Density functional theory study of the electronic structure of fluorite Cu$_2$Se

Mikael Råsander$^1$, Lars Bergqvist$^{1,2}$ and Anna Delin$^{1,2,3}$

$^1$ Department of Materials Science and Engineering, Brinellvägen 23 KTH (Royal Institute of Technology), SE-100 44 Stockholm, Sweden
$^2$ SeRC (Swedish e-Science Research Center), KTH, SE-100 44 Stockholm, Sweden
$^3$ Department of Physics and Astronomy, Uppsala University, Box 516, SE-751 20 Uppsala, Sweden

E-mail: mikra@kth.se

Received 13 November 2012, in final form 16 January 2013
Published 28 February 2013
Online at stacks.iop.org/JPhysCM/25/125503

Abstract

We have investigated the electronic structure of fluorite Cu$_2$Se using density functional theory calculations within the LDA, PBE and AM05 approximations as well as the non-local hybrid PBE0 and HSE approximations. We find that Cu$_2$Se is a zero gap semiconductor when using either a local or semi-local density functional approximation while the PBE0 functional opens up a gap. For the HSE approximation, we find that the presence of a gap depends on the range separation for the non-local exchange. For the occupied part in the density of states we find that LDA, PBE, AM05, PBE0 and HSE agree with regard to the overall electronic structure. However, the hybrid functionals result in peaks shifted towards lower energy compared to LDA, PBE and AM05. The valence bands obtained using the hybrid functionals are in good agreement with experimental valence band spectra. We also find that the PBE, PBE0 and HSE approximations give similar results regarding bulk properties, such as lattice constants and bulk modulus. In addition, we have investigated the localization of the Cu d-states and its effect on the band gap in the material using the LDA $+U$ approach. We find that a sufficiently high $U$ indeed opens up a gap; however, this $U$ leads to valence bands that disagree with experimental observations.

(Some figures may appear in colour only in the online journal)

1. Introduction

The copper chalcogenides Cu$_2$X (X = S, Se, and Te) are of possible technological interest because of their thermoelectric and photovoltaic properties as well as ionic conductivity. Cu$_{2-x}$Se, which is the focus of this study, has in particular received attention due to its high ionic conductivity, with possible applications in solar cells [1, 2] as well as being a good material for thermoelectric converters [3]. At room temperature, Cu$_{2-x}$Se is a rather good p-type conductor with an optical band gap of 1.23 eV [4]. The Cu$_{2-x}$Se system has a rather complicated atomic structure where the phase diagram consists of two phases: the low temperature $\alpha$-phase and the high temperature $\beta$-phase [5]. The $\beta$-phase with the space group $Fm\bar{3}m$ has the Se atoms in a face-centered cubic (fcc) environment while the superionic Cu atoms are randomly distributed on interstitial positions in the structure, where the majority of the Cu ions are positioned close to the tetrahedral interstitial sites [6, 7]. The low temperature phase is stable up to about 400 K and has a lower symmetry crystal structure, where the Cu atoms are not diffusing. We point out that the $\alpha$ to $\beta$ transition varies with the stoichiometry and for $x = 0.15–0.25$ the high temperature phase is stable at room temperature [8]. In addition, we note that both the high and the low temperature phases can be imagined as deviations from the fluorite crystal structure with the difference lying in the occupation of the tetrahedral interstitial positions.

Recently, Liu et al [3] showed that Cu$_{2-x}$Se exhibited excellent thermoelectric properties for a bulk material with a thermoelectric figure of merit of $zT = 1.5$ at 1000 K. The reasons for the favorable thermoelectric properties appear to be a low thermal conductivity due to the quasi-liquid behavior of the superionic Cu atoms combined with a rather high value of the power factor $S^2\sigma$, where $S$ is the Seebeck coefficient.

0953-8984/13/125503+07$33.00 © 2013 IOP Publishing Ltd Printed in the UK & the USA
The crystal structure of fluorite Cu$_2$Se, where Cu atoms are depicted by small (white) spheres and Se atoms by large (black) spheres. The Cu–Se bonds are shown in gray.

Figure 1. The crystal structure of fluorite Cu$_2$Se, where Cu atoms are depicted by small (white) spheres and Se atoms by large (black) spheres. The Cu–Se bonds are shown in gray.

The Kohn–Sham equation has been solved using the projector augmented wave method [12] as it is implemented in the Vienna *ab initio* simulation package (VASP) [13, 14]. Calculations have been performed using the local density approximation (LDA) [15], the generalized gradient approximation of Perdew, Burke and Ernzerhof (PBE) [16] as well as the AM05 functional of Armiento and Mattsson [17–19]. Since local and semi-local approximations to the XC functional are known to perform badly when determining the band gaps of semiconductors and insulators we have in addition performed calculations with the more advanced hybrid functionals of Perdew, Ernzerhof and Burke (PBE0) [20] and of Heyd, Scuseria and Ernzerhof (HSE) [21, 22]. These functionals have been found to be an improvement of the LDA and PBE with regard to, for example, bond distances and dissociation energies in molecules as well as structures and band gaps of bulk materials [21–24]. Interestingly, the AM05 has been found to yield the same level of accuracy as the hybrid functionals with regard to the bulk properties of crystals, such as lattice constants and bulk modulus [18].

The PBE0 and HSE are non-local hybrid theories where the exchange part of the XC functional includes some non-local contribution. In the PBE0 approximation the XC energy can be expressed by

$$E_{xc}^{PBE0} = \frac{1}{4}E_{xc}^{HF} + \frac{3}{4}E_{xc}^{PBE} + E_{xc}^{PBE0},$$

where $E_{xc}^{PBE}$ and $E_{xc}^{PBE0}$ are the exchange and correlation terms in the PBE approximation and $E_{xc}^{HF}$ is the Hartree–Fock exchange energy. In the HSE approximation the XC energy is given by [21, 22]

$$E_{xc}^{HSE} = E_{xc}^{HSE} + E_{xc}^{HSE},$$

where

$$E_{xc}^{HSE} = \alpha E_{xc}^{HF,SR}(\omega) + (1-\alpha)E_{xc}^{PBE,SR}(\omega) + E_{xc}^{PBE,LR}(\omega),$$

where LR and SR denote the long range and short range parts respectively, $\alpha$ is a mixing parameter governing the strength of the non-local exchange and $\omega$ is a screening parameter that controls the spatial range over which the non-local exchange part is important. The correlation energy in the HSE approximation, $E_{xc}^{HSE}$, is taken to be identical to the PBE correlation energy as in the PBE0 approximation. The amount of Hartree–Fock exchange in the HSE is the same as in the PBE0, i.e. $\alpha = 1/4$, while the range separation parameter, $\omega$, has to be determined by comparison with experimental data. It has been found that $\omega = 0.2–0.3$ Å$^{-1}$ gives good results with regard to structural as well as electronic properties of materials, with $\omega = 0.2$ Å$^{-1}$ being the optimum choice [21–23]. Unless otherwise specified, $\omega = 0.2$ Å$^{-1}$ has been used in the HSE calculations. We note that for $\omega = 0$ equation (2) is equivalent to the PBE0 and, furthermore, equation (2) asymptotically reaches the PBE for $\omega \rightarrow \infty$ [21]. We will return to this point in section 3.

An issue with the use of common density functional approximations is the description of strongly localized orbitals such as d- and f-orbitals. For this reason we have also investigated how the localization of the Cu 3d-states affects the electronic structure as well as the band gap in...
the system by employing the use of an on-site Coulomb interaction within the LDA + U approximation, using the approach of Dudarev et al [25]. We note that in the Dudarev et al approach the on-site Coulomb interaction, U, and on-site exchange interaction, J, do not enter separately but only in the combination of an ‘effective U’,  

\[ U_{\text{eff}} = U - J \]

However, throughout the presentation we will simply refer to the ‘effective U’ as U. The U has been applied solely to the Cu 3d-states.

For the main part of the calculations, the plane wave basis set was cut off at 1000 eV and we used a k-point mesh of 30 × 30 × 30 [26] for the primitive cell of Cu$_2$Se. However, since the hybrid functionals are much more computationally cumbersome than the local and semi-local approximations, we used a plane wave cut-off of 800 eV and a k-mesh of 10 × 10 × 10 in combination with the hybrid functionals.

The pseudopotential (PP) for Cu has the 3d and 4s electron states treated as valence states while the semi-core 3s and 3p states have been placed in the core of the PP. For Se the PP has the 4s and 4p electron states treated as valence states.

3. Results

The lattice constants and bulk moduli obtained using the various functionals are summarized in table 1. We note that the PBE, PBE0 and HSE functionals give very similar results in good agreement with experimental observations, whereas the LDA overbinds. The AM05 is the functional that gives the lattice constant closest to experiment, with a deviation that is less than 1%. When adding the on-site Coulomb interaction, the lattice constant increases. A reduced lattice constant may nevertheless appear since the population of strongly bonding s- or p-states may increase at the expense of the d-state occupation, resulting in an increased binding strength.

In figure 2, we show the electron density of states (DOS) as evaluated using the PBE functional. It is clear from the results in figure 2 that the valence band consists of three regions: a lower region between 14 and 15 eV below the Fermi level, which is mainly built up by Se 4s-states, a middle region in between 5 and 7.5 eV below the Fermi level, which is a mixture of states derived from both Cu and Se, and an upper region from about −2 eV to the Fermi level. This behavior of a Cu 3d peak centered in between regions of Cu 3d and Se 4p hybridized regions, the lower region between about −8 and −5 eV and the upper region from about −2 eV to the Fermi level. This behavior of a Cu 3d peak centered in between regions of hybridized Cu 3d and Se 4p states has been found experimentally by Domashevskaya et al [29], even though the exact positions of the peaks differ, which we will turn to shortly. We also note that the result presented in figure 2 is in agreement with the

| XC functional | a (Å) | B (GPa) | U (eV) | a (Å) | B (GPa) |
|---------------|-------|---------|--------|-------|---------|
| LDA           | 5.661 | 111     |        |       |         |
| PBE           | 5.844 | 82      | 2      | 5.650 | 108     |
| PBE0          | 5.833 | 81      | 4      | 5.637 | 105     |
| HSE           | 5.838 | 80      | 6      | 5.623 | 103     |
| AM05          | 5.722 | 97      | 8      | 5.605 | 100     |
|               |       |         | 10     | 5.583 | 98      |
|               |       |         | 12     | 5.554 | 97      |
| Exp.          | 5.759 |         |        |       |         |

Table 1. Calculated bulk properties of fluorite Cu$_2$Se obtained using the LDA, PBE, AM05, PBE0 and HSE approximations for the XC functional. a is the lattice constant and B is the bulk modulus. The lattice constants and bulk moduli are evaluated using a Birch–Murnaghan third order equation of state [28]. The lattice constants and bulk moduli in the second and third columns correspond to the XC functional in the first column while the fifth and sixth columns correspond to the U given in the fourth column within the LDA + U approximation.
Figure 3. Calculated density of states for PBE, AM05, PBE0 and HSE in the left column and for LDA and LDA + U, with $U = 4, 8$ and $10$ eV, in the right column. The vertical dashed line marks the position of the Fermi level $E_F$ for each case. The total DOS is shown in black and we also show the projected DOS on the two different atomic species, Cu in red and Se in blue.

previous tight binding calculation of Garba and Jacobs [10] as well as with the LDA result of Kashida et al [11]. A notable result is that the PBE functional yields a zero gap between the occupied valence bands and the unoccupied conduction bands. As was mentioned in section 1, optical studies have reported a band gap of 1.23 eV [4]. This is a rather small gap and density functional theory is known to underestimate the band gaps of semiconductors and insulators when using local and semi-local approximations. In order to investigate the band gap for this system further we will have to resort to more complex approximations to the XC functional.

In figure 3 we compare the DOS obtained using the LDA, PBE, AM05, PBE0 and HSE as well as LDA + $U$. We find that the overall shape of the DOS is very similar to the PBE, which was discussed previously, except when very large $U$-values have been applied. In the following discussion we divide the valence states into lower (Se 4s-states), middle (mainly Cu 3d- and Se 4p-states) and upper (including the main Cu 3d peak) valence regions. Compared to the PBE the predominant trend is a shift of the states towards lower energies. For the LDA and AM05 this shift is rather small. For the PBE0 and HSE we find that the lower valence region is between 15 and 16 eV below the Fermi level, compared to 14–15 eV for the PBE. The middle valence region is also shifted downwards by the same amount (≈1 eV). For the upper valence region the lower edge is shifted downwards by about 1 eV for the hybrid functionals. For very large $U$ the upper valence states are shifted more than the states in the middle valence region and for $U = 8$ and $10$ eV the upper and middle valence regions from the PBE description have merged into a single region. We note that the valence band DOS obtained by the PBE0 and the HSE functionals are in very good agreement with measured x-ray photoelectron spectra (XPS) [11, 29]. The main peak in the spectra at 3.5 eV comes from Cu 3d-states and is excellently reproduced by the main Cu peak obtained in the DOS from the PBE0 and HSE approximations as well as from LDA + $U$ with $U = 4$ eV, see figure 3. For larger $U$-values the Cu d-states are found at too low energies. The LDA, PBE and AM05 have the Cu d-states at slightly too high energy compared to the experiment. As regards the conduction bands and especially the band gap, we find that all approximations have a region of rather small DOS above the Fermi level.

Figure 4 shows the calculated band structure for the upper valence band as well as for a few conduction bands along high symmetry directions in the Brillouin zone. As is clear, only the PBE0 and LDA + $U$ with $U = 10$ eV calculations reveal a band gap. In all other cases the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) touch at the $\Gamma$-point. The LDA, PBE and AM05 have an almost flat conduction band along the $\Lambda$ line ($\Gamma$ to L), where the LUMO at L is only $\sim 0.1$ eV above the Fermi level. For these functionals the lowest conduction bands are degenerate with two valence bands at $\Gamma$. The same is also true for the HSE approximation as well as for LDA + $U$ with $U = 4$
Figure 4. Calculated band structures along directions of high symmetry in the Brillouin zone for Cu$_2$Se obtained using the LDA, PBE, AM05, PBE0 and HSE functionals. The vertical solid lines label high symmetry coordinates while the horizontal dashed line marks the position of the Fermi level, $E_F$. Note the common feature that in order for a gap to be open the HOMO-2 band, marked by the (red) dashed band, has to reach the Fermi level, which only happens in the case of the PBE0 and LDA + $U$ with $U = 10$ eV. The fat bands show the amount of Cu 4s character of the lowest conduction band and the three highest valence bands.

and 8 eV. However, as can be seen in figure 4, the HOMO-2 band at the Γ-point behaves differently depending on the XC functional. This band for the PBE band structure is found at 1.19 eV below the Fermi level, while for the HSE calculation it is found at 0.07 eV below the Fermi level. For the PBE0 this band has moved up to the Fermi level and the HOMO at the Γ-point is triply degenerate with a direct gap of 0.47 eV. The same situation is the case for $U = 10$ eV, but the gap is 0.30 eV.

When an on-site Coulomb exchange is added to the Cu 3d-states, the main effect is that the Cu 3d-states are pushed further down below the Fermi level, as witnessed by the projected DOS in figure 3. We find that the upper valence band in figure 4 is becoming broader and the conduction bands are shifted towards higher energies. The major effect in the band structure of figure 4 is a shift in the low-lying conduction band along the Γ-line (Γ to L). In order for a gap to be open very large $U$-values are required. The lower right panel of figure 4 shows the resulting band structure with $U = 10$ eV. The behavior of the valence and conduction bands with $U = 10$ eV is rather similar to the PBE0 results in the near Fermi level region, i.e. about −2 to 2 eV, with a direct band gap at Γ of similar size to the PBE0. We find that the HOMO-2 band is key for the formation of a band gap within the LDA + $U$ approximation. At $U = 8$ eV, this band just reaches the Fermi level and marks a transition situation, and a small increase of the Coulomb exchange interaction to 8.1 eV (not shown) gives a small gap at Γ.

Common features of the band structures shown in figure 4 are that the highest valence band, as well as the lowest conduction band, are found along the Λ-line and that the ordering of the bands is similar irrespective of approximation used. We also note that the valence bands obtained by the PBE0 and HSE are very similar, as is also witnessed by the DOS in figure 3. The difference between these two hybrid approximations lies in the obtained conduction bands: with PBE0 these bands are found higher above the Fermi level compared to the HSE. The band structure data shown in figure 4 are quantified in table 2, where we show the evaluated energy differences between the HOMO and LUMO levels at various high symmetry points in the Brillouin zone.

We have shown that the existence of a band gap is closely related to the position of the HOMO-2 level at the Γ-point. If this band reaches the Fermi level a gap is opened. Common for all calculations shown in figure 4 is that the triply degenerate state at the Fermi level at Γ is derived from hybridization between Cu 3d-states with $t_{2g}$ symmetry and Se 4p-states. The HOMO-2 band at Γ is derived from hybridized Cu 4s-
We find that by going below the optimized $\omega$ of the electronic structure of fluorite Cu$_2$Se using a variety of approximations for the XC energy functional. We find that the PBE, PBE0 and HSE approximations give very similar results regarding lattice constants and bulk modulus. The hybrid functionals PBE0 and HSE both show excellent agreement with experimental valence band spectra, although all functionals give rather similar results regarding the overall electronic structure, see figure 3. In addition, we find that the PBE0 is the only functional that yields a nonzero band gap. It is also possible to open a gap by adding an on-site Coulomb interaction to the Cu 3d-states. However, we conclude that localization of the Cu 3d-states cannot account for the formation of a gap since this requires very large $U$-values.

We also find that the presence of a band gap is dictated by the relative position of the Cu 4s and Se 4s hybridized band and the Cu 3d and Se 4p hybridized band at the $\Gamma$-point. When a gap is open, i.e. for the PBE0 and for very large $U$, the Cu 4s and Se 4s hybridized band is found in the LUMO above the Fermi level. As shown in figure 4, where we show the amount of Cu 4s character of each of the bands close to the Fermi level. As shown in figure 4, there is a region close to $\Gamma$ where the HOMO-2 band has a rather large Cu 4s character in the PBE, AM05 and LDA band structures. In the HSE band structure the Cu 4s character of this band is much narrower around the $\Gamma$-point; however, it is still present at $\Gamma$. For the PBE0 bands there is no Cu 4s character for this band at $\Gamma$. The same transition of the band character is found for the LDA result. The points for $\omega = 0.01, 0.05, 0.1$ and 0.3 Å$^{-1}$ have been evaluated using the lattice constant obtained with $\omega = 0.2$ Å$^{-1}$, and the points are connected by a fitted spline. The vertical dashed line marks $\omega = 0$.

4. Discussion and conclusions

We have performed density functional theory calculations of the electronic structure of fluorite Cu$_2$Se using a variety of approximations for the XC energy functional. We find that the PBE0 and HSE approximations give very similar results regarding lattice constants and bulk modulus. The hybrid functionals PBE0 and HSE both show excellent agreement with experimental valence band spectra, although all functionals give rather similar results regarding the overall electronic structure, see figure 3. In addition, we find that the PBE0 is the only functional that yields a nonzero band gap. It is also possible to open a gap by adding an on-site Coulomb interaction to the Cu 3d-states. However, we conclude that localization of the Cu 3d-states cannot account for the formation of a gap since this requires very large $U$-values and compared to experimental valence band spectra such large $U$-values push the Cu 3d-states too low in energy.

We also find that the presence of a band gap is dictated by the relative position of the Cu 4s and Se 4s hybridized band and the Cu 3d and Se 4p hybridized band at the $\Gamma$-point. When a gap is open, i.e. for the PBE0 and for very large $U$, the Cu 4s and Se 4s hybridized band is found in the LUMO above the triply degenerate HOMO that consists of Cu 3d and Se 4p hybridized bands. In all other cases the Cu 4s and Se 4s hybridized band is positioned below the Fermi level.

| $\Delta E$ | PBE | AM05 | PBE0 | HSE | LDA | $U = 4$ eV | $U = 8$ eV | $U = 10$ eV |
|-----------|-----|-----|------|-----|-----|----------|----------|----------|
| $\Gamma \rightarrow \Gamma$ | 0.00 | 0.00 | 0.47 | 0.00 | 0.00 | 0.00 | 0.00 | 0.30 |
| $\Gamma \rightarrow \Gamma$ | 0.10 | 0.14 | 1.91 | 1.29 | 0.12 | 0.61 | 1.14 | 1.42 |
| $L \rightarrow \Gamma$ | 0.63 | 0.70 | 1.33 | 0.82 | 0.75 | 0.86 | 0.95 | 1.27 |
| $L \rightarrow \Gamma$ | 0.73 | 0.85 | 2.77 | 2.11 | 0.87 | 1.47 | 2.09 | 2.39 |
| $L \rightarrow X$ | 1.94 | 2.02 | 3.78 | 3.11 | 2.01 | 2.35 | 2.64 | 2.76 |
| $X \rightarrow \Gamma$ | 1.82 | 2.03 | 3.00 | 2.44 | 2.17 | 2.66 | 3.25 | 3.57 |
| $X \rightarrow L$ | 1.92 | 2.17 | 4.44 | 3.73 | 2.29 | 3.27 | 4.39 | 4.69 |
| $X \rightarrow X$ | 3.13 | 3.34 | 5.45 | 4.73 | 3.43 | 4.15 | 4.94 | 5.05 |

Figure 5. Evaluated band gaps using various values for the range separation parameter $\omega$ within the HSE approximation. Note that $\omega = 0$ in the figure is the PBE0 result. Furthermore, as $\omega \rightarrow \infty$ the PBE0 result is obtained. The points for $\omega = 0.01, 0.05, 0.1$ and 0.3 Å$^{-1}$ have been evaluated using the lattice constant obtained with $\omega = 0.2$ Å$^{-1}$, and the points are connected by a fitted spline. The vertical dashed line marks $\omega = 0$. 

Table 2. Calculated transitions between the HOMO and LUMO levels at high symmetry points in the Brillouin zone. Energies are given in eV.
In comparison to experimental band gaps we conclude that the present calculations do not reproduce the obtained optical gap of 1.23 eV obtained by Sorokin et al. [4]. However, this could be due to several reasons, one of which is related to the structure of the system. It is possible that defects, most likely Cu vacancies or interstitials, affect the electronic structure in such a way that larger gaps are obtained, and further investigations along these lines are underway. We point out that the experiment was performed at room temperature and for the ordered low temperature phase of Cu$_2$Se, which has a lower symmetry than the fluorite structure. For Ag$_2$Te, which is similar to Cu$_2$Se, GGA calculations give a zero gap for the fluorite structure, while a gap opens up for the monoclinic structure [30]. We speculate that the same may also be true for Cu$_2$Se, i.e. that a sizable gap opens for the low temperature phase and that the fluorite structure has a vanishingly small gap.

Moreover, our calculations reveal that the band structure around the Γ-point is such that it would not create a clear peak in the optical spectrum but rather an energy independent low intensity signal which can easily be confused with a background. In addition, our DOS calculations shown in figure 3 reveal a region with very small DOS above the Fermi level irrespective of the XC energy functional that has been used.

Furthermore, it has been found that HSE is better compared to the PBE0 at describing the band gap in small gap semiconductors, where the latter is found to overestimate the size of the band gap [23]. Thus, in summary, despite the fact that PBE0 is the only functional opening up a gap, we believe that HSE with $\omega \sim 0.2$ Å$^{-1}$ is the functional that more correctly describes the electronic structure of Cu$_2$Se. In order to further analyze the optical spectra by theory it will be necessary to resort to solving the Bethe–Salpeter equation or using time-dependent DFT, as optical gaps can be described properly due to the inclusion of the electron–hole interaction in these methods.

Acknowledgments

This work was financed through the EU project NexTec, VR (the Swedish Research Council) and SSF (Swedish Foundation for Strategic Research). The computations were performed on resources provided by the Swedish National Infrastructure for Computing (SNIC) at the National Supercomputer Centre in Linköping (NSC).

References

[1] Okimura H, Matsumae T and Makabe R 1980 Thin Solid Films 71 53
[2] Chen W S, Stewart J M and Mickelsen R A 1985 Appl. Phys. Lett. 46 1095
[3] Liu H, Shi X, Xu F, Zhang L, Zhang W, Chen L, Li Q, Uher C, Day T and Snyder G J 2012 Nature Mater. 11 422
[4] Sorokin G P, Papshev Y M and Oush P T 1967 Sov. Phys.—Solid State 7 1810
[5] Massalski T B, Okamoto H, Subramanian P R and Kacprzak L 1990 Binary Alloy Phase Diagrams 2nd edn (Materials Park, OH: ASM International)
[6] Danilkin S A, Skomorokhov A N, Hoser A, Fauss H, Rajevac V and Bickulova N N 2003 J. Alloys Compounds 361 57
[7] Danilkin S A, Avdeev M, Sakuma T, Macquart R, Ling C D, Rusina M and Izaola Z 2011 Ionics 17 75
[8] Abrikosov N H, Bankina V F, Korzhuev M A, Demski G K and Teplov O A 1983 Sov. Phys.—Solid State 25 1678
[9] Snyder G J and Toberer E S 2008 Nature Mater. 7 105
[10] Garba E J D and Jacobs R L 1986 Physica B 138 253
[11] Kashida S, Shimosaka W, Mori M and Yoshimura D 2003 J. Phys. Chem. Solids 64 2357
[12] Blöchl P E 1994 Phys. Rev. B 50 17953
[13] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
[14] Kresse G and Joubert D 1999 Phys. Rev. B 59 1758
[15] Perdew J P and Zunger A 1981 Phys. Rev. B 23 5048
[16] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[17] Armiento R and Mattsson A E 2005 Phys. Rev. B 72 085108
[18] Mattsson T R 2008 J. Chem. Phys. 128 084714
[19] Mattsson A E and Armiento R 2009 Phys. Rev. B 79 155101
[20] Perdew J P, Ernzerhof M and Burke K 1996 J. Chem. Phys. 105 9982
[21] Heyd J, Scuseria G and Ernzerhof M 2003 J. Chem. Phys. 118 8207
[22] Heyd J, Scuseria G and Ernzerhof M 2006 J. Chem. Phys. 124 219906
[23] Matsushita Y I, Nakamura K and Oshiyama A 2011 Phys. Rev. B 83 075205
[24] Paier J, Hirschcl R, Marsman M and Kresse G 2005 J. Chem. Phys. 122 234102
[25] Dudarev S L, Botton G A, Savrasov S Y, Humphreys C J and Sutton A P 1998 Phys. Rev. B 57 1505
[26] Monkhorst H J and Pack J D 1976 Phys. Rev. B 12 5188
[27] Heyd J D 1986 Can. J. Chem. 84 44 1233
[28] Birch F 1947 Phys. Rev. 71 809
[29] Domashevskaya E P, Gorbachev V V, Terekhov V A, Kasharov V M, Panfilova E V and Shchukarev A V 2001 J. Electron Spectrosc. 114–116 901
[30] Zhang W, Yu R, Feng W, Yao Y, Weng H, Dai X and Fang Z 2011 Phys. Rev. Lett. 106 156808