First-principles Calculations of Effects of Pressure on Paramagnetic, Ferromagnetic and Antiferromagnetic spin-web Cu3TeO6

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Abstract

The structure, electronic and magnetic properties have been investigated by the first-principles calculations for paramagnetic, ferromagnetic and antiferromagnetic Cu_3TeO_6 under pressure from 0 to 100 GPa. The calculated lattice parameters at 0 GPa are in excellent agreement with the available calculated and experimental values. With increasing pressure, the lattice parameters and volume decrease, but Cu_3TeO_6 keep a stable cubic structure. The electronic calculations show that paramagnetic and ferromagnetic Cu_3TeO_6 are metallic, and antiferromagnetic Cu_3TeO_6 has the non-metallic nature with a direct band gap which decreases with the increasing pressure. Under the pressure, their non-locality of density of states enhances and the electrons becomes more active. Moreover, for antiferromagnetic Cu_3TeO_6, the spin moments of Cu atoms are affected obviously by pressures, and Te atoms show nonmagnetic performance. The total magnetic moment which is mainly contributed by Cu, reaches the maximum at 20 GPa, and decreases with the increasing pressure. The knowledge of these properties will provide reference and guidance for the subsequent study of Cu_3TeO_6.

1. Introduction

Cuprates have a variety of exotic physical properties, such as high-temperature superconductivity [1], layered crystal structures, magnetic insulating state [2], hybridization of Cu-d and O-p orbitals [3], and they show effects of strong electronic correlations [4]. Based on this wealth of fascinating properties, cuprates have attracted considerable attention both theoretically and experimentally [5–10], many researchers have done a lot of research on cuprates [11–21]. With $3d^9$ Cu^{2+} ions, Cu_3TeO_6 is a typical Te-based cuprate and exhibits an enormous diversity of magnetic structures [22–25] and variegated physical properties [2], displaying a long range antiferromagnetic order at $T_N \approx 61$ K [26–28]. As early in 1968 [7], the crystal structure of Cu_3TeO_6 was first determined, and it was modified in 1978 [12]. Herak *et al.* [7] identified the presence of a novel type of magnetic lattice which referred to as a 3D spin-web [22] by scrutinizing the neutron diffraction data crystal structure of Cu_3TeO_6. The existence of special manifestation attracts much interest to the study of Cu_3TeO_6. Moreover, in 2017, Li *et al.* [25] put forward that Dirac magnons may occur in Cu_3TeO_6. Yan *et al.* [2] predicted that the antiferromagnetic phase of Cu_3TeO_6 may be Slater insulator by investigating the electronic and magnetic properties in 2019.

Therefore, Cu_3TeO_6 is a very interesting material due to the fascinating properties, which worthy further studies. But from the available studies on Cu_3TeO_6, the most researches have been carried out on it in the antiferromagnetic state, up to now no comprehensive researches on Cu_3TeO_6 in other two magnetic (paramagnetic and ferromagnetic) states. On the other hand, the properties of materials will change in different degrees under different pressures. High-pressure studies of Cu_3TeO_6 are important to understand its properties under pressure, and it is possible to find new potential features of Cu_3TeO_6 under high pressures. In above context, it is of great significance to study the effects of pressure on paramagnetic, ferromagnetic and antiferromagnetic spin-web Cu_3TeO_6.

In this paper, based on density functional theory, we systematically studied the crystal structures, electronic and magnetic properties of paramagnetic (PM), ferromagnetic (FM) and antiferromagnetic (AFM) Cu_3TeO_6 under 0-100 GPa. We expect to fill in the blanks that studies about Cu_3TeO_6 in three magnetic states under different pressure and provide some references in the search for new features of Cu_3TeO_6 under pressures. This paper is organized as follows: we describe our first-principles calculations details in the next Computational methods section. In results and discussion section, we present the calculated results concerning the structural, electronic and magnetic properties of PM, FM and AFM Cu_3TeO_6, and discuss their properties in comparison under 0-100 GPa, the summary of our work is given in the last section.

2. Computational Methods

As a prized technique in condensed-matter theory, first-principles calculation has become one of the common research methods [29–31]. It can be used to predict the structures and other physical properties of materials under high pressure theoretically, which can provide guidance for the research under high pressure [31]. In our study, we used the first-principles method based on density functional theory (DFT) [32, 33] implemented in the Cambridge Sequential Total Energy Package (CASTEP) code [34]. The calculations adopted the generalized gradient approximation (GGA) with the Perdew-Wang 1991 (PW91) functional [35] to deal with exchange-correlation functional. The GGA + U approach was used to calculate the electronic properties of three magnetic states. The calculation of paramagnetic Cu_3TeO_6 was started without considering the spin polarization. The pseudoatomic calculations were performed on $3d^{10}4s^1$, $4d^{10}5s^25p^4$ and $2s^22p^4$ of Cu, Te and O atoms. In order to ensure the convergence of total energy, the cutoff energy of plane-wave was set to be 400 eV. The Brillouin zone integration was performed using the Monkhorst-Pack [36] method with a k-point grid of 2×2×2 for Cu_3TeO_6. We introduced the different pressures (0-100 GPa) during the geometry optimization (the different pressures were set using the CASTEP code) to study the effect of pressure on crystal structure, electronic and magnetic properties.

3. Results And Discussion

3.1. Crystal structures

In order to verify the reliability of the obtained results, the lattice parameters of antiferromagnetic Cu_3TeO_6 at 0 GPa along with the available data [2, 24, 28, 37] are shown in Table 1 for comparison. The results show that the lattice parameters are in good agreement with these values, showing the accuracy of the structural optimization. The crystal structure of Cu_3TeO_6 at 0 GPa is shown in Figure 1, it is a cubic structure with the space group Ia3(—) [5]. In this structure, each Te atom is surrounded by six O atoms, and they form a regular TeO_6 octahedra,[38] as shown in Figure 1(c). Per unit cell contains eight TeO_6 octahedras and twenty-four Cu^{2+} ions [7, 24]. Six Cu atoms form a planar hexagon [24, 25], surrounded by six O atoms, and they form a distorted octahedron [4, 5, 38], as shown in Figure 1(d). A regular TeO_6 octahedra is connected to irregular CuO_6 octahedras, forming a unique three-dimensional structure [27,

39]. There are two types of Cu-O bonds and Te-O bonds, resulting in the coupling of CuO_6 octahedrons and TeO_6 octahedrons [2]. In three different magnetic states (paramagnetic, ferromagnetic and antiferromagnetic), Cu_3TeO_6 crystals are all cubic structures with the space group Ia3(—) analyzing the optimization results.

Table 1. Space group and calculated lattice parameters along with available experimental data.

Type	Space group	a/Å	Method	Reference
Cu_3TeO_6	$Ia\bar{3}$	9.629	GGA+U	This work
	$Ia\bar{3}$	9.799	GGA+U	[2]
	$Ia\bar{3}$	9.511	LSDA+U	[2]
	$Ia\bar{3}$	9.537	Experiment	[24]
	$Ia\bar{3}$	9.538	Experiment	[28]
	$Ia\bar{3}$	9.513	Experiment	[37]

To find out the specific differences in structure among three magnetic states under different pressures, the next step is to analyze the lattice parameter of three magnetic states from 0 to 100 GPa. The effects of pressure on lattice parameter and volume of Cu_3TeO_6 are shown in Figure 2. It can be seen that these parameters have the similar change trend, namely, the lattice parameter and volume decrease monotonically with the increasing pressure and this is because the pressure compresses the crystal structures. In addition, it could be found that FM state possess greater lattice parameter and cell volume than other two states at the same pressure. With the increasing pressure, the lattice parameter and cell volume of AFM state are larger than that of PM state.

3.2 Electronic structures

The band structures of PM, FM and AFM states and the effect of pressure on band gaps of antiferromagnetic Cu_3TeO_6 from 0-100 GPa are shown in Figure 3 and Figure 4. The vertical dashed line at 0 eV is the Fermi level. For FM and AFM band structures, the pink, yellow and purple lines represent the spin up. The blue, green and orange lines represent the spin down. The spin polarization of the PM state is not considered. From the calculated results of electronic structures, it can be observed that PM and FM band structures have no bandgap at 0 GPa, indicating that they are metallic [2]. As shown in Figure 3(a) and Figure 3(b), with the increasing pressure, they retain their metallicity character. For AFM state, as in Figure 4(a) (only the important Brillouin points are shown in the abscissa), there is an insulation gap at the Fermi level, indicating that it has the non-metallic nature [23]. The valence band maximum (VBM) and

conduction band minimum (CBM) are both located at H point for AFM band structure, this indicates that the insulation gap of antiferromagnetic Cu_3TeO_6 is direct band gap. The value of this direct band gap at 0 GPa is 1.784 eV and this result is basically consistent with that obtained in the literature [23]. Figure 4(b) show the pressure dependence of the band gap of AFM state. Its band gap decreases monotonically with the increasing pressure, which means that its nonmetallic property is weakened. Moreover, in the low pressure section (0-50 Gpa), the band gap decreases fast with the increase of pressure; in the high pressure section (50-100 GPa), the band gap decreases slowly with the increase of pressure.

Next, we adopt the energy range from −25 eV to 25 eV to analyze the effects of pressure on total density of states (TDOS) of three states, as shown in the Figure 5. Comparing the total density of states at the Fermi level under different pressures, we discover that the peak at the Fermi level increases with the increasing pressure for PM state. This results show that its conductivity increases with the increasing pressure. For FM state and AFM state, the pressure has little effect on the total density of states at their Fermi level. From the whole, for three magnetic state states, the bandwidths of TDOS broaden and the TDOS dispersion increases with the increasing pressure. It indicates that the non-locality enhances and the electrons become more active under higher pressure. In other words, the hybridization is enhanced under pressures.

In order to analyze the electronic properties under pressure in detail, the partial density of states (PDOS) under pressure of 0, 40 and 80 GPa is plotted in Figure 6, which can well reflect the variation of PDOS with pressure. For PM state, the density of states at Fermi level originates predominantly from Cu-d and O-p states, and the density of states of Te atom orbits is approximately zero at Fermi level. When the density of each electron orbital is in the same energy range, it indicates that there is hybridization between them. Here, the hybridization is mainly generated by the Te-p and O-p states from −8.0 to −6.5 eV. There is a pseudo-gap between the peaks of O-p states to the left of the Fermi level. At 0 GPa, the density of states in the range of -19.3 eV to -17.4 eV originates predominantly from O-s states; in the range of 4.5 eV to 6 eV, it is predominantly contributed by Te-p states. With the increasing pressure, the peak of Cu-d states at -3 eV decreases and the pseudo-gap decreases. For FM state, there is no significant contribution of Te states around the Fermi level. The electrons from Cu-d and O-p states contribute little to the DOS near the Fermi level. At 0 GPa, the density of states in the range of -8 eV to -4 eV mainly consists of the Cu-d state. the Cu-d, Te-s, Te-p and O-s states have peaks around -5.4, -5.2, -6.5, and -17.5 eV, respectively. When pressure increases, the peaks of Cu-d, Te-s, Te-p and O-s states decrease and the bandwidths become broad. This implies that the electrons in these states are active under pressure [40]. For AFM state, it can be seen that the peak in the valence band near Feimi level is mainly contributed by Cu-d and O-p states, Te atom orbits is approximately zero at Fermi level [3]. At 0 GPa, the density of states in the range of -8 eV to -3 eV originates predominantly from Cu-d and O-p states, which indicates that strong hybridization between Cu-d and O-p states [5, 23]. In addition, O-s states are mainly located between −19 and -18 eV, -16.7 and -14.4 eV. The Te-s and Te-p states also appear in these two ranges, respectively. This suggests that the hybridization between Te and O atoms [5]. With the increasing pressure, the peaks of Cu-d, Te-s, O-s and O-p states decrease and the non-locality enhances. In summary,

the pressure not only affects the crystal structures but also impact the electronic properties of Cu_3TeO_6 in three states.

3.3. Magnetic properties

Because the ground state of Cu_3TeO_6 is antiferromagnetic state [27], we analyze the magnetic properties of antiferromagnetic Cu_3TeO_6 under different pressures. Figure 7 shows the spin moments dependence of pressure and the total magnetic moment dependence of pressure. In Figure 7(a), the spin magnetic moment of the Cu atoms at 0 GPa is 0.76 μ_B, which is larger than experimental value of 0.64 μ_B [7] and smaller than calculated value of 0.81 μ_B in literature [23]. The spin contribution of O atoms is small and Te atoms show nonmagnetic feature, Cu atom contributing the most to the total magnetic moment. With the increasing pressure, the spin contribution of Cu atoms decreases remarkably, and the spin moments have little change for Te and O atoms. This illustrates that the spin moment of Cu atoms is affected obviously by the pressure, while the spin moments of Te and O atoms are insensitive to pressures. In Figure 7(b), the total magnetic moment reaches the maximum at 20 GPa and decreases monotonously with increasing pressure from 20 to 100 GPa.

In order to get more information from the magnetic properties, the orbital projected DOS of Cu-d, O-p, Te-s and Te-p states under 0, 40 and 80 GPa are shown in Figure 8, the positive and negative values on the y axis stand for spin-up and spin-down, respectively. The calculated magnetic moments of O-s [23], Cu-s and Cu-p states are small and it is negligible, so they are not shown here. It can be seen that there are spin down states of Cu and O atoms around 2.5 eV, which indicates that strong hybridization between Cu-d and O-p states [5]. For Cu-d states, most of the spin moments are totally occupied and a few spin moments are partially occupied, showing the high spin state of Cu ions in Cu_3TeO_6 [5]. The spin contribution of Te atoms is small because the distribution of the spin-up and spin-down densities are substantially symmetric for different orbital. Total magnetic moment is mainly from the spin down states of Cu-d and O-p states, and these results are in good agreement with previous results. For Cu and O atoms, the spin up states and spin down states are decreased with pressure. The spin up states and spin down states of Te atoms move sideways under the pressure. The total magnetic moment varies mainly with the spin contribution of Cu and O atoms.

4. Summary

Based on the density functional theory, we have studied the structural, electronic and magnetic properties of paramagnetic, ferromagnetic, and antiferromagnetic spin-web Cu_3TeO_6 in pressure range 0-100 GPa. The results of the calculations reveal that Cu_3TeO_6 crystals are all cubic structures in three magnetic states, and their lattice parameters decrease monotonically with the increasing pressure. The calculated band structures show that PM and FM Cu_3TeO_6 behave in a metal manner at all pressures of interest. For AFM state, it exhibits a non-metallic nature with a direct band gap, and its nonmetallic property is weakened with the increasing pressure. For the three states, the bandwidths of TDOS broaden obviously,

and the electrons become more active under higher pressure. We have also investigated the magnetic properties of antiferromagnetic Cu_3TeO_6, finding that the value of spin magnetic moment of the Cu atoms is in good agreement with other reliable results. Total magnetic moment reaches the maximum at 20 GPa, and it decreases monotonously with the increasing pressure from 20 to 100 GPa. The total magnetic moment is mainly from the spin down states of Cu and O atoms with light contribution of Te atoms.

Declarations

Funding

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Conflicts of interest/Competing interests

All authors declare that we have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this manuscript.

Availability of data and material

The data sets supporting the results of this work are included within the article, the other datasets generated during the current study are available from the corresponding author on reasonable request.

Code availability

Not applicable

Authors' contributions

Yi-Hua Du：Writing - original draft, Formal analysis, Investigation, Methodology, Software

Wei Zeng：Investigation, Methodology, Writing - review & editing

Bin Tang：Methodology, Software, Writing - review & editing

Mi Zhong：Data curation, Writing - review & editing, Visualization

Qi-Jun Liu：Conceptualization, Project administration, Resources, Supervision, Writing - review & editing

Fu-Sheng Liu: Data curation, Methodology, Writing - review & editing

Xiao-Juan Ma：Data curation, Methodology, Conceptualization, Visualization

Ethics approval

Not applicable

Consent to participate

Not applicable

Consent for publication

Not applicable

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Figures

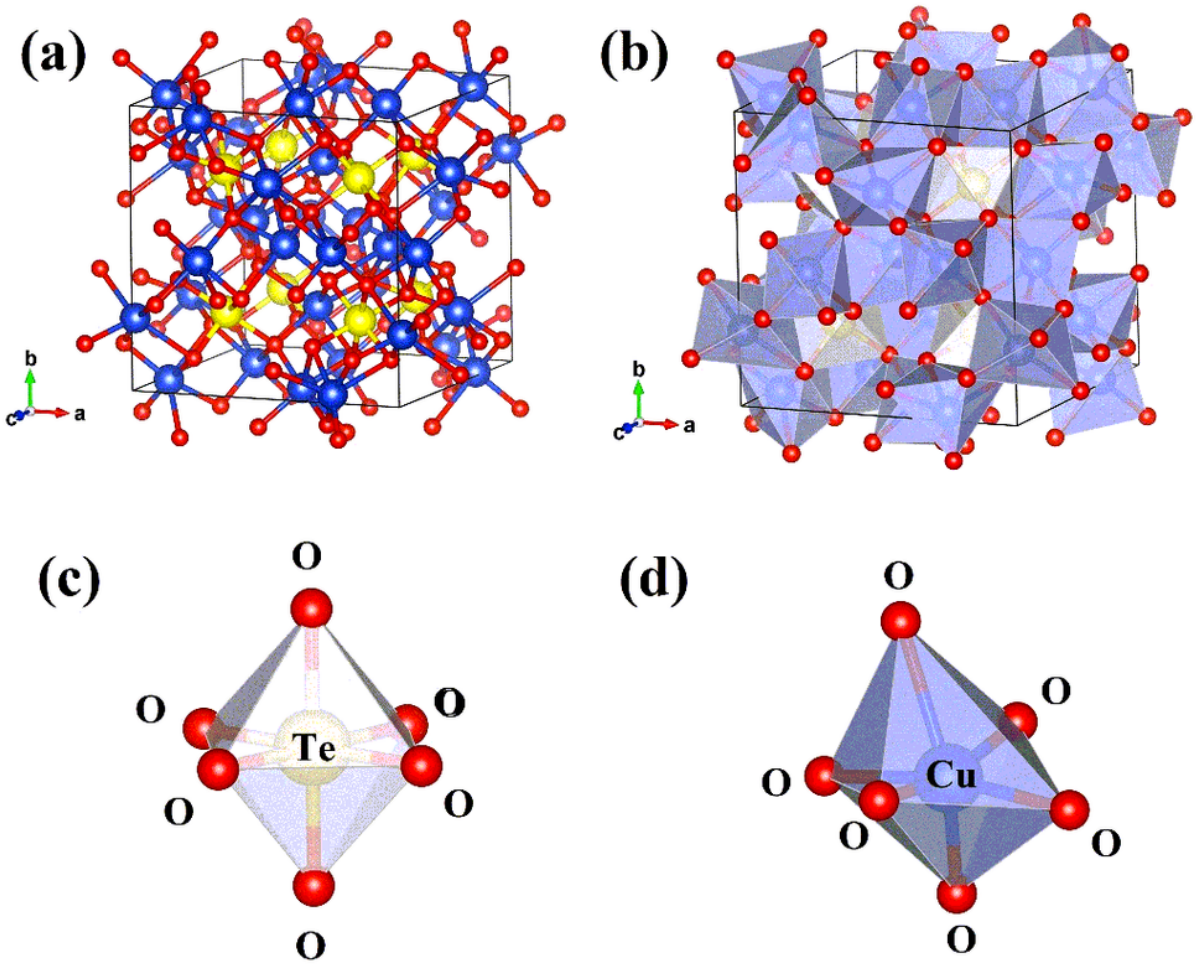

Figure 1

(color online) Fig. 1 (a) The unit cell of Cu3TeO6 at 0 GPa; (b) the structure of Cu3TeO6 at 0 GPa; (c) TeO6 regular octahedra; (d) CuO6 irregular octahedra.

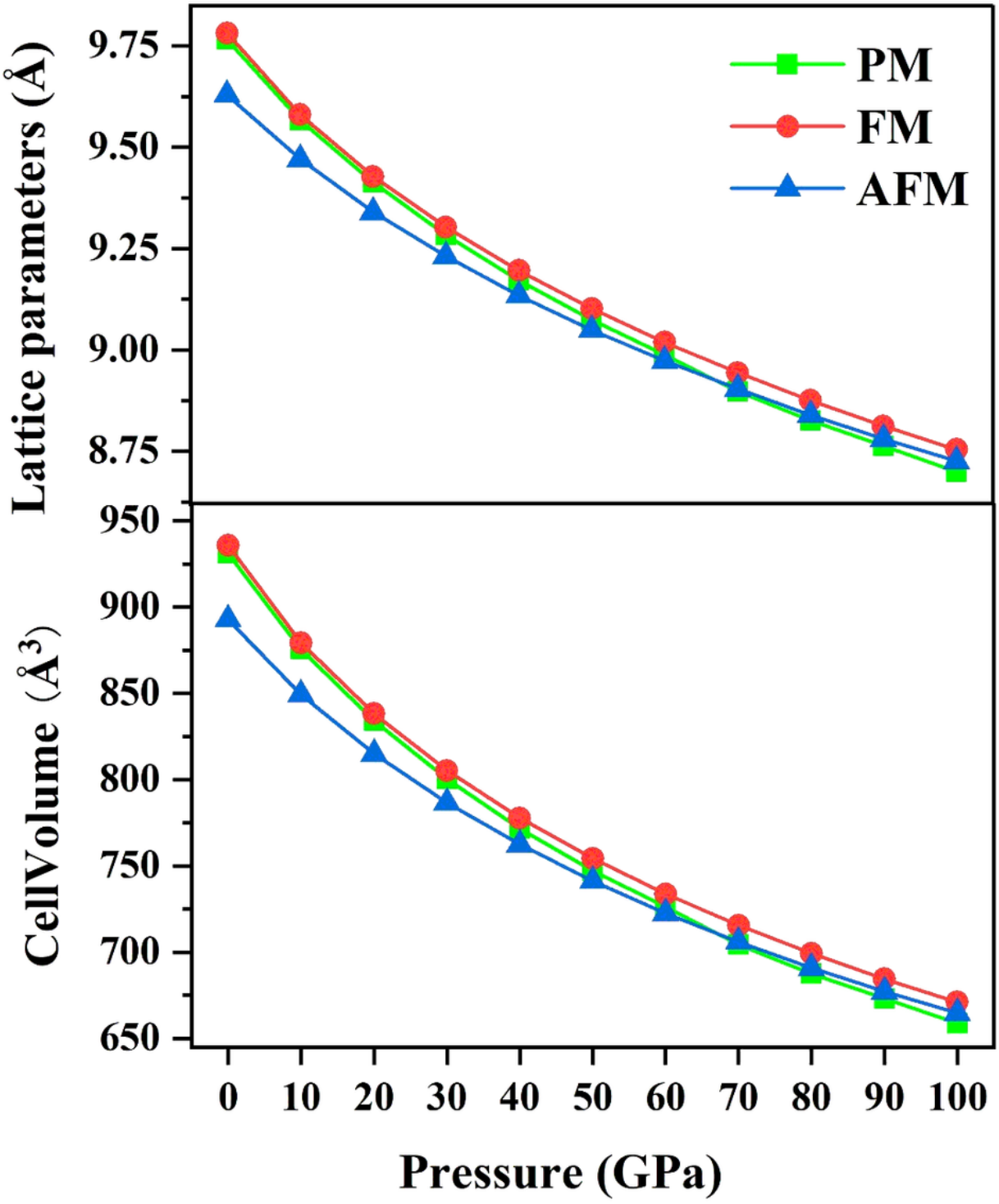

Figure 2

(color online) Fig. 2 The effects of pressure on lattice parameter and volume.

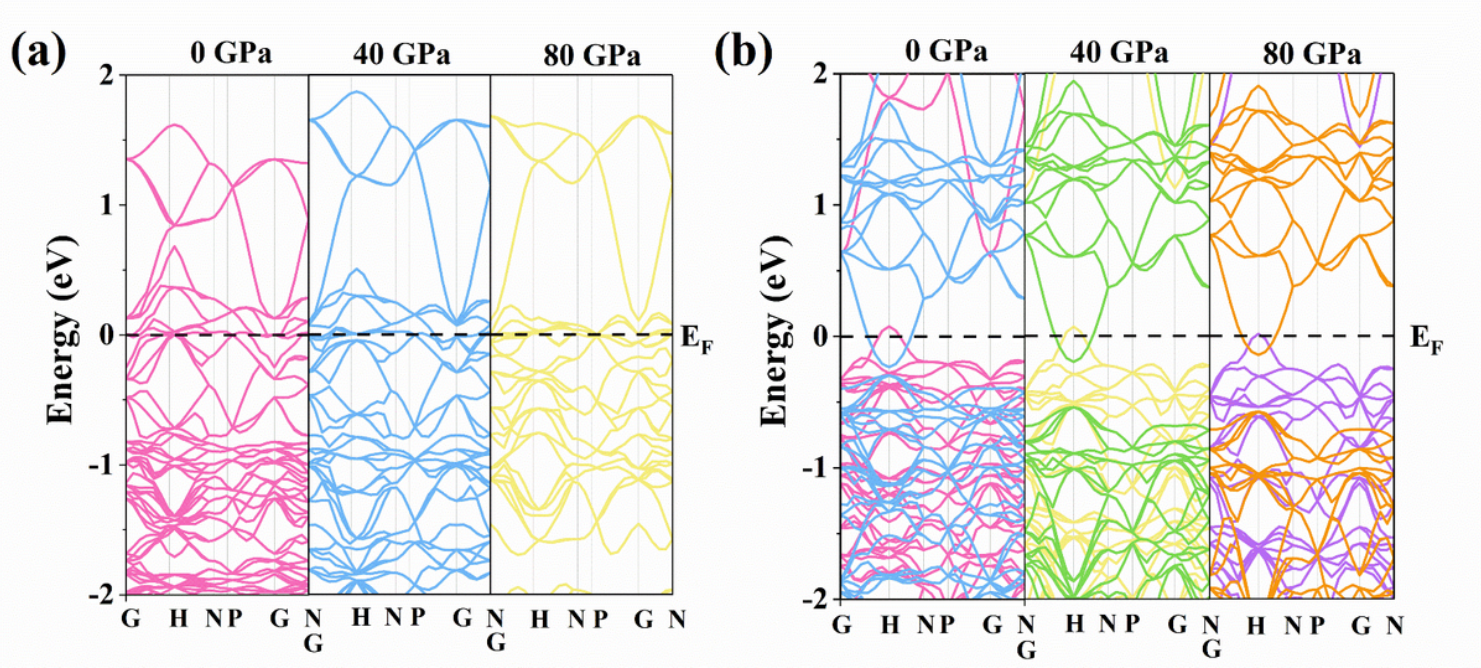

Figure 3

(color online) Fig. 3 Band structures of (a) paramagnetic and (b) ferromagnetic Cu3TeO6.

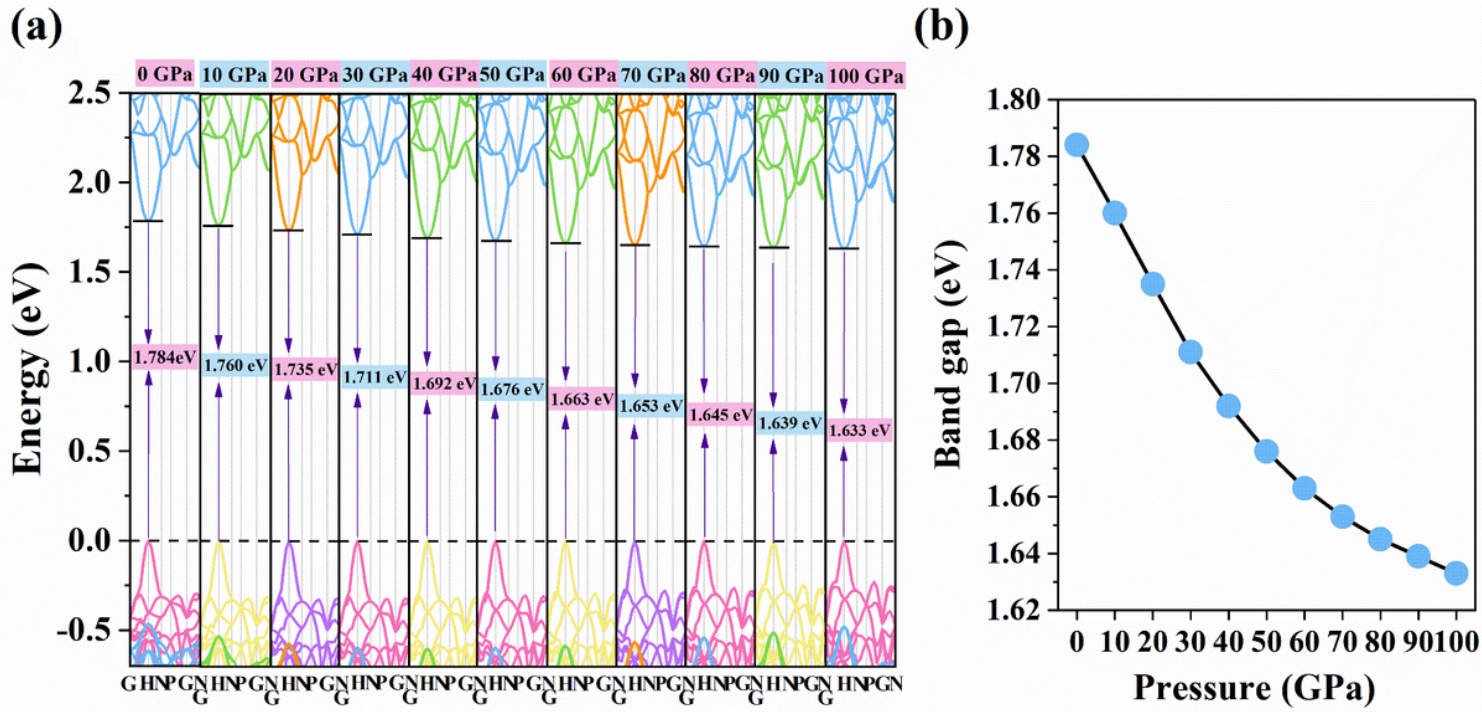

Figure 4

(color online) Fig. 4 (a) band structures of antiferromagnetic Cu3TeO6 from 0-100 GPa; (b) the effect of pressure on band gap of antiferromagnetic Cu3TeO6.

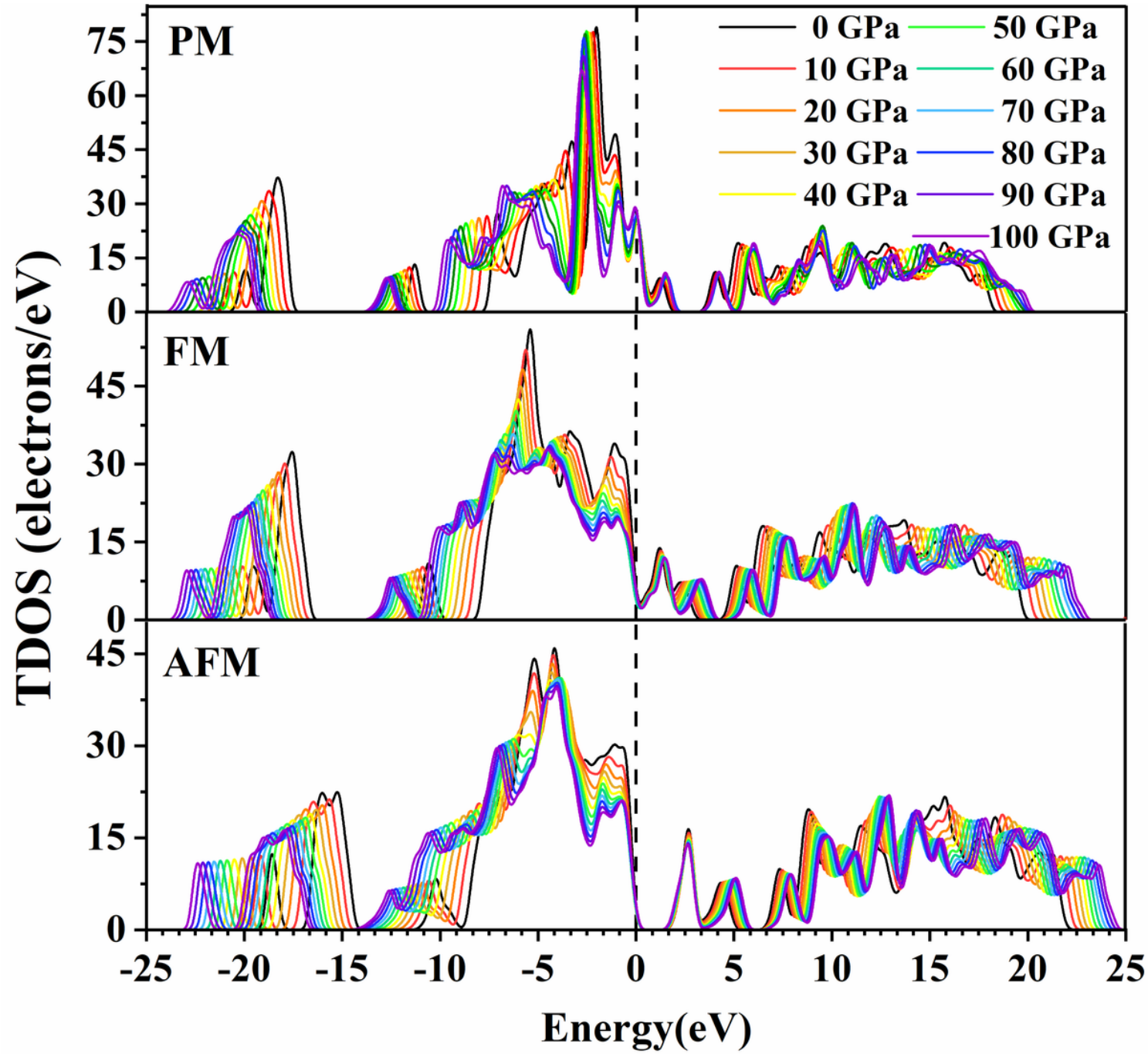

Figure 5

(color online) Fig. 5 The effects of pressure on total density of states of paramagnetic, ferromagnetic and antiferromagnetic Cu3TeO6.

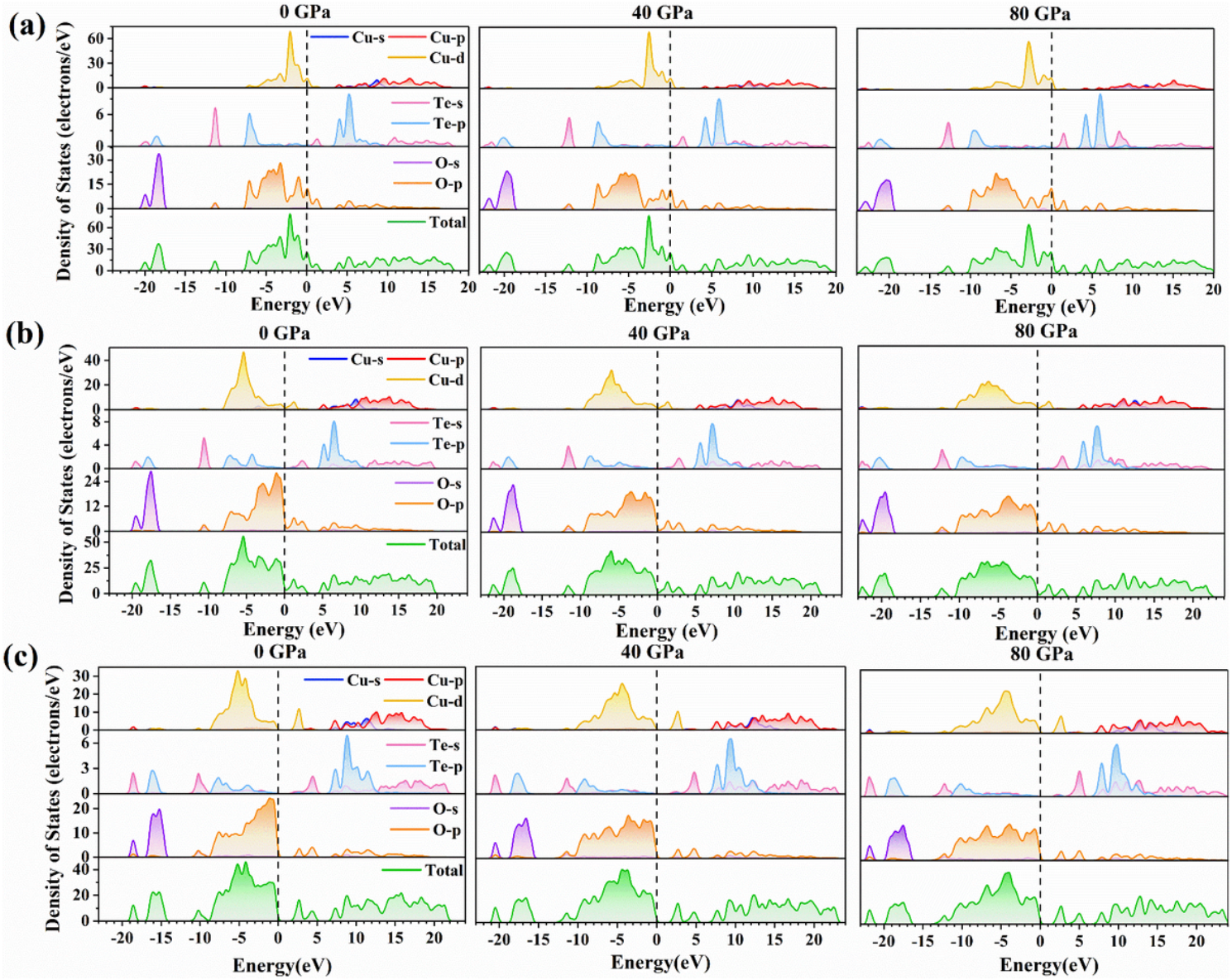

Figure 6

paramagnetic, (b) ferromagnetic, and (c) antiferromagnetic Cu3TeO6.

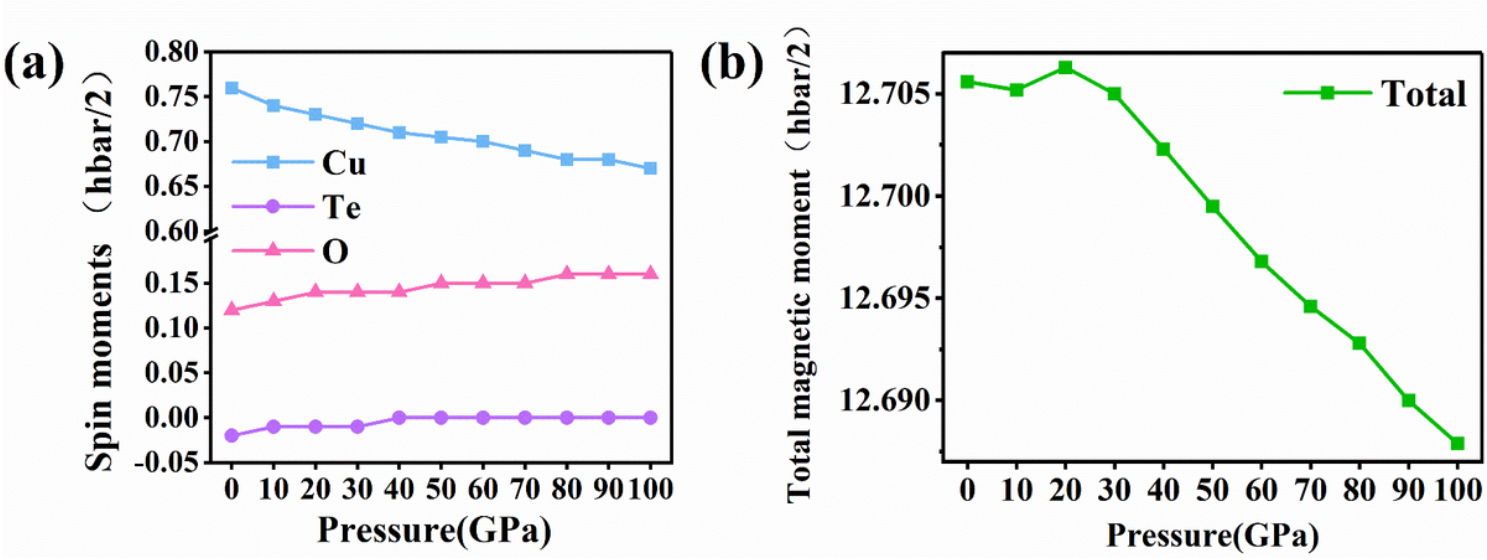

Figure 7

(color online) Fig. 7 Antiferromagnetic Cu3TeO6: (a) the spin moments dependence of pressure; (b) the total magnetic moment dependence of pressure.

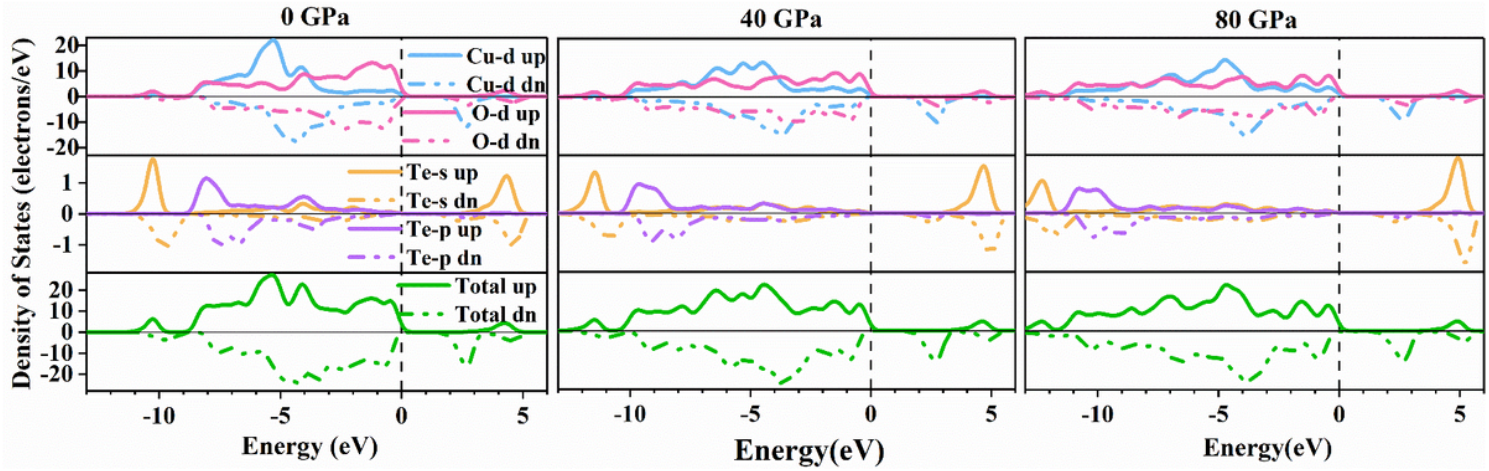

Figure 8

(color online) Fig. 8 The orbital projected DOS of Cu-d, O-p, Te-s and Te-p states under 0, 40 and 80 GPa for antiferromagnetic Cu3TeO6.