

First Principles Calculation of Magnetic Resonance Properties of $\text{Cu}_{2-\delta}\text{X}$ (X = Se, S, Te)

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Abstract

In order to have a better understanding of the electronic structures and physical properties of $\text{Cu}_{2-\delta}\text{X}$ (X = Se, S, Te) copper chalcogenides. First principles were performed to calculate the chemical shift, band structure, and electron density of states of $\text{Cu}_{2-\delta}\text{X}$ (X = Se, S, Te). By comparing our calculation results with previous experimental works, we found that the predicted electronic structures of Cu_2Se , Cu_2Te and Cu_2S transform from semimetal to semiconductor after adding on-site Coulomb U, which reflects the real properties of the materials. By using (Density Functional Theory) DFT + U method, the calculation result is close to the real electronic structure. The calculation result of chemical shift of adding U does not reach the ideal expectation, and the reason is not clear at present. In this paper, the theoretical electronic structures of Cu_2Se , Cu_2Te and Cu_2S are better calculated by DFT + U method and compared with the actual properties. The effect of Cu-s electron on the chemical shift is understood, and a theoretical result of the chemical shift is calculated, which provides a powerful reference for the subsequent research and understanding of the electronic structure and physical properties of the compounds with S groups of Cu.

Keywords

Copper Chalcogenides, Chemical Shift, First Principles Calculation

1. Introduction

Copper chalcogenides represented by Cu_2Se , Cu_2S , Cu_2Te , have received more and more attentions in recent years for their potential applications in photovoltaic, semiconductor, supercapacitor and thermoelectric materials [1] [2]. For example, Cu_2Se is a kind of promising thermoelectric materials. It can make a direct conversion between heat and electricity. The special liquid-like behavior

of Cu ions in the Se atomic crystalline sublattice results in low thermal conductivity and high ZT (thermoelectric figure of merit) [3] [4] [5] [6], which is beneficial for the performance of such thermoelectric materials [7] [8]. The development of thermoelectric technology provides an efficient and emission-free method for the recycling of industrial waste heat [9] [10] [11]. Moreover, Cu₂Se is a typical P-type semiconductor with an indirect band gap of 1.23 eV, which is close to the ideal value for solar cell applications. Therefore, Cu₂Se is considered as a possible energy conversion material in photovoltaic as well [12]. These excellent performances of Cu₂Se provide a good way to solve the global energy shortage and improve the efficiency of energy conversion and utilization.

The crystal structure of Cu₂Se is complex. There are two different phase structures for Cu₂Se, which are distinguished by low temperature α -phase and high temperature β -phase, respectively [13] [14]. Below 400 K, the low temperature α -phase Cu₂Se has several possible crystal structures. The Cu sublattice changes from ordered to disordered as the temperature increases, but the details of the process are still not very clear [15] [16]. The high temperature and low temperature phases of Cu₂Se have been studied. But crystal structure of the low temperature monoclinic phase is relatively complex and is still not fully understood [17] [18]. The high-temperature phase has been identified as the cubic phase (space group Fm-3m) [19]. The superior performance of Cu₂Se (ZT) is influenced by its electrical transport property, which in turn strongly correlated with the electronic structure of it. Therefore, the properties of Cu₂Se, Cu₂S and Cu₂Te are closely related to their electronic structures, better understanding of their electronic structures can help optimizing the performance of such materials. Nuclear magnetic resonance (NMR) is considered as an important technique for investigating the local chemical environment of certain isotropic. It is also a local probe for observing the ionic diffusion [20] [21]. Moreover, NMR chemical shift can well reflect the related characteristics of electronic structure. The study of this paper is based on first principles, using VASP, CASTEP and other software; some parameters of NMR were calculated theoretically. The theoretical calculation results of chemical shift in NMR are compared with those of energy band structure and electron density of states, The theoretical results of NMR chemical shift and electronic structure are calculated by different methods, and the electronic structure characteristics of S group compounds of Cu are analyzed and compared theoretically from different angles, It is helpful to deepen the understanding of structural properties of S group metal materials such as Cu₂Se [22].

There have been studies on NMR based on sulfur-based metal compounds, on this basis, Cu₂Se's high temperature phase is selected as the research system (space group is Fm-3m), There are two Cu crystallographic sites in the average structure of Cu₂Se, namely 8(c) and 32(f) sites [23] [24]. The structure of Cu₂Se calculated in this paper only considers the 8(c) bits of Cu atom. Asadov *et al.* summarized the previous experiments of Cu₂Te phase. There are many different phases at different temperatures, and phase transitions occur with temperature, Cu₂Te has a cubic antiferroite structure at 835 K [25] [26]. Cu₂Se and Cu₂S also

have complex phase transitions with different temperatures [27] [28]. Cu_2S is a face-centered cubic phase structure at 700 K, so the space group of Cu_2S is also selected as Fm-3m to do relevant calculations [29]. The high temperature opposite fluorite structure of Cu_2Se is shown in **Figure 1**. The NMR chemical shift characteristics of Cu_2Se are studied by VASP and CASTEP, and compared with the theoretical calculation of electronic structure.

Previous NMR experiments can measure Chemical Shifts, which can reflect some electronic properties and characteristics, but have no way of associating Knight shift with specific atoms. In recent years, the method of matching chemical shifts with specific atoms has been developed, and the chemical shifts calculated by NMR simulation have been compared with the theoretical calculations of electronic structures, which provide a new perspective and reference for the understanding of the properties of electronic structures, making the calculation results more reliable and meaningful.

Therefore, the purpose of this paper is to explore how to obtain the electronic structures of Cu_2Se , Cu_2Te and Cu_2S that are more consistent with the actual conditions through first-principles calculation. The chemical shifts of the three materials are also calculated to obtain the information of electronic structure. The main contribution of this paper is that the calculation using (Density Functional Theory) DFT + U can better reflect the real electronic structures of the three materials. Through the analysis of the electron density of states of the materials, it is known that Cu-s electrons should have the greatest influence on the chemical shift, but the results calculated by VASP and CASTEP do not meet the expectation.

2. Computational Details

The calculation of this work is based on density functional theory (DFT) [30] and implemented in the Vienna Ab initio Simulation Package (VASP) [31] [32]. We use the Perdew-Burke-Ernzerhof (PBE) type of generalized gradient approximation (GGA) as the exchange-correlation functional [33] [34] [35]. The

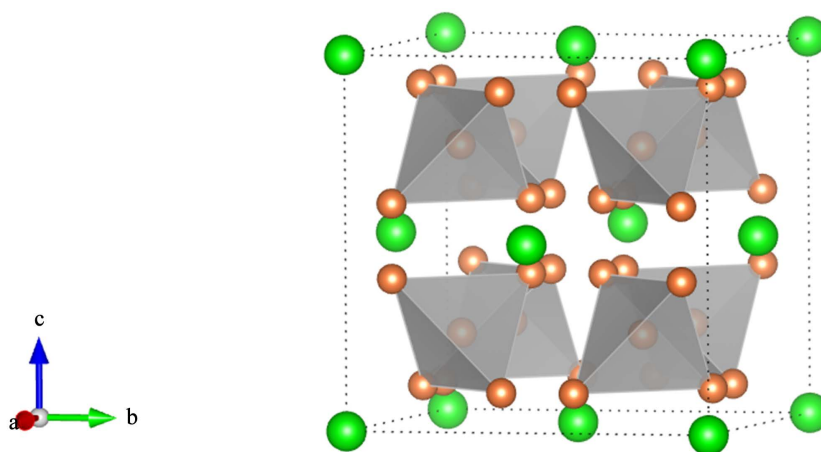


Figure 1. High temperature phase structure of Cu_2Se .

valence electron configurations employed in our calculations are Cu ($3d^{10}, 4s^1$), Se ($4s^2, 4p^4$), Te ($5s^2, 5p^4$) and S ($3s^2, 3p^4$). The interaction between the core electrons and the valence electrons is included by the standard frozen-core projector augmented-wave (PAW) potentials provided within the VASP package [36]. In this paper, we use the PBE + U method to calculate the band structure, density of states, and chemical shifts. During Cu_2Se Structure optimization, we adopt the Monkhorst-Pack scheme k-point mesh from gamma to the $21 \times 21 \times 21$ point and use finer k-points to further calculate the electronic structures; the convergence precision of ions and electrons is 1×10^{-6} eV, and the cut-off energy is set to 500 eV. VASP and CASTEP were used to calculate the NMR chemical shifts, the cut-off energy is set to 1000 eV, and the Automatic mesh k-points grid was $21 \times 21 \times 21$.

3. Results and Discussion

It is found that the ^{63}Cu NMR chemical shifts of existing literature of Cu_2Se samples remain almost unchanged above 400 K [20]. As we know, the addition of Cu atoms in Cu_2Se will provide more free electrons. Different concentrations of Cu will lead to different concentrations of electrons provided by Cu. However, different concentrations of electrons should have an impact on the chemical shift. So using VASP software to do the first principles of calculation can help us more understand characteristics of materials. The partial wave densities and total densities of states of Cu_2Se , Cu_2S and Cu_2Te with different Cu contents were calculated and analyzed, and the effects of the three materials plus U on the chemical shifts were also analyzed.

The observed Chemical shift can be derived from three parts, Ks, Kd and Kp [37], which are correlated to the contributions of s, p and d electrons. Among these three parts, the contribution of s electrons, namely Ks, has the most significant effect on the chemical shift [38]. While the contributions of s and d electron are somewhat relative weak, it had been observed that the chemical shift of Cu in Cu_2Se kept unchanged between 300 K - 400 K. The experimental results showed a much smaller value of the chemical shifts of Cu, compared with that of elemental Cu metal. In this paper, partial density of states focused on Cu atom was performed to clarify the contribution to chemical shift. Therefore, VASP is used to calculate the partial wave state density of different components s, p and d, the contribution of p electrons to chemical shift is generally negative, Because of the influence of Van Vleck paramagnetism, and the contribution of d electron to chemical shift is small.

The chemical shift in elemental Cu is much larger than that in Cu_2Se , indicating that it is mainly the d electron bonding of Cu. By calculating the electron state density of Cu_2Se with different Cu composition ratio, it can be found that with the increase of Cu content in Cu_{2-x}Se , the electron state density of different Partial wave state increases with the increase of Cu ratio. It is d electron that increases the density of states most significantly, and Ks that increases the chemi-

cal shift most significantly. Therefore, in theory, although the increase of copper proportion will lead to the increase of electron density of states, the increase of K_s electrons has little effect on the chemical shift.

3.1. NMR Chemical Shift Calculation Results

In order to further understand its electronic structure, energy band structure and other characteristics, we used different software to calculate the theoretical results of NMR chemical shift, and analyzed the changes of solid NMR chemical shift after adding U.

The calculated NMR isotropic chemical shifts are listed in **Table 1**. Various on sites Coulomb U values are added to search the effect of U on the calculated chemical shifts. Generally, the calculated chemical shifts of Cu_2S , Cu_2Se , and Cu_2Te using VASP program are close. With increasing U values, the calculated shifts became smaller and smaller. Thus, according to the results of VASP, the effect of on-sites Coulomb U cannot be neglected. The results of CASTEP are different. The calculated chemical shifts are much more different from each other. Moreover, the varied U values had nearly no effect on the calculated chemical shifts. The differences between these VASP and CASTEP are not very clear.

3.2. Density of Electronic States

Figure 2 shows the calculated density of states of Cu_2S , Cu_2Se and Cu_2Te . Since we will discuss the chemical shifts of Cu, only the contribution made by Cu atoms are shown. According to the calculation results of PBE method, it can be seen from -4 eV to Fermi level, the density of states is mainly contributed by Cu-3d electrons. It can be seen that among the three kinds of materials, the

Table 1. Calculated chemical shift of Cu_2Se , Cu_2S and Cu_2Te by DFT + U.

Calculated value of chemical shift of Cu in VASP first principles				
	U = 0 eV	U = 4 eV	U = 7.5 eV	U = 10 eV
	PBE ISO_SHIFT	PBE + U ISO_SHIFT	PBE + U ISO_SHIFT	PBE + U ISO_SHIFT
Cu_2Se	647.9390	-236.8034	-647.5071	-874.4668
Cu_2S	598.7500	-90.2254	-537.0861	-775.6825
Cu_2Te	543.2066	-124.2206	-522.5469	-740.6468
Calculated value of chemical shift of Cu in CASTEP first principles				
	U = 0 eV	U = 4 eV	U = 7.5 eV	U = 10 eV
	PBE ISO_SHIFT	PBE ISO_SHIFT	PBE ISO_SHIFT	PBE ISO_SHIFT
Cu_2Se	2131.94	2128.97	2131.38	2129.37
Cu_2S	205.90	205.99	206.43	206.67
Cu_2Te	874.90	874.82	874.86	874.35

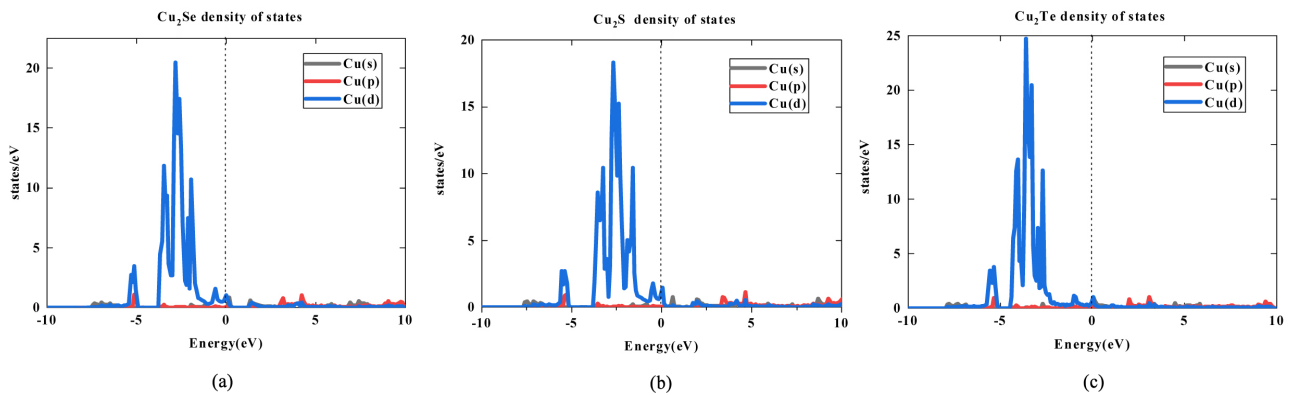


Figure 2. The density of states contributed by Cu atom in Cu_2Se , Cu_2S and Cu_2Te . Calculated using PBE method by VASP.

contribution of Cu's d electron to the density of states is the largest, and the contribution of s electron and p electron to the d electron is very small. This result can also be obtained in the calculation results of electron state density of Cu_2Se with different Cu proportions in **Figure 3**. Thus it can be concluded that the electron state density of Cu_2Se , Cu_2S and Cu_2Te mainly comes from the d electron of Cu.

For Cu_2Se with different Cu ratios, the electron densities of s, p and d of Cu varied with the content of Cu. The calculated results show that the change of d electron of Cu with Cu content is significant, and the effect of d electron should be considered if the chemical shift changes greatly. **Figure 3** electron state density of Cu_2Se with different component ratios. It can be seen that the electron state density in Fermi surface increases with the increase of Cu content. As the number of Cu atoms increases, the density of electron states provided by Cu atoms also increases. The magnitude of chemical shift in NMR is mainly affected by the extranuclear electrons. Therefore, the calculated value of electron density of states increases with the increase of Cu content, which is useful for analyzing the effect of electron density of states on chemical shift.

The calculated partial density of states of Cu in Cu_{2-x}Se has been shown in **Figure 3**. With the increase of Cu concentration, the states of d electrons increased significantly. Compare with d electrons, there is little increment of the states of s and p electrons. Therefore, with the increase of Cu content, the increment of d-electron density is much larger than the increment of s and p-electron density.

Cu_2Se electronic state density by theory calculation, we compare the different software computing Cu_{2-x}Se NMR chemical shift theory as a result, the contribution of the further understanding of the copper electronic Cu_2Se chemical shift change, through the analysis of the calculation results NMR chemical shift, we can from the new dimension more reliable further understand the electronic structure of materials. In conclusion, understanding the electronic structure of the material can help us understand the physical properties and structure of Cu_2Se .

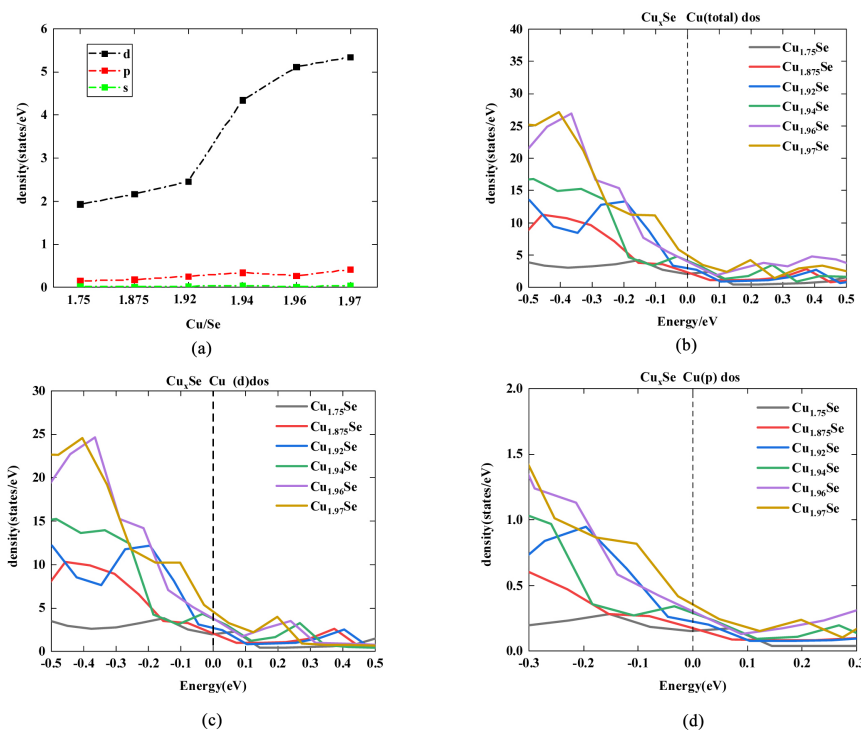


Figure 3. Density of electron states at Fermi surfaces of Cu₂Se with different Cu ratios. Figure (a) shows the partial wave state densities of Cu₂Se with different Cu ratios; (b) shows the total density of Cu states at Fermi surfaces of Cu₂Se with different Cu ratios; (c) and (d) show the d-electron and p-electron densities of states at Fermi surfaces of Cu in Cu₂Se with different Cu ratios.

3.3. Band Structure

In the calculation of energy band structure and electronic density of states, VASP is used to calculate Cu₂Se, Cu₂S, Cu₂Te with various on-site Coulomb U . The method of PBE + U ($U = 10$ eV) has been used to explore the electronic structure of Cu₂Se, and reliable results have been obtained by Rasander M, Bergqvist L, Delin A. [39]. According to the works of Rasander M. 4 eV, 7.5 eV and 10 eV are applied in this work. The cut-off energy was set to 1000 eV. **Figure 4** shows the band structure diagram of the high-temperature phase of Cu₂Se, Cu₂S, Cu₂Te. It can be seen that when U is not added, there is no band gap in the band structure of Cu₂Se, so it is predicted as a semimetal. When U is added to 10 eV, the band gap appears obviously. That is to say, its band structure is considered as a semiconductor. Therefore, the band gap generated when U is added more accurately reflects the real band structure, indicating that adding U can make the theoretical results closer to the real band structure. It can be seen **Figures 4(c)-(f)**, the same situation occurs when Cu₂S and Cu₂Te U were added in the calculation of energy band. Therefore, when calculating the band structure of such materials and calculating the electronic density of states, it is necessary to add U appropriately to ensure the accuracy of calculation. With the consideration above, DFT + U method were performed to the calculation of chemical shifts of these copper chalcogenides.

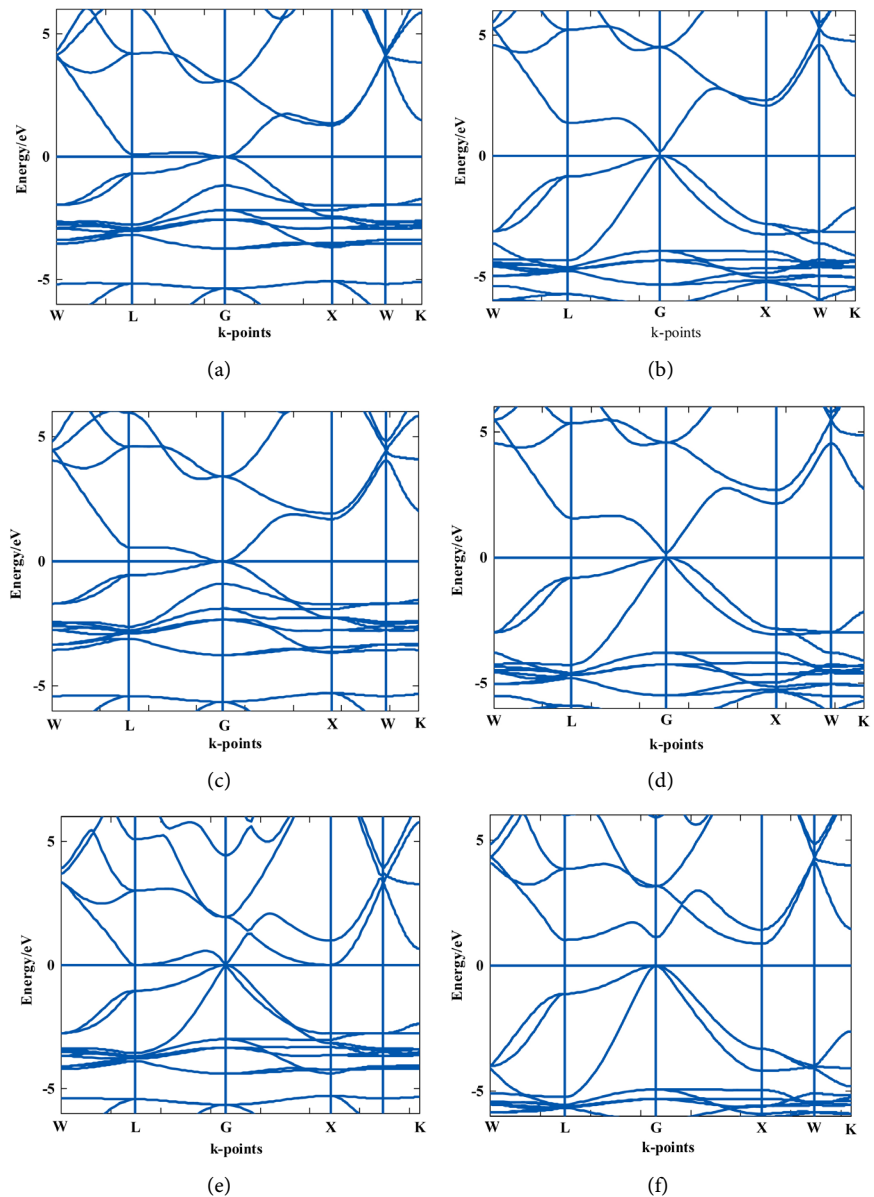


Figure 4. (a) and (b) show the band structure of PBE and PBE + U ($U = 10$ eV) of Cu_2Se ; (e) and (d) shows the band structure of PBE and PBE + U ($U = 10$ eV) of Cu_2S . (e) and (f) shows the band structure of PBE and PBE + U ($U = 10$ eV) of Cu_2Te . (a) Cu_2Se PBE + U ($U = 0$ eV); (b) Cu_2Se PBE + U ($U = 10$ eV); (c) Cu_2S PBE + U ($U = 0$ eV); (d) Cu_2S PBE + U ($U = 10$ eV); (e) Cu_2Te PBE + U ($U = 0$ eV); (f) Cu_2Te PBE + U ($U = 10$ eV).

4. Conclusion

In this paper, the density of states, band structures and NMR chemical shifts of Cu_2Se , Cu_2S and Cu_2Te have been systematically studied by first principles calculation. By performing a DFT + U calculation, the band gap of Cu_2X opened and showed semiconductor structures. Our calculation of DOS shows that the density of states of Cu_2Se , Cu_2S and Cu_2Te is mainly contributed by the d electrons. However, due to the influence of Van Vleck paramagnetization, the d electron has little effect on the chemical shift. However, the contribution of p-electron

chemical shift is generally negative, so among the contributions of K_s , K_p and K_d . The contribution of s electron to chemical shift should be the most significant, but the state density of s electron is small, so its influence on the chemical shift is also small. The isotropic chemical shifts of Cu_2Se , Cu_2S and Cu_2Te were calculated by using VASP and CASTEP with various on-site Coulomb U values. The chemical shifts of Cu_{2-x}X calculated by CASTEP with different U values are basically the same. However, the isotropic chemical shift calculated by VASP is becoming smaller with increase U values. Subsequently, some experimental results can be obtained from the NMR chemical shifts of Cu_2Se , Cu_2Te and Cu_2S in the direction of the experiment. Referring to the calculated results, it will better promote the understanding of the structural properties of the materials.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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