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NUCLEAR SCIENCE AND TECHNIQUES

Nuclear Science and Techniques, 19 (2008) 365-369

Influence on electron energy loss spectroscopy of the niobium-substituted uranium atom: A density functional theory study

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Abstract We present the electronic structure and electron energy loss spectroscopy (EELS) for uranium, niobium and U_3Nb in which uranium is substituted by niobium. Comparing the electronic structures and optical properties for uranium, niobium and U_3Nb , we found that when niobium atom replaces uranium atom in the center lattice, density of state (DOS) of U_3Nb shifts downward to low energy. Niobium affects DOS for *f* and *d* electrons more than that for *p* and *s* electrons. U_3Nb is similar to uranium for the electronic energy loss spectra.

Key words Uranium, Niobium, Electron energy loss spectroscopy, Electronic structure, Local density approximation **CLC numbers** 0482.3, TL817⁺.9, TL271⁺.99

1 Introduction

Uranium oxides and uranium alloy are important nuclear fuel^[1]. Uranium oxides are widely used in pressurized water reactor, boiling water reactor, light water reactor, supercritical water-cooled reactor, etc. Pure uranium is of bcc structure γ phase at 776~1132°C and transforms into β and α phase during cooling^[2]. To keep the bcc structure at ambient temperature, uranium alloys were developed with Mo, Nb, Zr, Ti, etc. At ambient temperature, metastable γ phase uranium is made by quick cooling of γ phase uranium added with alloying elements, though solubility of the elements is low. Among the alloys, U-Nb alloy has good anti-oxidation and ductility, and lower Young's modulus^[3].

On the other hand, electron energy loss spectroscopy (EELS) has become a powerful tool for determining structure-property relationships at interfaces and grain boundaries, and for probing local stoichiometry, impurity segregation and electronic structure^[4]. And local density approximation (LDA) is a credible and effective density functional theory (DFT) method to explore electronic structures and properties of condensed matter. Buck et al. [5, 6] studied plutonium behavior in nuclear waste materials by EELS. Dudarev et al.^[7] calculated EELS spectra of nickel and uranium oxides with the LDA+U method. Progresses have also been made with ASW (Augmented Spherical Waves) and LDA. Davis et al. [8-10] studied electronic structure of uranium compounds such as U₂T₂X (T is a transition metal, X is a p-metal) and UFeSi. Matar et al.^[11-16] reported the calculated electronic properties and hybrid effect of intermetallic compounds such as UMn₂Ge₂ by DFT. Nourbakhsh et al.^[17] calculated electronic properties of intermetallic compound UIn₃ by LDA. Rusz at al.^[18,19] studied electronic structure of intermetallic compounds such as UTX (T and X as above) and UPtAl by LDA+U method. Lu Lei ^[20] used EELS on an Auger electron spectrometer to analyze U or U-Nb alloy surface with different oxidation degrees. They found it difficult to clearly distinguish EELS of

Supported by the National Key Laboratory Foundation of China (9140C6601010804) and Sichuan Provincial Key Laboratory for Applied Nuclear Technology in Geology Foundation (27-7).

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Received date: 2008-07-10

U in uranium metal from that in U-Nb alloys. In this paper, LDA is used to study Nb influence on electronic structure of U-Nb alloys, in which the center U atom in lattice is substituted by Nb atom, in an attempt to explain theoretically that EELS of U from uranium metal and U-Nb alloy is similar.

2 Computational method

Assume the center U atom of α -U lattice is substituted by a Nb atom to form U₃Nb, the model of U₃Nb with PMMM space group (No. 47) is established (Fig.1), with the lattice constants of a = 0.2854nm, b = 0.587 nm and c = 0.4955 nm. The electronic properties of U₃Nb, α -U and α -Nb are obtained using LDA. CASTEP^[21] code is employed to perform the calculation within framework of the argument plane wave method. CA-PZ exchange-correlation^[22] and ultra-soft potential are used in the calculation. The calculations were carried out with 9×4×5 *k*-points for uranium and U₃Nb and 8×8×8 *k*-points for niobium in the entire Brillouin Zone.



Fig.1 Schematic model of niobium-substituted uranium atom holding center of lattice.

3 Result and discussion

3.1 Electronic structure

The energy bands for U_3Nb are plotted in Fig.2. It indicates that U_3Nb is still a metal, of which some bands cross the Fermi level. The plots of density of states (DOS) show that bands of 5f electrons play a main role among energy bands around the Fermi level. Fig.3 presents more details. The metal f states form a



Fig.2 Energy bands and state of density for U₃Nb.



Fig.3 Projected density of states. (A): f electrons, (B): d electrons, (C): p electrons, (D): s electrons.

main band between -5 and 2.6 eV (Fig.3A), and DOS for 5*f* electrons shifts slightly to lower energy after the center uranium atom is substituted by niobium atom. Moreover, because *d* electrons of niobium affect electronic structure, DOS for *d* electrons also shift slightly to lower energy and the degree of overlap increases. The d electrons of uranium contribute DOS around -20 eV (Fig.3B). Compared with *d* electrons, Fig.3C and Fig.3D show that *p* and *s* electrons barely affect the electronic structure. The *p* electrons of niobium contribute DOS around -30 eV.

3.2 EELS and optical properties

The optical properties can be obtained from the dielectric function $\varepsilon(\omega) = \varepsilon_{\text{Re}}(\omega) + i\varepsilon_{\text{Im}}(\omega)$, which is calculated by the approach of Ehrenreich and Cohen^[23]. The imaginary part, $\varepsilon_{\text{Im}}(\omega)$, is given as function (1).

$$\varepsilon_{\rm Im}(\omega) = \frac{e^2}{\pi m^2 \omega^2} \times \sum_{\rm i} \sum_{\rm f} \int_{\rm BZ} |eP_{\rm if}|^2 \,\delta(E_{\rm f}^k - E_{\rm i}^k - \hbar\omega) \,d^3k \quad (1)$$

where e is the polarization vector of the electric field,

k is the point in the IBZ (irreducible Brillouin zone), and E_i and E_f are the binding energies of the initial and final states, P_{if} is the momentum matrix elements. The real part $\varepsilon_{Re}(\omega)$ can be derived from the imaginary part $\varepsilon_{Im}(\omega)$ by the Kramer–Kronig transformation. All the other optical parameters, such as the absorption coefficient $I(\omega)$, the refractive index $n(\omega)$, the extinction coefficient $k(\omega)$, the energy-loss spectrum $L(\omega)$, and the reflectivity $R(\omega)$ can be all calculated from $\varepsilon_{Re}(\omega)$ and $\varepsilon_{Im}(\omega)^{[24]}$. In this study, only the imaginary part $\varepsilon_{Im}(\omega)$, which determines the other parameters and discribes electronic states between occupied and unoccupied orbits, is discussed.

For static dielectric function, $\varepsilon(0) \approx \varepsilon_{\text{Re}}(0)$ in low frequency zone. From Fig.4, $\varepsilon_{\text{Re}}(0)$ is 589.86, then we can obtain the refractive index due to $n^2 = \varepsilon$. Fig.5 shows the dielectric functions of uranium and U₃Nb. They are very similar, with just a few differences in low frequency region. LDA was used to calculate electron energy loss spectra (Fig.6). The EELS of uranium and U₃Nb are similar, but there is some difference between the U₃Nb and niobium EELS.

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Fig.5 Real and imaginary parts of dielectric constants.



Fig.6 Electron energy loss spectra of U_3Nb , U and Nb.

Electronic density around the center atom changes slightly after the Nb substitution (Fig.7). Moreover, change of the electronic density around neighboring atoms is less than that of the center atom. Optical properties such as EELS and the electronic density change slightly in system after the Nb substitution. This is main reason why LU Lei^[20] cannot distinguish EELS of uranium in uranium and from that in U-Nb alloys.







Fig.7 Scheme of electronic density of U_3Nb , α -U and α -Nb.

4 Conclusion

In this paper, the ground state properties of U_3Nb , α -U and α -Nb are studied. Comparing the density of states of uranium, we found that DOS of U_3Nb tends to shift to lower energy because of the influence of niobium. The influence of *f* electrons is more evident than *d*, *p* and *s* electrons. In low frequency zone, the EELS of U_3Nb differs little from that of uranium, but differs distinctly from that of niobium. The calculated results demonstrate that optical and electronic properties of U_3Nb are similar to those of uranium. The fundamental electronic structure determines optical and energy spectra. When determining the EELS of uranium, we must scan and determine simultaneously the EELS of other elements in the same specimen.

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