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Electronic Structure, Magnetism and Phase Stability of Heusler Alloy Mn_2CuAl

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ABSTRACT

It completely decomposes to a mixture of a tetragonal phase and a Cu9Al4 phase. Electronic structure, magnetism and face stability of new Mn-based Heusler alloys Mn2CuAl has been studied and synthesized by first-principles calculations and by the melt-spinning method. Firstly, the calculations suggest that Mn2CuAl crystallizes in the Hg_2CuTi type of structure, in which the Cu atoms have Al as nearest neighbors. As a consequence, the Mn atoms occupy two nearest neighbors' sub lattices A and B. Like the well knownHeusler alloyCu2MnAl, the magnetic moment of ,Mn2CuAl also comes from the 2Mn atoms in the lattice, while the Cu atom is almost nonmagnetic .At equilibrium lattice constant, Mn2CuAl is a ferrimagnetic with moment of 0.22uB. The partial spin moments of Mn (A) and Mn (B) are -3.52uB and 3.74uB, respectively. The small total moment comes from the antiparallel configurations of the Mn partial moments. With a small contraction of the lattice, the total moment becomes near zero and half-metallic antiferromagnetic state is observed. Secondly, It has an ordered bcc structure and is a ferrimagnet with a saturation moment of 1.44mB/f.u. at 5 K. The magnetization mainly comes from the contributions of the antiparallel aligned Mn spin moments.

A compensation point is observed at 630 K, indicating the antiferromagnetic between the two Mn sublattices. The Curie temperature of the ribbons is 690 K When heated to 740 K, the Mn_2CuAl.

1. INTRODUCTION

Electronic Structure and Magnetism: The study of the Heusler alloys has increased considerably in recent years due to new phenomenon, such as half-metallicity and shape memory effect, in this alloy family. The Full– Heusler alloy has a stoichiometric composition of X2YZ, where X and Y are transition metal elements, and Z is a main group element. the Heusler structure can be looked on as four interpenetrating face-centered-cubic lattices and has four unique crystal sites

in Wyckoff coordinates, respectively. It is found that the site preference of the X and Y atoms is strongly influenced by the number of their valence electrons. For example, Mn-based Heusler alloys Mn_2YZ, the Y atom will occupy B site (Cu_2MnAl-type structure) or A site (Hg_2CuTi-type structure) due to Y atom having less or more valence electrons compared with Mn. Among these alloys, the case of the Mn-based Heusler alloy is particularly interesting. In 1999, Mn_2VAl was predicted to be a half-metal from band theory calculations, which was the first half-metallic material in Mn-based Heusler alloys. Mn_3Ga, Mn_2FeZ and also Mn_2CoSb have also been predicted as half-metallic materials by theoretical and experimental studies. Meanwhile, a new ferromagnetic shape memory alloy Mn_2NiGa has been found in the Mn-based Heusler alloys, which has a Curie temperature as high as 588 K and is suitable for technical applications. these attracted much attention and people take great efforts in searching for new functional materials in this series of alloys. Till now, the electronic structure and site preference of the Mn_2YZ have been thoroughly studied. In case Mn_2CuZ alloys is still unclear yet. It is known that Cu atom has a filled d subshell and leaves the 4s with one electron. This is different from the other 3d elements like Fe or Co, which has an unfilled d subshell. It may be expected that the different electronic configuration will have influence on the site preference as well as the electronic structure. Investigations on the electronic structure of the Mn_2CuZ alloys can be helpful for finding new functional materials. the electronic structure and site preference of the Mn_2CuAl alloy was investigated by first-principles calculations and the stable structure was determined compensated total spin moment is observed.

Phase Stability: The research interest mainly focuses on the half-metallic materials and ferromagnetic shape-memory alloys in the Mn_2YZ alloys, where Y is a transition metal element and Z is a main group element. Mn_2VAl was the first half-metallic material observed in Mn2-based Heusler alloys. In succession, Mn_3Ga and Mn_2FeZ have also been predicted as half metals by theoretical and experimental studies. Mn2NiGa and MnNiIn have been reported as newly discovered FSMAs . They make Mn2-based Heusler alloys a promising family for investigating new materials and phenomena. However, the properties of Mn_2CuZ, which has Cu as the Y atom. The Cu atom has a filled d subshell and leaves the 4s with one electron. This is different from other 3d elements like Fe or Co, which have an unfilled d subshell. It may be expected that the different electronic configurations will have an influence on their electronic structure and magnetic properties. Li et al studied the electronic structure of Mn_2CuAl theoretically. It shows a half-metallic antiferromagnetic character with a small contraction of the equilibrium lattice.

2. EXPERIMENTAL METHOD

We carried out the electronic-structure calculations using the pseudopotential method with a plane-wave basis set based on density-function theory . The calculations have been performed within the CASTEP (Cambridge Serial Total Energy Package) code. The interactions between the atomic core and the valence electrons were described by the ultra-softpseudo potential. The electronic exchange-correlation energy was treated under the local-density approximation. The plane-wave basis set cut-off was used as 500 eV for all the cases. In the irreducible Brillouin zone 182 k points are employed. These parameters ensure good convergences for total energy.

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The convergence tolerance for the calculations was selected as a difference on total energy within 1 10– 6 eV/atom.

The Mn2CuAl ingots were prepared by arc melting the constituent elements in a high-purity argon atmosphere. The purity of the starting materials was 99.9% or higher. The ingots were melted at least three times for homogenization. The ingots were then wrapped in molybdenum foil and sealed in a quartz tube and annealed at 1073 K for 3 days under protection of an argon atmosphere. The melt-spun ribbons were prepared by a single-wheel technique with the substrate velocity (Vs) of 20 m/s, under protection of an Ar atmosphere. Then X-ray powder diffraction (XRD) with Cu Ka radiation was used to verify the crystal structure and to determine the lattice constants. The temperature dependence of the magnetization was measured using a vibrating-sample magnetometer .The magnetization curves were measured by a SQUID magnetometer with applied fields up to 5 T.

3. RESULTS AND DISCUSSION

The equilibrium lattice parameter was derived by minimizing the total energy. Here, in order to determine the site preference, we considered two possible crystal structures: one is the Cu atom entering the A sites (Hg2CuTi-type structure); the other is the Cu atom occupying the B site (Cu2MnAl-type structure). All the calculations were carried out for paramagnetic (PM) and ferromagnetic (FM) states, which is also the common case in Mn-based Heusler alloys . In Table 1, DE1 gives the energy difference between the FM and PM states when Mn2CuAl forms the Cu2MnAl- or Hg2CuTi-type structure. It is clear that in the two structures, the FM state is always lower in energy and more stable. This agrees with the findings in other Mn-based Heusler alloys well. DE2 represents the energy difference between the Cu2MnAl- and Hg2CuTi-type of structure at their equilibrium lattice constants. When Mn2CuAl forms Hg2CuTi-type structure, the total energy is 0.32 eV, lower than Cu2MnAl-type structure. This suggests that the Cu atom also prefers the A sites like Co or Ni in Mn-based Heusler alloys. Similar result has also been found in Fe3Si. From neutron diffraction and NMR studies, it has been found that Mn tends to occupy the B site due to its fewer electrons than that of Fe. So we will discuss the electronic structure of Mn_2CuAl with Hg2CuTi-type structure.

Table 1
The energy of difference between the FM and PM states ΔE_1, the energy of difference between the Cu_2MnAl- and Hg_2CuTi-type of structure at their equilibrium lattice constants ΔE_2, the total calculated moment M_{cal} and the moments M_{Mn}, M_{Cu}, M_{Al} of different atoms.

Compound	ΔE_1 (eV)	ΔE_2 (eV)	M_{cal} (μ_B)	M_{Mn} (μ_B)	M_{Cu} (μ_B)	M_{Al} (μ_B)
Mn_2CuAl				−3.52 (A)		
	−0.61	−0.32	0.22		−0.04	0.02
Hg_2CuTi- type Mn_2CuAl				3.74 (B)		
	−0.98	–	5.68	3.24	−0.32	−0.48
Cu_2MnAl- type Cu_2MnAl	–	–	3.59	4.14	−0.2	−0.18

Fig 1 gives the calculated total and partial density of states (DOS) of Mn2CuAl for the stable Hg2CuTi-type of structure. It is known that Cu2MnAl is an analog of Mn2CuAl and has been thoroughly studied . In order to understand the electronic structure of Mn2CuAl deeply, we also present the DOS of Cu2MnAl in Fig. 2 for comparison

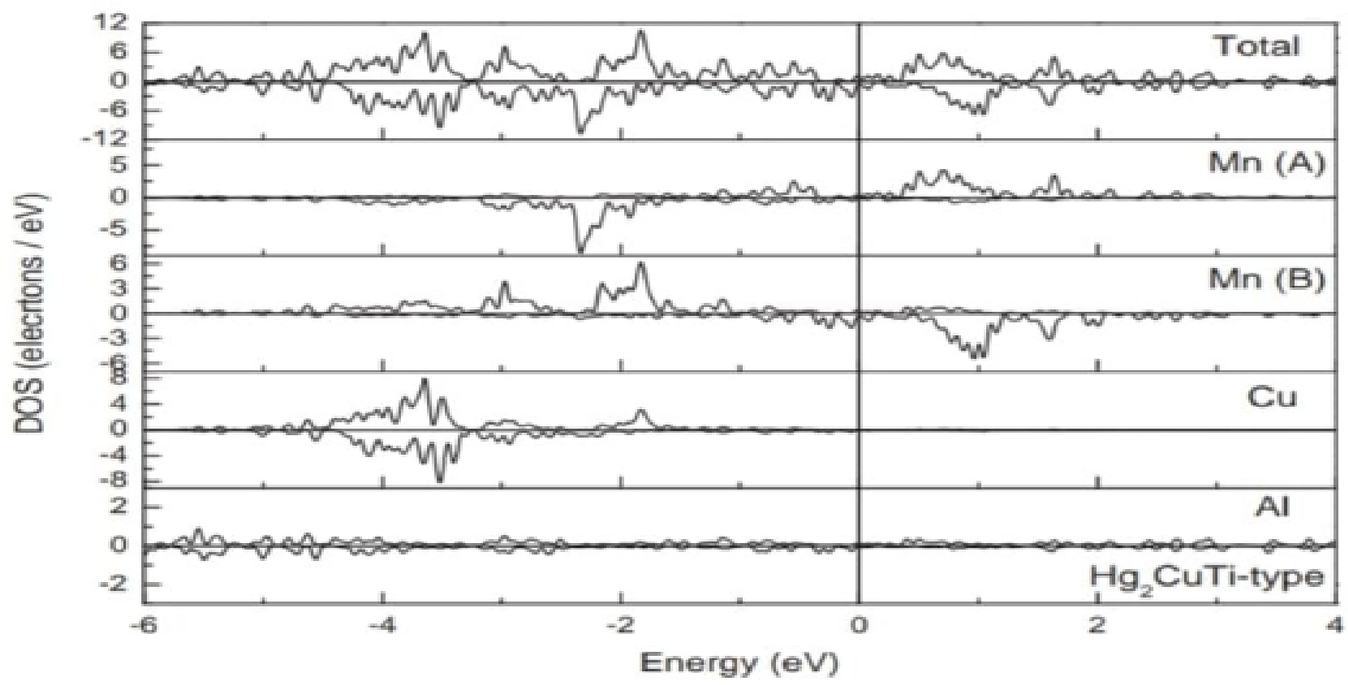


Fig. 1. The calculated spin-projected total and partial DOS plots for Mn_2CuAl.

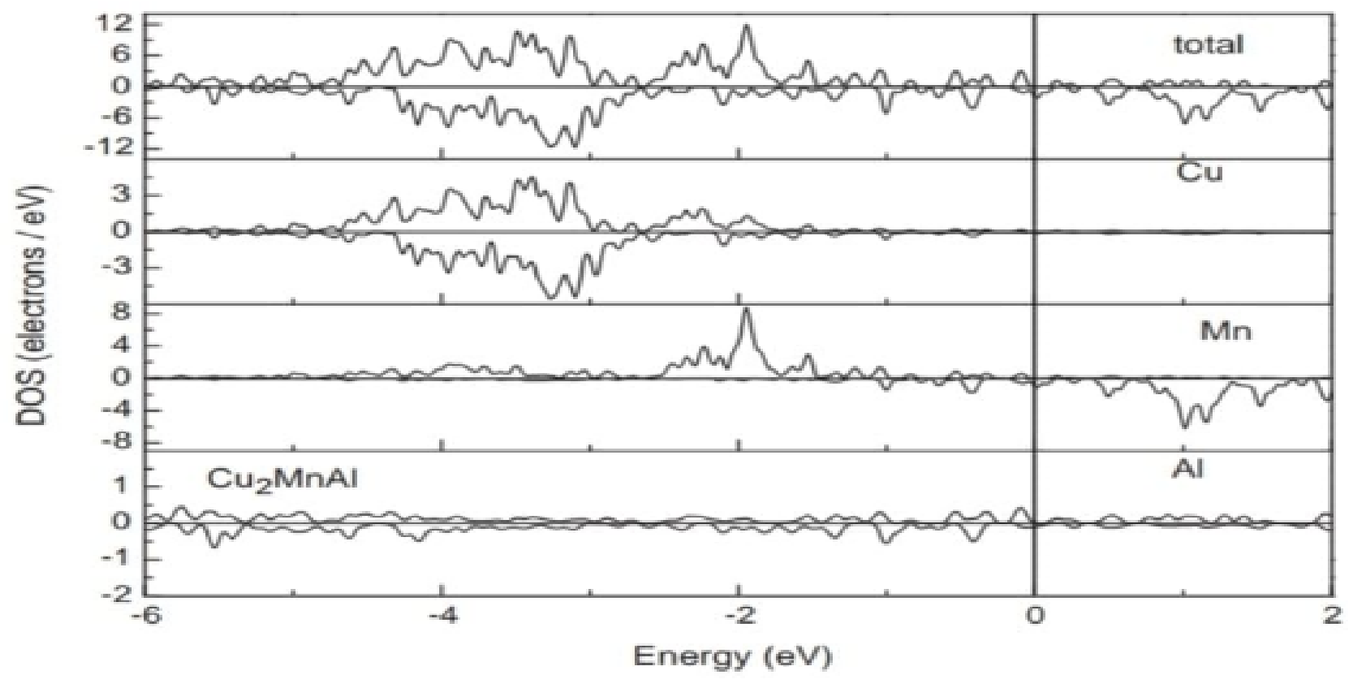
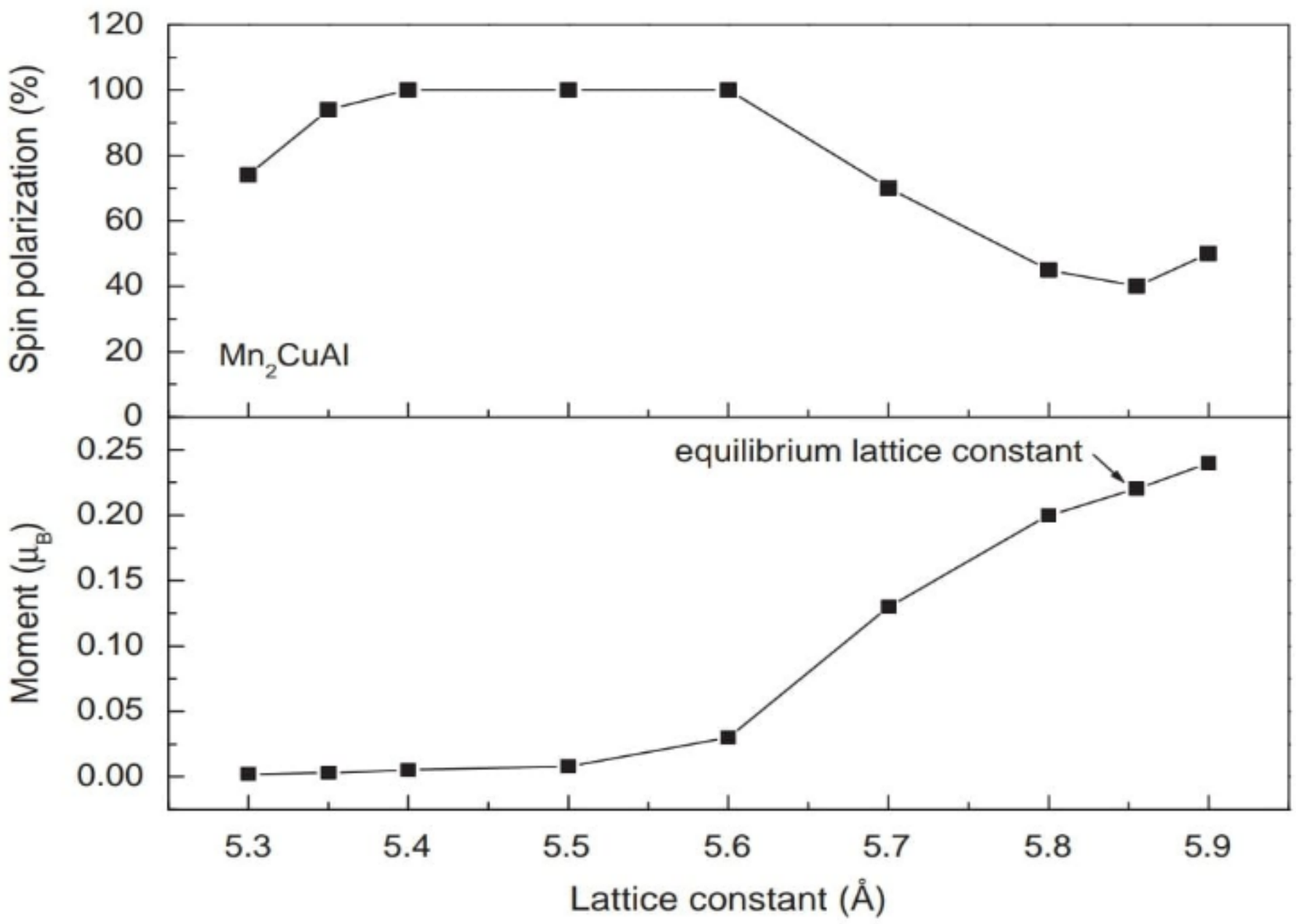


Fig. 2. The calculated spin-projected total and partial DOS plots for Cu_2MnAl.

in both figures a magnetic splitting is clearly observed in the total DOS, indicating the ferromagnetic ground state. In the minority-spin band, the cases in Mn2CuAl and Cu2MnAl are similar. The Fermi level locates in a low-density region and separates the bonding and antibonding orbitals. In the majorityspin states, the high-density region of Cu2MnAl is far below the Fermi level. But in the majority DOS of Mn2CuAl, the antibonding peak is about 0.75 eV above the Fermi level. This difference can be traced back to the partial DOS of these alloys. For the two alloys, these states of the Al atom are mainly below 7 eV and have no contribution to the total spin moments. So they are omitted from plotting to give the detail of d states. The energy region between 5 and +2 eV consists mainly of the d electrons of Cu and Mn atoms. It is clear that the Cu and Mn 3d states behave quite differently. In both Cu2MnAl and Mn2CuAl, the d states of Cu locate in the region of 5 to 2 eV and are almost identical in both spin directions. The Cu 3d states are almost completely occupied and show no exchange splitting. So the Cu atom only has a small moment and contributes little to the magnetism of the two alloys. The Mn 3d states extend from 3 to +2 eV, and a clear exchange splitting is observed between majority- and minorityspin states. This is the main source of the magnetic moment in Cu2MnAl or Mn2CuAl. In the two alloys the partial DOS of the Mn atom at the B site shows a two-peak structure. This may

be traced back to the eg– t2g splitting in cubic crystal field. In the majorityspin band, the bonding and antibonding peaks of Mn (B) are both below EF. While in the minority-spin band, the antibonding peak is high above EF. This large exchange splitting in DOS between majority and minority states leads to a large localized spin magnetic moment at the Mn (B) sites. This has been confirmed by experimental studies in Cu2MnAl. In Mn2CuAl, besides the Mn atom at the B site, there is also a Mn atom at the A site. Its minority states are situated below the Fermi level.

t is clearly seen that the magnetic moments of the Mn atoms are similar and compensated each other in the alloys, while Cu is almost nonmagnetic. This is similar to the case in half-metallic antiferromagnets, in which the spin moments from different atoms cancel each other and lead to a near zero total spin moment and keep high spin polarization. A typical example is Mn3Ga. Its composition is similar to Mn2CuAl in this work. So it may be expected that with a small change of the lattice constant, the moments in Mn2CuAl can exactly compensate each other. Meanwhile, modern methods for the synthesis of thin films such as MBE make it possible to prepare materials as multilayers in which the lattice constant is strongly affected by the lattice of substrate. It is meaningful to study the effect of lattice constant on the magnetism and electronic structure of Mn2CuAl.



The change in the total and partial moments for Mn_2CuAl as a function of lattice constant is shown in Fig. 3. It is found that with a small contraction of the lattice constant a, both the absolute values of the moments of Mn (B) and Mn (A) decreased.

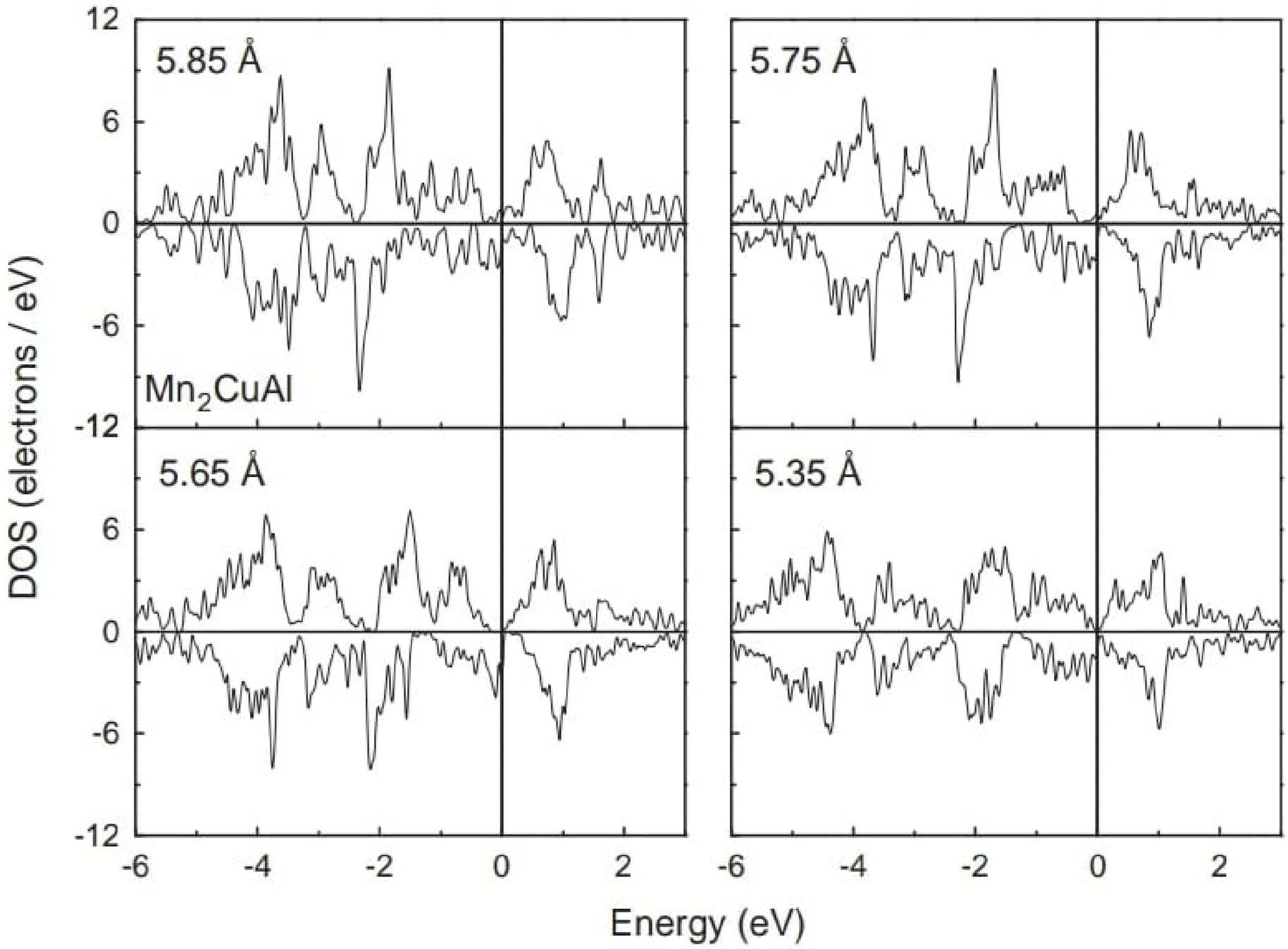


Fig. 4. The calculated total DOS for Heusler alloy Mn_2CuAl at different lattice constants.

As an example, Fig. 4 gives the variation of the total DOS of Mn_2CuAl with lattice constant. It is clear that the lattice distortion leads to an interesting change of the DOS.

4. CONCLUSIONS

The electronic structure , magnetic properties, and thermal stability of a new Mn based Heusler alloy Mn2CuAl melt spun ribbons have been studied by first principle calculation. The metastable Heusler alloy Mn2CuAl can be obtained by the melt spinning technique and is a ferrimagnet with a saturation moment mainly comes from the two Mn atoms in its lattice. A compensation point is observed at 360 K in the M-T curve . The curie temperature of Mn2CuAl ribbons is 690 K that' s exchanges interactions between the 3d atom which is strong. The magnetic moment at 5 K clearly decreases after decomposition. These antiparallel configuration compensated each other to small total moment which becomes near zero and half metallic antiferromagnetic is observed.

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