures, i.e., in hcp, fcc, and bcc structures. The energy-volume correlations of pure Co with respective structures were acquired by *ab initio* calculations and then fitted to the Murnaghan equation of states¹⁸ (EOS). The cohesive properties of each structure are thus obtained and are listed in Table I. First, the most stable structure of Co is calculated to be hcp. Second, the fcc Co has a little higher energy than hcp, matching well with the well-known fact. Third, the bcc Co has the highest heat of formation and therefore is hard to be stabilized. In addition, the calculated lattice constants of hcp ($a=2.49$ Å, $c/a=1.62$) and fcc

TABLE I. Cohesive properties of pure Co in different structures obtained from the present *ab initio* calculations. Available experimental values are given in parentheses. (E_{\min} : minimum total energy; ΔH : heat of formation; V_0 : equilibrium average atomic volume; a : lattice constant; c/a : relaxed c/a ratio; MM: magnetic moment of Co at the equilibrium volume.)

| Structure | hcp | fcc | bcc |
|--------------------------|--------------------------|---------------------------|--------------------------|
| E_{\min} (eV/atom) | -6.998 | -6.975 | -6.890 |
| ΔH (eV/atom) | 0 | 0.023 | 0.108 |
| V_0 (\AA^3) | 10.827 | 10.919 | 11.036 |
| a (\AA) | 2.49(2.50 ^a) | 3.52(3.544 ^a) | 2.81 |
| c/a | 1.62 | | |
| MM (μ_B) | 1.57(1.71 ^b) | 1.63(1.74 ^c) | 1.69(1.80 ^d) |

^aReference 19.

^{b-d}Extrapolated from Refs. 20, 21, and 22, respectively.

(3.52 \AA) Co are in good agreement with the experimental values of 2.50 \AA ($c/a=1.62$) and 3.544 \AA , respectively.¹⁹ Although the above calculation results for the Co are well-known facts, the agreement between the VASP calculation and the experimental data confirms the relevance or serves as a calibration of the calculation performed in the present work.

Prior to studying the magnetic behavior of the possible metastable Co-Ag alloys, the structural stability, i.e., the relatively stable structures, of the respective alloys should be identified. In the present work, three representative alloy compositions, i.e., Co_3Ag and CoAg_3 , and CoAg , were selected and some relatively simple structures, i.e., $A15$, $D0_{19}$, $L1_2$, and $L6_0$ at Co_3Ag and CoAg_3 , and $B1$, $B2$, and $B3$ at CoAg , respectively, were calculated. The criteria of choosing the limited alloy compositions and some relatively simple structures in calculations have been described in details in some of our previous publications.^{15-17,5}

For the CoAg_3 alloy, Table II lists the spin polarized (SP) and spin unpolarized (SUP) calculation results, from which one can easily find that the CoAg_3 alloys in all the calculated structures prefer to be ferromagnetic, as the heats of formation of the respective structures obtained by SP calculation is lower than those from SUP calculation. We take the preferred

SP results to discuss the structural stability of the four possible structures. Apparently, the $A15$ structure has the highest positive heat of formation. The $L6_0$ structure has the second highest positive heat of formation, which is much lower than that of the $A15$ structure. The $L1_2$ and the $D0_{19}$ structures are in a same low energy level and the $D0_{19}$ structure has the lowest heat of formation among the four possible structures. Interestingly, the *ab initio* predicted most stable $D0_{19}$ CoAg_3 state has ever been observed in experiments, i.e., a metastable CoAg_3 alloy of hcp structure was obtained in thin films upon ion irradiation and its lattice constants were determined by diffraction analysis to be $a=2.84$ \AA and $c/a=1.65$.²³ Comparing to the present SP calculation results of $a=2.76$ \AA and $c/a=1.632$, a difference is only about 3%. It is known that in a routine diffraction analysis, an inevitable error is at least 3-5%, the agreement between the *ab initio* calculation and experiment, in this respect, is therefore excellent. Incidentally, Liu *et al.*¹⁶ have studied the structural stability of the CoAg_3 alloy by first-principles calculation based on the Vanderbilt-type ultrasoft pseudopotential,²⁴ in which the magnetic interactions have not been taken into account. It is noted that their calculations predicted the same stability order for the CoAg_3 alloy among the possible structures as revealed in the present work, though the calculated formation energies and the lattice constants showed some difference probably due to the different pseudopotentials used in the calculations. In addition, the calculated properties obtained in the present work are believed to have an improved precision.

For the Co_3Ag alloy, similar results are obtained and are listed in Table III. Comparing the SP and SUP results, it is concluded that a ferromagnetic state is also energetically favored. Regarding to the metastability of the possible structures, a same energy order is also found as in the CoAg_3 case. The $A15$ structure has the highest energy. The $L6_0$ structure has a second highest energy. While the $L1_2$ and $D0_{19}$ structures have a lower energy than the above two structures and share an approximately same energy level. The heat of formation of $D0_{19}$ structure is calculated to be 0.383 eV/atom, which is 0.011 eV/atom lower than that of $L1_2$.

TABLE II. Cohesive properties of CoAg_3 in different structures obtained from the present *ab initio* calculations. The symbols in the table are the same as used in Table I.

| | Structure | $A15$ | $D0_{19}$ | $L1_2$ | $L6_0$ |
|-------------------------------|--------------------------|--------|-----------|--------|--------|
| Spin unpolarized calculations | E_{\min} (eV) | -4.285 | -4.406 | -4.409 | -4.401 |
| | ΔH (eV/atom) | 0.558 | 0.436 | 0.4335 | 0.442 |
| | V_0 (\AA^3) | 15.070 | 14.680 | 14.644 | 14.676 |
| | a (\AA) | 4.94 | 2.75 | 3.88 | 4.07 |
| | c/a | | 1.632 | | 0.868 |
| Spin polarized calculation | E_{\min} (eV) | -4.319 | -4.449 | -4.443 | -4.431 |
| | ΔH (eV/atom) | 0.523 | 0.393 | 0.399 | 0.411 |
| | V_0 (\AA^3) | 15.260 | 14.824 | 14.805 | 14.832 |
| | a (\AA) | 4.96 | 2.76 | 3.90 | 4.09 |
| | c/a | | 1.632 | | 0.867 |
| | MM (μ_B) | 1.48 | 1.43 | 1.31 | 1.36 |

TABLE III. Cohesive properties of Co_3Ag in different structures obtained from the present *ab initio* calculations. The symbols in the table are the same as used in Table I.

| | Structure | A15 | $D0_{19}$ | $L1_2$ | $L6_0$ |
|-------------------------------|--------------------------|--------|-----------|--------|--------|
| Spin unpolarized calculations | E_{\min} (eV/atom) | -6.340 | -6.470 | -6.482 | -6.456 |
| | ΔH (eV/atom) | 0.686 | 0.556 | 0.544 | 0.570 |
| | V_0 (\AA^3) | 11.561 | 11.335 | 11.290 | 11.325 |
| | a (\AA) | 4.52 | 2.52 | 3.56 | 3.68 |
| | c/a | | 1.630 | | 0.906 |
| Spin polarized calculations | E_{\min} (eV) | -6.537 | -6.64 | -6.632 | -6.601 |
| | ΔH (eV/atom) | 0.489 | 0.383 | 0.394 | 0.425 |
| | V_0 (\AA^3) | 11.874 | 11.612 | 11.597 | 11.665 |
| | a (\AA) | 4.56 | 2.55 | 3.59 | 3.75 |
| | c/a | | 1.628 | | 0.882 |
| | MM (μ_B) | 1.62 | 1.62 | 1.60 | 1.61 |

For the CoAg alloy, similar SP and SUP calculations are carried out for three selected possible structures, i.e., $B1$, $B2$, and $B3$. It turns out that a ferromagnetic state is also energetically favored rather than a paramagnetic one in three possible structures and among the possible structures, the most stable one is predicted to be the $B2$ structure. Nonetheless, the heat of formation of the most stable $B2$ phase is rather large being 0.573 and 0.695 eV/atom in SP and SUP calculations, respectively. It is therefore anticipated that it is probably necessary to have a far-from-equilibrium processing technique capable of providing a considerable extra energy during the processing procedure to obtain such a highly energetic metastable CoAg alloy predicted by *ab initio* calculation.

B. Magnetic properties of Co and metastable Co-Ag alloys

Referring again to the magnetic properties illustrated in Table I, one sees that the equilibrium hcp Co is indeed calculated to be ferromagnetic with a magnetic moment (MM) of $1.57\mu_B$, and that the MMs for the fcc and bcc Co are predicted to be $1.63\mu_B$ and $1.69\mu_B$, respectively, which are both greater than that of the equilibrium hcp Co. The above calculations clearly show the variation of MM of Co atom in hcp, fcc, and bcc structures. The next question is to find out what is the relevant parameter(s) pertinent to such a variation. Naturally, the MM of a Co atom could be influenced by its surrounding environment. Viewing a structure at an atomic scale, the number and the distance of the neighboring atoms to an atom should be considered. Virtually, changing the number and the distance of the neighboring atoms of the atom would result in varying the average atomic volume of the atom. The average atomic volume is therefore used as an intrinsic parameter to reflect the atomic environment of a Co atom concerned. Consequently, we plot a two-dimensional figure with the calculated MMs of Co in different structures against the corresponding average atomic volumes as displayed in Fig. 1(a). Obviously, the plot shows that an expansion of the average atomic volume tends to enhance the MM of the Co atom, which is in accordance with that reported by Moruzzi.¹ To examine if fcc Co also features such a trend while varying its average atomic volume, the MMs of fcc Co

are also calculated by using the lattice constants of Cu and Ag, which are both greater than 3.52 \AA of the relatively stable fcc Co discussed above, and the calculated MMs ($1.64\mu_B$ and $1.85\mu_B$, respectively) are indeed a little greater than $1.63\mu_B$. Incidentally, the calculated MMs are fairly compatible with those ($1.68\mu_B$ and $1.86\mu_B$, respectively) reported by Nogueira.²⁵

It is of importance to compare the calculation results with those obtained from experiments. Concerning the MM of hcp

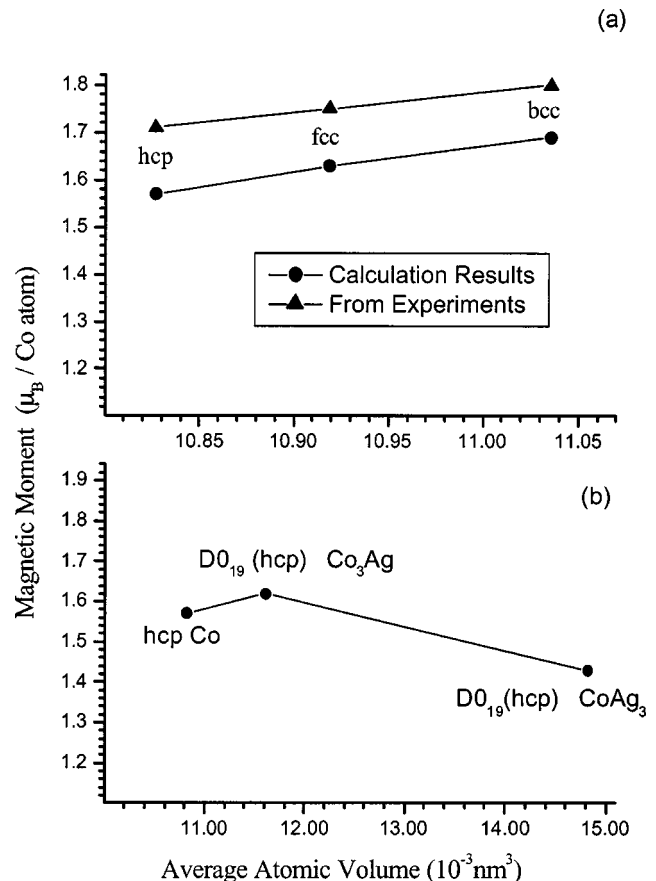


FIG. 1. Correlation of MM of Co atom vs average atomic volume in (a) pure Co metal with different structures and (b) hcp structured Co-Ag alloys at different compositions.

Co, Myers has measured the MM of a single crystal Co in a temperature range from liquid oxygen (-183°C) to hcp-to-fcc transition temperature (450°C) of Co and obtained a MM-temperature correlation.²⁰ Extrapolating the MM-temperature correlation to 0 K, the MM of hcp Co is deduced to be $1.71 \pm 0.05\mu_B$. Referring again to the calculated values listed in Table I, the smallest difference between the calculated and extrapolated values from experiments is about 5.4%. For the case of fcc Co, Crangle has studied a series of fcc structured Co-Cu alloys and obtained a correlation between MM and Co concentration.²¹ By extrapolating the experimentally obtained MM-Co correlation to pure Co, the MM of Co in the fcc structure is deduced to be $1.74 \pm 0.05\mu_B$. Similarly, the smallest difference between the calculated value and the experimental one is about 3.6%. For the case of bcc Co, Bardos has reported the measured MMs of some bcc structured Fe-Co alloys,²² and from his published data, the MM of Co in bcc structure is figured out to be $1.80 \pm 0.05\mu_B$. Incidentally, Collins has also obtained an approximately the same value ($1.80\mu_B$) for bcc Co.²⁶ Comparing the experimentally determined MM of bcc Co with our calculated value, the smallest difference is 3.5%. With these data in hand, the experimentally determined MMs of Co in three different structures versus the corresponding average atomic volumes are also plotted in Fig. 1(a), and it is highly interesting that the correlation shows a similar trend as that observed from the calculated ones.

Naturally, by introducing some alloying atoms into the Co lattice, the atomic environment of Co could be changed and we now turn to study the alloying effect of Ag in the metastable Co-Ag alloys. From the data displayed in Table II, it is found that the MMs of Co calculated for the CoAg_3 alloys in four possible structures are predicted to be smaller than that of pure hcp Co, e.g., MMs are $1.43\mu_B$ and $1.31\mu_B$ in $D0_{19}$ (hcp) and $L1_2$ (fcc), respectively. Coincidentally, the calculated MMs of Co in the CoAg_3 alloys are in accordance with the verdict of a proposed mean field model that the MM of Co would decrease with increasing the Ag neighbors.²⁷ For the Co_3Ag alloys, the MMs of Co calculated for the four possible structures are sitting in between those of pure hcp and fcc Co, as is shown in Table III. For example, for the $D0_{19}$ (hcp) and $L1_2$ (fcc) Co_3Ag alloys, the MMs are calculated to be $1.62\mu_B$ and $1.60\mu_B$, respectively. Coincidentally, Morkowski have calculated the MMs of some hypothetical hcp/fcc ordered structures by the SP tight binding linear muffin-tin orbital (TB-LMTO) method and reported that the MMs of hcp and fcc $\text{Co}_{75}\text{Ag}_{25}$ alloys were $1.5490-1.7204\mu_B$ and $1.675\mu_B$, respectively.²⁸ Though the reported calculation method and condition were not the same as in the present work, the calculated MMs matched the present results reasonably well. After all, both calculations

did confirm an energetically favored ferromagnetic state of Co in the above described atomic environments. For the CoAg alloys, the calculated MMs of Co in different possible structures are all much larger than that of pure Co and in particular, the predicted MM of Co in $B3$ CoAg alloy could be as large as $1.87\mu_B$. As has been mentioned before, the CoAg alloy has a rather large positive heat of formation and therefore could only be stabilized under some strict conditions.

The variation of the MMs of the Co-Ag alloys revealed by *ab initio* calculations is not as straightforward as in the case of pure Co to correlate with its crystalline structure, because of the involving of the nonmagnetic element Ag. As described above, the expansion of the average atomic volume tends to enhance the MM of Co atom, while the increasing of the number of Ag neighbors is prone to reduce the MM, which is in accordance with the previous observations.^{3,27} The resultant magnetic moment is therefore attributed to a combining effect of the two competitive factors. Take the hcp structured Co-Ag alloys as an example, Fig. 1(b) shows the variation of the MM of Co atom versus the average atomic volume for pure Co and two hcp structured Co-Ag alloys at different compositions. In the Co_3Ag alloy, the atomic volume expansion plays more important role than the Ag alloying effect and the MM of Co in Co_3Ag is therefore larger than that in pure Co. In contrast, for the CoAg_3 alloy, the reduction of MM of Co originated from increasing Ag neighbors dominates, leading to a smaller MM of Co in the alloy than that of pure Co.

III. SUMMARY

In summary, *ab initio* calculations reveal that the pure Co metal in hcp, fcc, and bcc structures could all be ferromagnetic and the metastable fcc and bcc Co could possess greater magnetic moments than the equilibrium hcp Co. It also reveals that the CoAg_3 , Co_3Ag , and CoAg alloys are energetically favored to be in $D0_{19}$, $D0_{19}$, and $B2$ structures, respectively, and all prefer to be ferromagnetic rather than paramagnetic. The present calculation results seem to suggest that the variation of the magnetic moment of Co is governed by a combining effect of two competitive factors, i.e., an atomic volume expansion enhances whereas an Ag alloying reduces the magnetic moment of Co.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from the National Natural Science Foundation of China, The Ministry of Science and Technology of China (Grant No. G20000672), and the Administration of Tsinghua University.

*Email address: dmslbx@tsinghua.edu.cn

¹V. L. Moruzzi and P. M. Marcus, Phys. Rev. B **34**, 1784 (1986).

²L. M. Sandratskii and J. Kübler, Phys. Rev. B **47**, 5854 (1993).

³V. S. Stepanyuk *et al.*, Phys. Rev. B **49**, 5157 (1994).

⁴Y. S. Shi *et al.*, Phys. Rev. B **65**, 172410 (2002).

⁵B. X. Liu, W. S. Lai, and Q. Zhang, Mater. Sci. Eng., R. **29**, 1

(2000).

⁶G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

⁷A. E. Berkowitz *et al.*, Phys. Rev. Lett. **68**, 3745 (1992).

⁸J. Q. Xiao, J. S. Jiang, and C. L. Chien, Phys. Rev. Lett. **68**, 3749 (1992).

⁹M. Negrier *et al.*, Philos. Mag. A **81**, 2855 (2001).

- ¹⁰U. Ebels *et al.*, Phys. Rev. B **58**, 6367 (1998).
- ¹¹M. Gester, J. A. D. Matthew, S. M. Thompson, and G. Beamson, Phys. Rev. B **59**, 15 654 (1999).
- ¹²G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
- ¹³G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
- ¹⁴G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996).
- ¹⁵J. B. Liu *et al.*, Phys. Rev. B **63**, 132204 (2001).
- ¹⁶J. B. Liu *et al.*, Phys. Rev. B **64**, 054102 (2001).
- ¹⁷L. T. Kong, J. B. Liu, and B. X. Liu, J. Phys. Soc. Jpn. **71**, 141 (2002).
- ¹⁸J. P. Poirier, *Introduction to the Physics of the Earths Interior* (Cambridge University Press, Cambridge, 1991).
- ¹⁹X-Ray Powder JCPDS Diffraction Files 5.0727 and 15.0806.
- ²⁰H. P. Meyers and W. Sucksmith, Proc. R. Soc. London, Ser. A **207**, 427 (1951).
- ²¹J. Crangle, Philos. Mag. **46**, 499 (1955).
- ²²D. I. Bardos, J. Appl. Phys. **40**, 1371 (1969).
- ²³S. Amirthapandian *et al.*, J. Phys.: Condens. Matter **14**, L641 (2002).
- ²⁴D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
- ²⁵R. N. Nogueira and H. M. Petrilli, Phys. Rev. B **63**, 012405 (2000).
- ²⁶M. F. Collins and J. B. Forsyth, Philos. Mag. **8**, 401 (1963).
- ²⁷Z. S. Shan *et al.*, J. Appl. Phys. **73**, 6057 (1993).
- ²⁸J. A. Morkowski and A. Szajek, Acta Phys. Pol. A **98**, 447 (2000).