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Correlation –induced anomalies and extreme sensitivity in fcc-Pu[1]

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Abstracts

We have used GGA + U density functional theory to study the effects of correlation on the properties of fcc-Pu. We found that the structural and elastic properties of fcc-Pu are highly sensitive to the Hubbard U parameter. Within an interval of 0.1 eV of the U parameter, the equilibrium lattice constants of fcc-Pu can change from 0.44 to 0.47 nm. While the bulk modulus can drop by a factor of 5 to 10. The pressure derivative, dB/dp, of the bulk modulus can rise dramatically from 5 to 16 and then drop to a negative value before recovering to a more normal value. These observations are partially supported by existing experiments and the prediction of a negative dB/dp needs to be tested in future experiments.

Keywords: Pu, DFT, correlation, Hubbard U, bulk modulus, pressure derivative, localization, itinerancy

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Introduction

As Jim L. Smith and E. A. Kmetko [1] indicated long time ago that Pu lies near the borderline of instability of magnetism, superconductivity and phase instability. Pu and other actinides seem to derive these properties from neither fully localized nor fully itinerant nature of the 5*f* electrons. Their structural, elastic, and electronic properties can be changed by a slight shift to their temperature, pressure and small amounts of alloying elements [2-3]. It is likely the manifestation of the correlated nature of the electron interaction is the central part of the mystery in understanding the behaviors of Pu and other actinides. Many experiments and theories have been advanced to explain these complicated behaviors with different levels of success [3-15]. In particular, the dynamical mean field theory (DMFT) approach [5, 9] seems to be able to explain the large lattice parameters of fcc-Pu without invoking either the ferro-magnetism or antiferro-magnetism [7] in Pu that was never observed in experiments. From these studies, it seems that one of the effects of the correlation is to cause the spin-up electrons and spin-down electrons to be separated in the energy levels that they occupy. Through the repulsion of these electrons of different spins, the lattice expands. Here, without assuming any underlying mechanisms for the correlation changes, we study carefully the sensitivity of the correlation parameter, Hubbard U, that was used in the GGA + U approach as that was implemented by Dudarev et al [16] successfully to calculate the spectroscopic, elastic and structural properties of many materials in the VASP [17-18].

Calculations

We have used the density functional theory, in particular the GGA +U [17] approach to study the effects of the effective correlation in fcc-Pu. The generalized gradient Approximation (GGA) [19] With the projector augmented wave potential (PAW) have been used. The Monkhorst and Pack [20] k-point sampling was used with 8x8x8 k points (and checked on another 12x12x12 calculations) are used to ensure good convergence. While accurate total energy calculations were performed by means of the linear tetrahedron method with Blo¨chl's correction [21]. The electron configuration for Pu is $[Xe6S^2 5P^6]6d^8 5f^6 7S^2$ with 16 electrons treated as valence electrons. The effective correlation effects were incorporated in the average Hubbard U as proposed by Dudarev et al [16] in a rotationally invariant form. The additional simplified rotationally invariant Hamiltonian due to the U is incorporated as follows

$$E_{GGA+U} = E_{GGA} + (U/2)^* \sum_\sigma [(\sum_{m1} n^\sigma_{m1,m1}) - (\sum_{m1,m2} n^\sigma_{m1,m2} n^\sigma_{m2,m1})] \qquad \text{(eq .1)},$$

where U is the average Hubbard U onsite Coulomb repulsion parameter, and $n^\sigma_{m1,m2}$ is the PAW onsite occupancies [16]. The average U parameter is only applied to the 5*f* electrons. A convergence of 1 meV/atom was achieved.

In the beginning we calculated the properties of fcc-Pu with the average U = 0 eV in nonmagnetic, antiferro-magnetic (AF), and ferro-magnetic (F) conditions. The equilibrium lattice constants are 0.41531, 0.45282, and 0.47466 nm respectively. The corresponding bulk moduli are 154.26, 57.95 and 34.23 GPa respectively. As previous theoretical calculations [3-15], these values for both the AF and F systems are in reasonable agreement with experimental values of lattice constant a_0 = 0.46371 nm at 320C [23] and bulk moduli of 29.9 [24] and 29.6 to 30.7 [25]. But the magnetic moments are 5.5 Bohr magnetons which are not consistent with experimental observations [2-3] of no magnetic moments at all. For our GGA+U calculations, a value of U of 3.55 eV gives a equilibrium lattice parameter of 0.46031 nm that is very close to the experimental value of 0.46371 nm [23]. For U = 3.55 eV, we have also performed the calculations with both ferro- and antiferro-magnetic arrangement. The detailed results will be presented elsewhere and we only present a summary of these calculations here. These ferro- and antiferro-magnetic calculations yield the equilibrium lattice constants at 0.52309 nm and 0.49566 nm, respectively. The corresponding magnetic moments are 5.73 and 4.96 Bohr magneton , respectively. Both the lattice parameters and the magnetic moments are significant larger than the nonmagnetic case. These results are not consistent with experimental observations and will not be discussed further here.

Savrasov et al. [5] have chosen the value of U = 4 eV for their DMFT calculations that give them good results. We have done the GGA+U calculations from 0 to 6 eV. For the very sensitive region, a fine 0.01 eV interval was used. For every value of the average U, we calculated the energy vs volume curve. From 5 or 6 of these data points we fitted them to the Birch-Murnagham [22] curve to calculate the equilibrium lattice constants (a_0), bulk moduli (B), and its pressure derivative (B' = dB/dp) through the minimum and the derivatives. We repeat these processes for every value of the average U from 0 to 6 eV.

In figure 1, we plotted the equilibrium lattice constant. a_0, as a function of the average U. There is a slow increase of the a_0 as the U value is increased. The increase of the a_0 starts to accelerate as the U value increases past 3.0 eV and suddenly jumps up at 3.55 eV within an interval of 0.1 eV (a0 is 0.439 nm for U=3.50 eV, 0.460 nm for U=3.55 eV, and 0.467 nm for U=3.60 eV). After that the increase starts to slow but still maintains a roughly linear dependence at 5.0 eV.

For the bulk modulus, B, the value starts to decrease as the U value is increased (figure 2). A steeper drop was observed as U increases past 3.0 eV to a minimum of 12 (near U=3.60 eV) or so before bouncing back to a value of 20 and then starts the downward trend again.For the pressure derivative (figure 3), B', the values stay pretty flat at around 5 from U value of 0 to 2 eV. Then B' dips and rises to 16 and drops to negative 8 (around U= 3.60 eV area) before recovering to a more normal value of 4 or 5. In light of the abnormal values of B and B' that were calculated from fcc-Pu for various values of U as seen in figure 2, We have also calculated these quantities for other fcc metals and listed them together with some experimental values [26-27] in table 1 to demonstrate the uniqueness of the abnormal values of B and B' for Pu. For all the calculations, the DFT

values are very close to the experimental value both in B and B'. It is clear that the values of Pu as shown in figure 2 and 3 are anomalous. Some of the experimental values for Pu are listed in table 2 for comparison [28-30]. The value for the bulk modulus is very low and the pressure derivative, B', is about three times larger than the usual metals.

We have also calculated the density of states at Fermi energy and onsite charges and split them into *s, p, d, f* contributions in order to determine their behaviors for many cases without and with the average Hubbard U (=3.55 eV) correlations. Four cases were studied: A – at GGA minimum a_0; B – at GGA minimum a_0 plus U correlation,; C – at GGA+U minimum a_0, but without U correlation; D – at GGA+U a_0 with full GGA+U correlations. There are bigger change of +0.12 d electrons from case A to case B (at a_0 of 0.41531 nm) as the U is turned on, while roughly a half of the change in -0.09 f electrons were observed. In contrast, as the U is turned on at the larger a_0 of 0.46031 nm, a smaller change at +0.07 d electrons and +0.03 f electrons are observed. Overall, no drastic changes at Fermi energy or charges were observed for the cases considered. The occupation of the 5 *f* electrons are right at the the 5.0 that is consistent with many previous calculations [11-15]. Overall, the inclusion of the U is to effectively make the DOS split into two pieces and move one of that into a higher energy level as seen at 2 eV, 3.55 eV and 6.0 eV as shown in figure 4. The DOS at the Fermi energy for 2.0 eV (fig 4(a) already shows the beginning of a peak at the Fermi energy. The DOS for the U= 3.55 eV (fig 4(b) clearly exhibit the prominent peak at the Fermi energy as demonstrated in the photoemission spectroscopy data [2, 6] that can not be captured by the conventional DFT calculations [10-11]. Our agreement with the photoemission data is by no means unique as previous theoretical models have shown [10-15]. For the case with U= 6.0 eV (fig 4(c)), the DOS at the Fermi energy is not at the peak and the band width is much smaller with the spike in the DOS about 0.6 eV below the Fermi energy.

Discussion

The effect of the inclusion of the Hubbard U is to split the bonding and anti-bonding states further apart in the energy. This effect can be seen from the density of states as shown in fig. 4 as the U value is increased from 2 eV to 6 eV. One of the effect of this change is that a new energy minimum is slowly created at higher a_0 (at 0.460 nm or above). For the values that are near the transition around 3.55 eV, the energy landscape is very flat. With a small change in the correlation (due to any changes in temperature, pressure or alloying element concentration) near the transition point, the a_0 can take a sudden jump to a much larger value like what we observed here. From the flatness of the energy landscape, we would expect the bulk modulus, which is the second derivative of the ererngy, to be very small. From fig 4b, we also noticed that a cusp of the DOS is right at the Fermi energy which indicates a high sensitivity to any potential perturbation of pressure, temperature and alloying changes. From our current calculations we can understand the peculiar drop of the bulk modulus, B to a very small value and the extremely large value of B' due to the introduction of correlations. These abnormal behaviors in the structural, elastic and spectroscopic properties should apply to many

actinides and other materials that have been identified to be near the 'transition' zone in the seminal paper of Smith and Kmetko [1]. Even though we expect to see a change from the lower value of a_0 to a larger value of a_0 with the introduction of the correlation U, we did not expect to see such a dramatic change over such a small change (of 0.1 eV) in U. We would have expected a much smoother change in the lattice parameter than what was observed here. The localization (for large U above 3.55 eV) favors systems with large lattice constants that are combined with small Bs and extreme or unusual values of B's. While for materials with a small U will behave like an itinerant material and thus have a smaller a_0 with a larger B and a somewhat normal value of B'. The exact value of the U when this transition occurs will depend on how the effective correlation is incorporated into the theory and calculations, but the sensitivity identified in our study would most likely be preserved.

The calculations of U or its effective number have been attempted for many materials [3]. The value of 4 eV seems to be reasonable for fcc-Pu, but the extreme sensitivity of the properties to the value of U makes it harder to make predictions about the properties of Pu a priori. If this extreme sensitivity were common for these models and theories, then one has to be really very careful about the predictions coming out from many of the models or theories [10-15]. Can we find support for our predictions for the small values of B and large values or negative values of B'? For the B, it is easy. From table 2 and references [3-10, 28-30], the bulk modulus of Pu in its alpha or delta (fcc) forms all have very low bulk modulus values ranging from 25 - 54 GPa and in good agreement with our calculations. While normal metals tend to have B values from 72 - 252 GPa as shown in table 1. For B' values, no experimental B' for fcc-Pu exist. We have tabulated the values for various kinds of Pu in table 2. The B' values range from 10 to 15 that match the extreme values of 16 in our figure 3. For normal metals, the B' values are in the range of 4.9 to 6.4 as seen in table 1. It will be very beneficial to have the B' values of many fcc-Pu materials (with or without small amounts of alloying elements) measured and compared with our predictions. In doing so, we would be able to understand more thoroughly the extreme sensitivity that was identified in our current study. This may offer future paths for controlling this extreme sensitivity more intelligently.

In summary, we have used GGA + U density functional theory to study the effects of correlation on the properties of fcc-Pu. Our calculations are consistent with available experimental data and other theoretical models in many aspects, while we predict new phenomena that can be checked by future experiments. From our study, we found that the effective U parameter to describe the delta-Pu successfully is about 3.55 eV. We found that a non-magnetic arrangement with the right structural, elastic and spectroscopic properties can be described by GGA+U approach that is consistent with several previous theoretical models [10-15]. We found that the structural and elastic properties of fcc-Pu are highly sensitive to the Hubbard U parameter. Within an interval of 0.1 eV of the U parameter, the equilibrium lattice constants of fcc-Pu can change from 0.44 to 0.47 nm. While the bulk modulus can drop by a factor of 5 to 10. The pressure derivative, dB/dp, of the bulk modulus can rise dramatically from 5 to 16 and then drop to the negative values before recovering to the more normal values. These observations are partially

supported by existing experiments and the prediction of a negative dB/dp needs to be tested in future experiments.

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Tables:

Table 1. Calculated and experimental values for bulk modulus, B, and its pressure derivative, B' for selected metals.

Metal	B (GPa) (expt.)#	B' (expt.)%	notes
Ag	89.99 (100.7)	5.76 (6.18)	# = ref 26
Au	133.78 (173.2)	6.33 (6.43)	%= ref 27
Cu	136.87 (137)	5.10 (5.59)	

Table 2. Experimental values of B and B' for Pu.

B (GPa)	B'	notes
47.6 (B_T)	10.17	Ref 28
54.1 (B_S)	11.36	Ref 28
42.2(7)	10.5(2)	Ref 29
43(2)	15(2)	Ref 30

Figure captions:

Fig. 1. The equilibrium lattice constant, a_0, as as a function of U in fcc-Pu. The horizontal line indicates the experimental value for fcc Pu at 320C.

Fig. 2. The bulk modulus, B, as a function of the average U in fcc-Pu.

Fig. 3. The pressure derivative of the bulk modulus, B', as a function of the average U in fcc-Pu.

Fig. 4. The DOS of fcc-Pu when the average U is at (a) 2.0 eV (at 0.42036 nm), (b) 3.55 eV at 0.46031, and (c) 6.0 eV at 0. 53191 nm. The Fermi energy is at 0 eV.

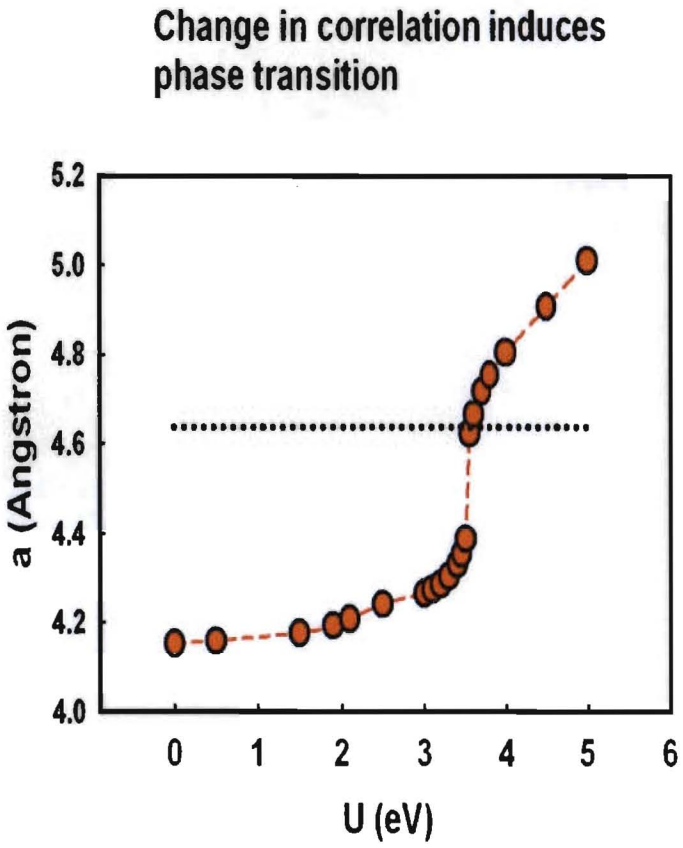

Fig. 1

The bulk modulus changes drastically as U increses.

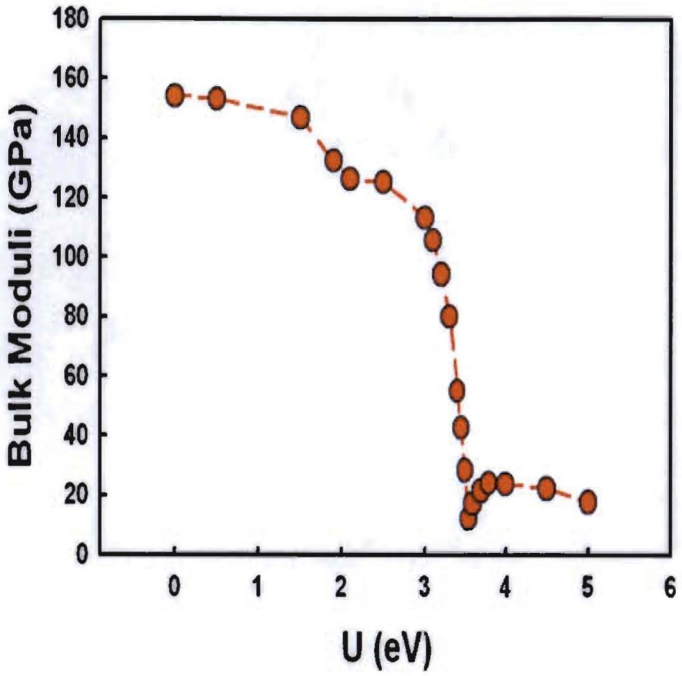

Fig. 2

The pressure derivative of the bulk modulus changes dramatically as U increases.

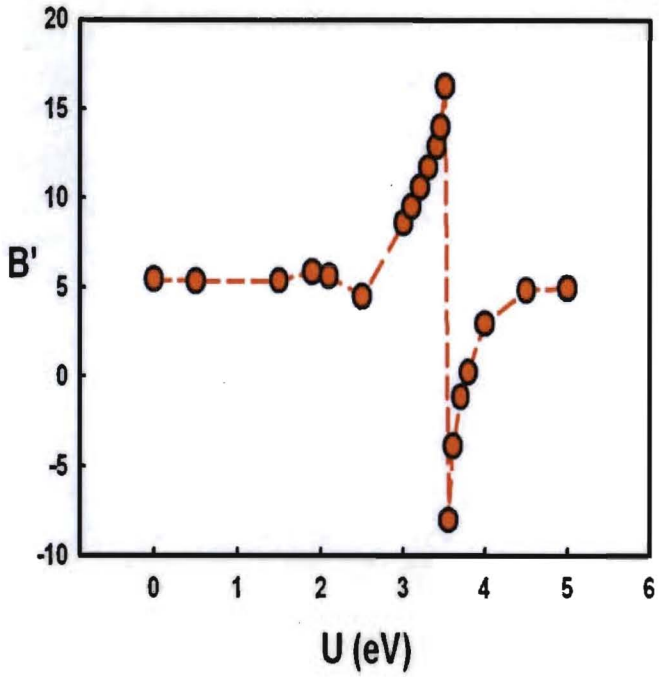

Fig. 3

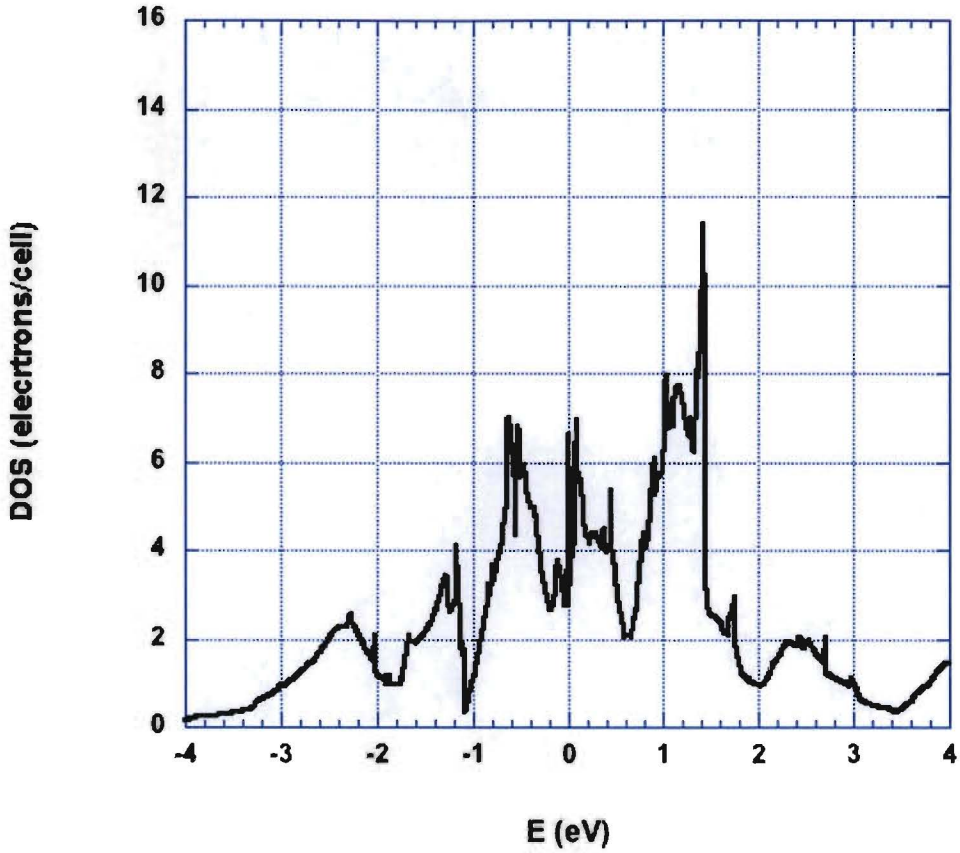

Fig. 4a

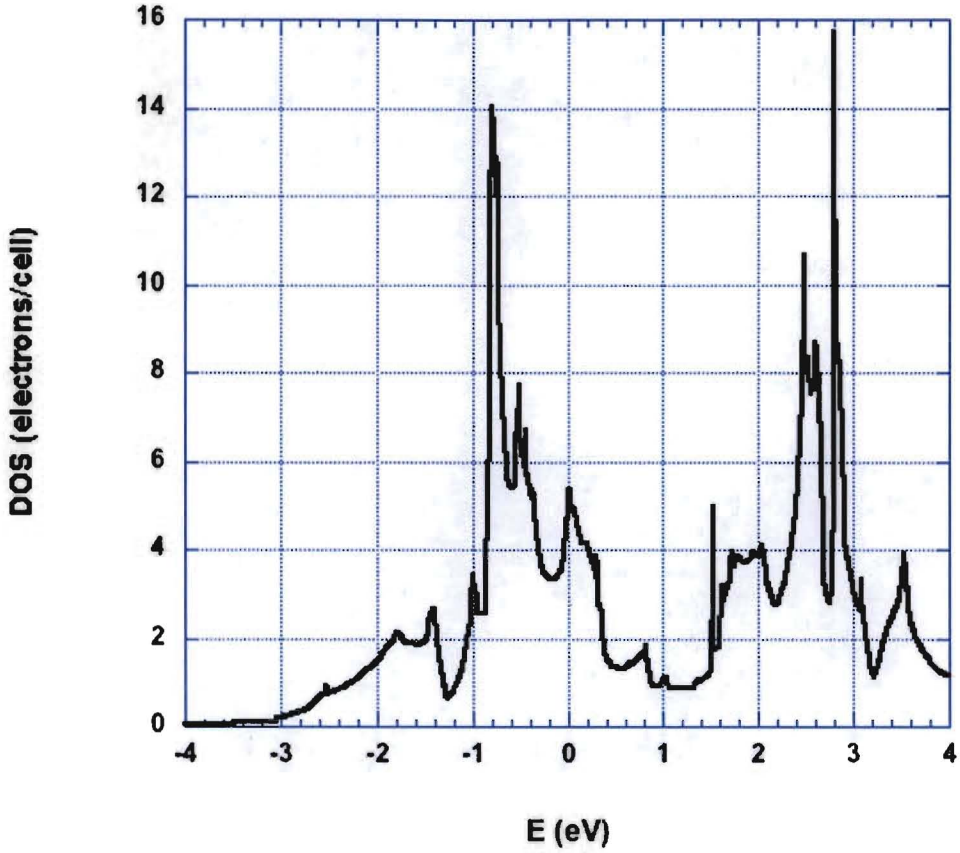

Fig. 4b

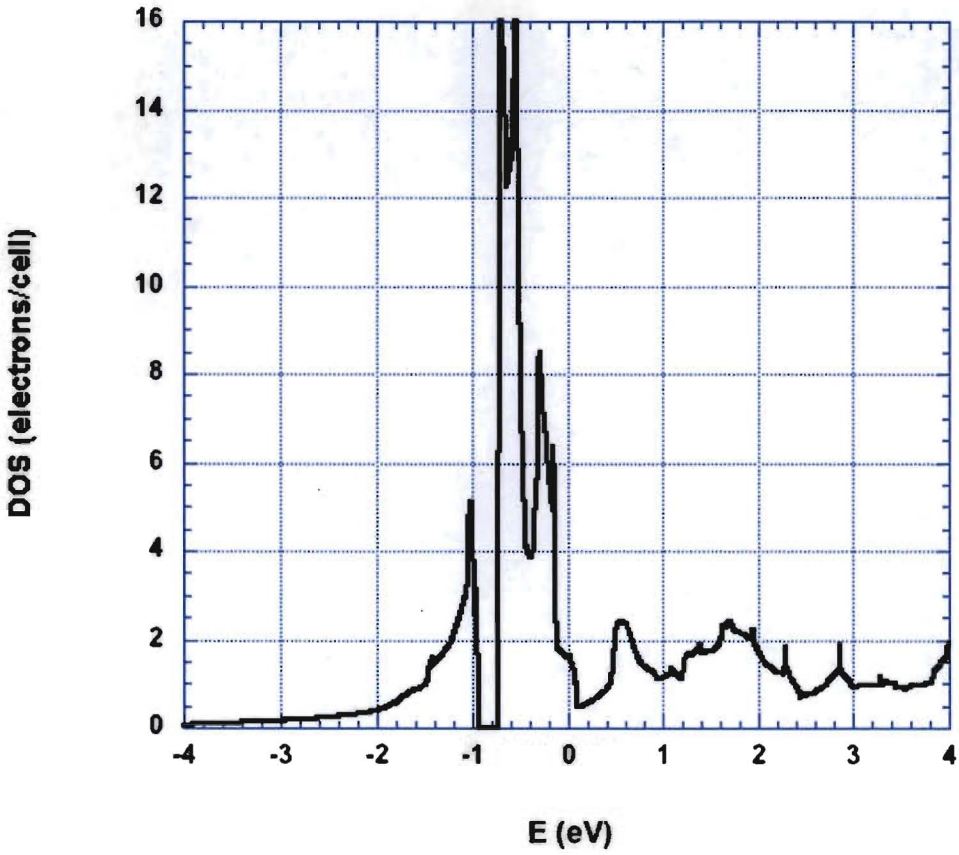

Fig. 4c