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August 7, 2015

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Phonon and magnetic structure of δ -plutonium from density-functional theory

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Abstract

We present phonon properties of plutonium metal obtained from a combination of density-functional-theory (DFT) electronic structure and the recently developed compressive sensing lattice dynamics (CSLD). The CSLD model is here trained on DFT total energies of several hundreds of quasi-random atomic configurations for best possible accuracy of the phonon properties. The calculated phonon dispersions compare better with experiment than earlier results from dynamical mean-field theory. The density-functional model of the electronic structure consists of disordered magnetic moments that are treated fully relativistic with explicit orbital-orbital correlations. The magnetic disorder is accomplished in two ways: (i) a special quasi-random structure and (ii) the disordered-local-moment (DLM) method within the coherent potential approximation. Magnetism in plutonium has been debated intensely, but the magnetic approach for plutonium is validated by the close agreement between the predicted magnetic form factor and that of recent neutron-scatter experiments.

Introduction

The properties of plutonium metal are rather extraordinary with perhaps the most striking being its ambient pressure phase diagram [1]. The fact that on one hand the material exist in a very low symmetry and high density phase, the monoclinic α phase, and on the other, in a high symmetry and low density cubic δ phase, is remarkable and unlike any other condensed matter system. To make plutonium even more intriguing, there are four more phases (β , γ , δ' , and ϵ) before melt that we illustrate in Figure 1.

The plutonium phase diagram is of course a challenge for theory; consider its lighter friend cerium and its *one* isostructural phase transition (α to γ) that is still a focus of debate, experiment, and modeling [2]. Nonetheless, the Letter by Söderlind and Sadigh [3] clearly showed that the main features of the plutonium phase diagram could be understood in terms of itinerant (delocalized) $5f$ electrons that support formation of magnetic moments. In a series of papers [3-6] the authors explain that the magnetic moments must be disordered in the δ phase because any magnetic order is mechanically destabilizing. This conclusion naturally resolves why δ -plutonium does not exist at lower temperatures below the magnetic ordering temperature. Another piece of the puzzle was added when it was realized [7, 8] that the spin and orbital moments cancel each other, rendering δ -Pu effectively nonmagnetic, while the electronic structure agrees very well with photo emission spectra [9].

There has been some criticism [10] leveled against the DFT because of its prediction of magnetic moments in plutonium. It was pointed out that neutron scattering data showed no evidence of ordered or disordered moments and the case was made that the magnetic moments are completely absent in plutonium [10]. Because of a new development in experimental measurements on plutonium we will return to this issue below.

In spite of the critique regarding plutonium magnetism, it is clear from the phase-diagram energetics [3] and elastic-constant calculations [11] that the DFT total energies are accurate and reliable for plutonium metal. Hence, we are here taking advantage of this in an advanced scheme to compute plutonium lattice dynamics from first-principles theory. The compressive sensing lattice dynamics (CSLD) method determines force

constants and lattice dynamics and it combines well with total-energy calculations [12]. We utilize the robust and mathematically rigorous framework of compressive sensing (CS), a new technique in the field of information science for recovering sparse solutions from incomplete data [13], to resolve which harmonic and/or anharmonic terms are important and find their values simultaneously. From CSLD we calculate phonon dispersions for δ -plutonium for two separate implementations of DFT that we describe in the modeling section below. The most important difference between them is their treatment of magnetic disorder that is modeled by either a special quasi-random structure (SQS) or the disordered-local-moment method within the coherent-potential approximation (CPA). The latter approach can easily be extended to also model solid solutions of δ -Pu-Ga or other alloys.

In the modeling section below we detail the electronic-structure calculations as well as aspects of our lattice-dynamics approach for the δ -Pu phonons. The results section show calculated phonon dispersions and make contact with existing experimental data and other theoretical modeling. Lastly, in the discussion section, we return to the issue of magnetism in plutonium and compare the previously calculated magnetic form factor with that obtained very recently from neutron scattering.

Modeling

Within the density-functional theory approach one important and necessary assumption is that of the electron exchange and correlation energy and potential. Because of the success of the generalized-gradient approximation (GGA) for actinide metals in general [14] it is applied here generally for the δ -plutonium electronic structure. We are employing two distinct implementations of DFT-GGA for the calculations of the total energies required for the CSLD. First, we employ the full-potential linear muffin-tin orbital method (FPLMTO) [15] for best possible accuracy of energetics related to atomic displacements. Second, the exact muffin-tin orbitals (EMTO) methodology [16] is applied similarly, but with a somewhat less accuracy with respect to atomic displacements, EMTO has the advantage, however, to exploit the CPA for modeling of magnetic as well as atomic disorder.

The FPLMTO method has been tested thoroughly for plutonium metal [3, 11] and most of the details of the present calculations replicate that of Söderlind and Sadigh [3]. The magnetic disorder for δ -Pu in [3] was accomplished by an eight atom special quasi-random structure while here we are applying a 32-atom cell for this purpose, similar to what was used for paramagnetic face-centered-cubic iron in the report by Körmann *et al.* [17]. Spin-orbit interaction and orbital polarization are here exactly as earlier [3] except that the orbital polarization correction is only acting on the $5f$ states (not also the $6d$ states). This difference is less important because the orbital moments from the $6d$ states are small ($\sim 0.1 \mu_B$). Because of the application of random displacements of the atoms, necessary for the CSLD, the crystal has no symmetry and a total of 32 k points are applied for the electronic structure in the full Brillouin zone. Finally, the FPLMTO calculations are carried out at the theoretical equilibrium lattice constant (4.635 Å) that is very close to established handbook data (4.637 Å) [18].

The details of the EMTO computations are identical to those presented in an earlier report [19]. Here they are performed for a 64-atom supercell for the EMTO equilibrium lattice constant (4.669 Å). The Brillouin zone is sampled on a $3 \times 3 \times 3$ Monkhorst-Pack grid. The Green's function has been calculated for 40 complex energy points distributed exponentially on a semicircle with a 1.9 Ry diameter enclosing the occupied states. Notably, spin-orbit coupling is not included while the spin disorder is that of a paramagnetic disordered-local-moment model [20]. This state uses a random mixture of two distinct magnetic states (spin up and down) on the same atomic species.

To train the CSLD model and compute harmonic force constants for δ -Pu, total-energy calculations are performed for supercells with (1) random atomic displacements between 0.05–0.26 Å and (2) a few select frozen-phonon configurations. The total number of configurations is rather large and about 250 and 150 for FPLMTO and EMTO, respectively.

For the FPLMTO-SQS configurations, we apply relatively large displacements to avoid the mechanical instability that may occur for any particular SQS arrangement. The second (harmonic), third, and fourth order force constants of the lattice are taken into account in the CSLD fitting, resulting in 109 independent parameters after considering constraints on the forces due to crystal symmetry and translational invariance [12]. By

considering the anharmonic (third and fourth) order force constants the fit is accurate even though the displacements are relatively large. We divide the training data into a fitting and a prediction (validation) subset, obtaining CSLD force constants with the fitting data and then computing the prediction error on the prediction subset at a given μ parameter [12, 21]. An average is then calculated by repeating the above procedure 10 times. Finally, the optimal force constants are obtained by minimizing the prediction error ($\sim 6\%$) over μ .

Results

Assuming that the Taylor expansion [12] that is fitted to the total energies in the CSLD scheme is converged, we calculate the lattice dynamics corresponding to our two DFT approaches, FPLMTO and EMTO. Because the former method provides a more accurate electronic structure, with the caveat that magnetic disorder may be better modeled within EMTO, we focus first on the results from FPLMTO.

In Figure 2 we show the FPLMTO-CSLD phonon dispersions for δ -Pu together with experimental data from Wong *et al.* [22] and dynamical mean-field theory (DMFT) [23]. Our result (solid line) generally agrees quite well with inelastic x-ray scattering [22], particularly all longitudinal branches. The Γ -X [001] longitudinal (L) and transverse (T) branches slope at the Γ point correspond to the c_{11} and c_{44} elastic moduli, while similarly the T_1 slope at Γ -X [011] relates to $c' = \frac{1}{2}(c_{11}-c_{12})$. A close inspection of Figure 2 reveals that our calculations slightly overestimate c_{11} and c' , while c_{44} and c_{12} are in good accord with experiment. That is also the conclusions from our previous investigation of the elastic moduli for δ -plutonium [11]. Furthermore, in Figure 2, we are able to compare our DFT result (solid line) with that of DMFT (dashed line) [23]. The authors of [23] state that DFT “have limited applicability” but in reality the DFT result agrees better with the experimental data [22] than DMFT does.

Next, in Figure 3, we show the lattice dynamics obtained from EMTO total energies combined with CSLD. The EMTO method predicts somewhat larger zone-boundary phonons than FPLMTO [18] and for a closer comparison we scale the EMTO phonon frequencies so that their L-point L phonon coincides. The high-energy phonons

agree very well between the two methods but for some of the softer transverse phonons there are differences. It is also for these softer phonons where both FPLMTO and DMFT diverge from the experimental phonons by Wong *et al.* One reason for this discrepancy may be that the sample used for the inelastic x-ray scattering was a δ -Pu-Ga alloy, while all theory so far models unalloyed δ -Pu. A sophisticated investigation of the δ -Pu-Ga alloy system, applying the EMTO-CPA and CSLD methods, is forthcoming.

Discussion

We have shown that combining a new efficient scheme for lattice dynamics with density-functional-theory gives quite good phonon properties for δ -plutonium that agree better with inelastic x-ray scattering than that of the dynamical mean-field theory. The DFT-CSLD methodology has distinct advantages over the DMFT in that it is entirely parameter free and it easily couples to advanced modeling of alloys by the CPA.

The critique against DFT for plutonium has generally been that no magnetic moments exist in plutonium contradicting the theory. The belief that magnetic moments are absent in plutonium is reasonable based on the body of experimental evidence against its existence [10] while it is equally reasonable to argue that the complex magnetism predicted by DFT has been too illusive or complex to discover. Certainly, the magnetic disorder and cancellation of spin and orbital moments make the magnetism obscure for most experimental probes. Lander [24] agrees that anti-parallel spin and orbital moments is a more complex situation but explains [10] that even in the complete cancellation scenario, where the total magnetic moment is equal to zero, “the difference in their [spin and orbital] spatial extent would still allow a measureable signal to be seen in neutron scattering”. Apparently, no such signal was detected in neutron-scattering work up to that point.

It is actually rather straightforward to calculate the magnetic form factor, at least within the dipole approximation. From the band-structure computation one obtains spin- and orbital-moment densities and the magnetic form factor (magnetic scattering amplitude) from a Fourier transform of the magnetization density

$$F(\mathbf{Q}) = \int M(\mathbf{r}) e^{i\mathbf{Q}\mathbf{r}},$$

where \mathbf{Q} is the scattering vector. In the dipole approximation [25] it can be expressed as

$$F(\mathbf{Q}) = [\langle j_0 \rangle_s \mu_s + \langle j_0 + j_2 \rangle_l \mu_l].$$

Here $Q = |\mathbf{Q}|$ and $\langle j_n \rangle$ are averages of Bessel functions over the plutonium-atom spin density and μ_s and μ_l are magnetic spin and orbital moments, respectively. In the cancellation model [8] both these moments are anti-parallel with the same magnitude so that $\mu_s + \mu_l = 0$. In this special case, F reduces to a scaled j_2 function and one therefore expects the magnetic form factor to behave like j_2 with a shoulder at finite Q vector and vanish as Q approaches zero. This behavior has also been observed for α -Sm where there is a very close magnetic cancellation [26].

In Figure 4 we show the DFT prediction [8] of the magnetic form factor (full line) that shows the behavior of the j_2 Bessel function. In this figure we also plot very recent magnetic form factor data for δ -Pu obtained from neutron-spectroscopy experiments with two incident neutron energies (250 and 500 meV) [27]. Most error bars on the experimental data in the original plot (Fig. 2 in [27]) are small and here removed for clarity. There is obviously a very good agreement between the measurement and the prediction from DFT made some years ago [8]. One important feature of both the DFT and the experimental data is that both have a shoulder close to $Q \sim 0.25-0.3$ and approaches zero for smaller Q values. This behavior indicates a very efficient destruction of the net total magnetic moment in δ -Pu because the $Q = 0$ value corresponds to the magnetic moment integrated over the full crystal. The DMFT model [27] agrees relatively well with the neutron-spectroscopy data but seems to lack the correct functional form for small Q .

Janoschek *et al.* make the point that spin moments exist in δ -Pu, contrary to the conclusion by Lashey *et al.* [10], and they are fluctuating by means of valence fluctuations. This conclusion is consistent with DFT because magnetic disorder simply represents a frozen (static) state of the fluctuations. One important difference in the DMFT interpretation of the measurements [27] and the present theory lies in the description of the $5f$ electrons. The DMFT [27] characterization is a superposition of

localized $5f$ wave functions with screened magnetic moments while DFT describes the $5f$ electrons as itinerant with spin and orbital moments effectively cancelling each other.

The delocalization of the $5f$ electrons not only explains the atomic volume for the δ phase but also the volumes for all the other phases as well [3]. The DMFT interpretation, on the other hand, cannot explain the lattice constant for δ -Pu (or any other phases) because here the localized $5f$ electrons do not provide sufficient bonding. This has been shown by spin polarized and strongly correlated (GGA + Hubbard U) calculations that severely overestimate the atomic volume for δ -Pu [28, 29].

Acknowledgments

We thank B. Sadigh, F. Körmann, and T. Björkman for helpful discussions. A. L. thanks A. V. Ruban and M. Dehghani for EMTO development. This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

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Figure Captions

Figure 1. The experimental phase diagram for plutonium metal. Redrawn after [1].

Figure 2. FPLMTO-CSLD (full line), DMFT (dashed line) [23], and experimental [22] phonons for δ -plutonium.

Figure 3. FPLMTO-CSLD (full line), EMTO-CSLD (red line), and experimental [22] phonons for δ -plutonium.

Figure 4. DFT (full line) [8], neutron-spectroscopy (solid symbols) [27], and DMFT (dashed line) [27] magnetic form factor for δ -plutonium.

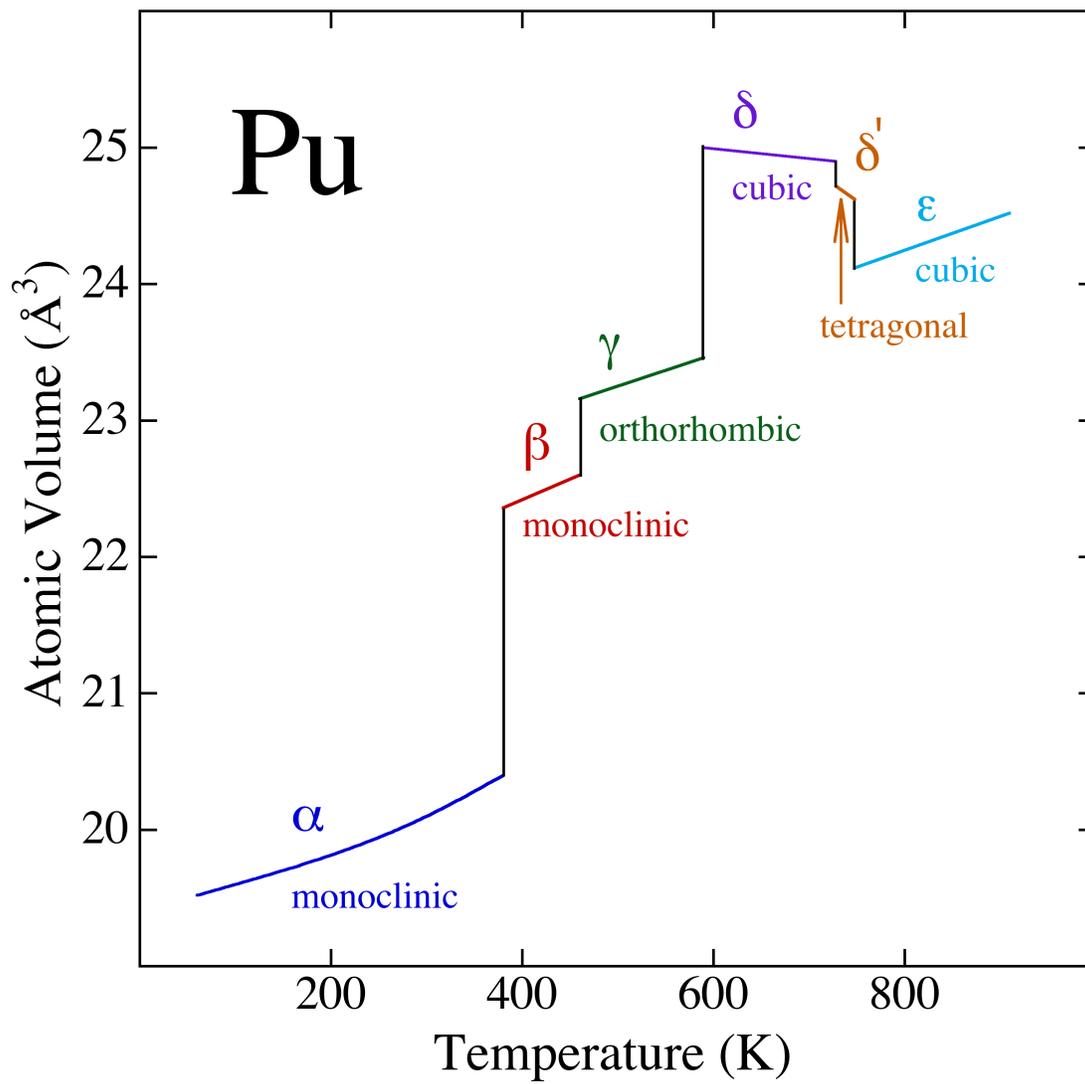


Fig. 1

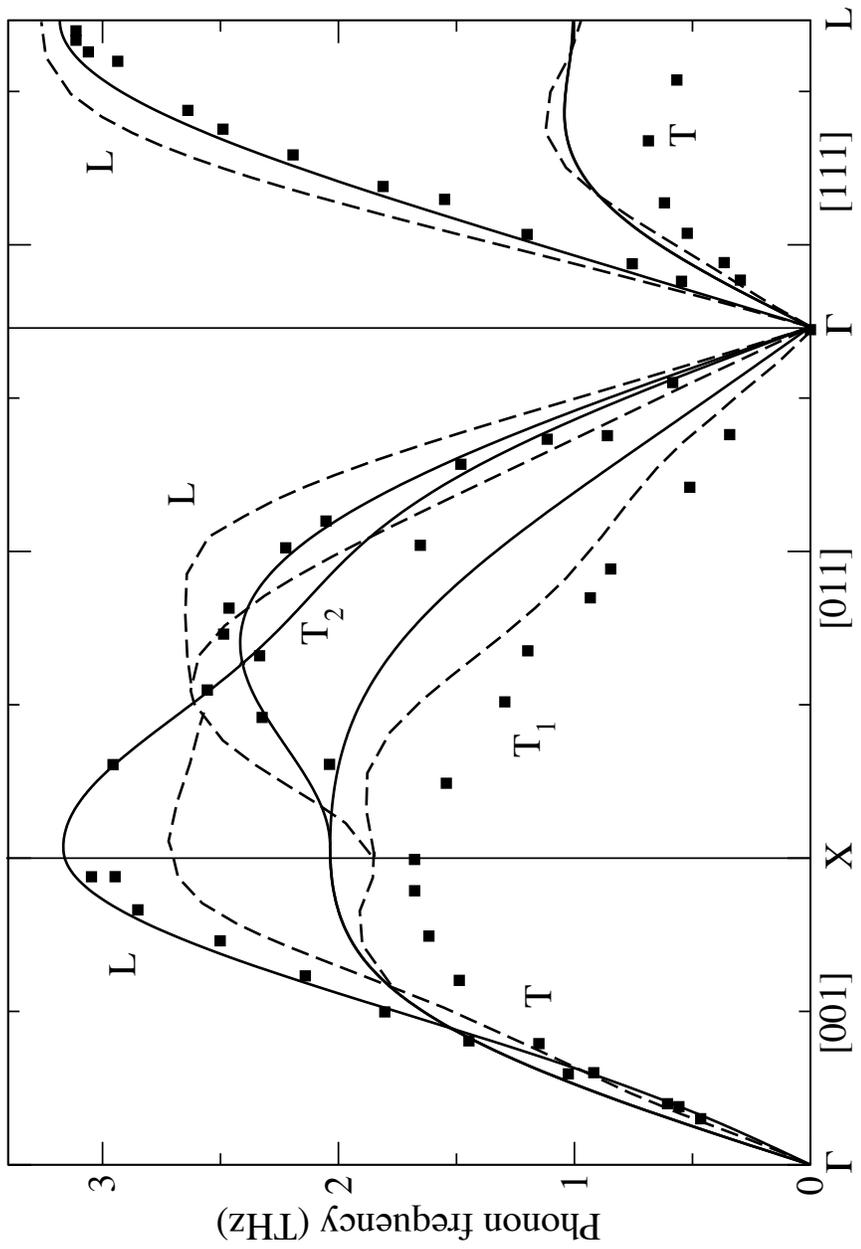


Fig. 2

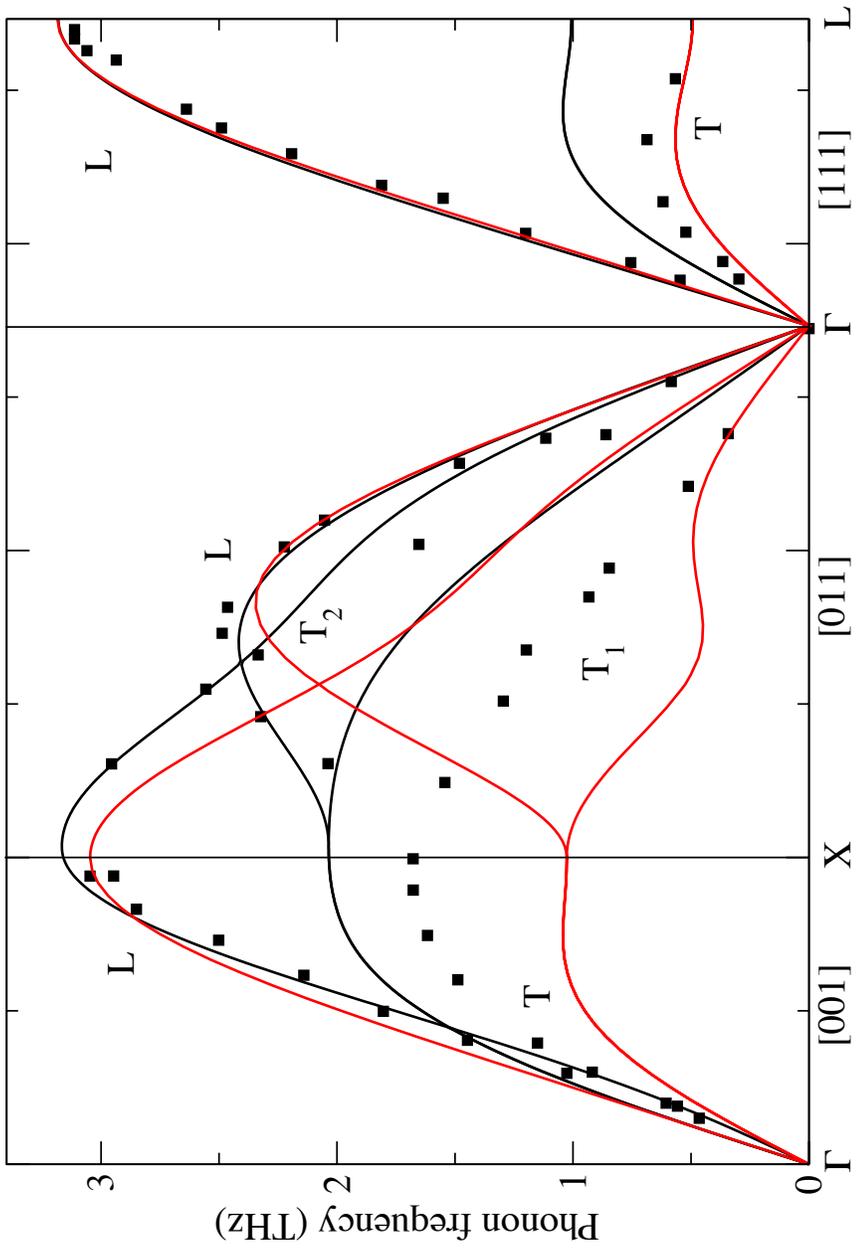


Fig. 3

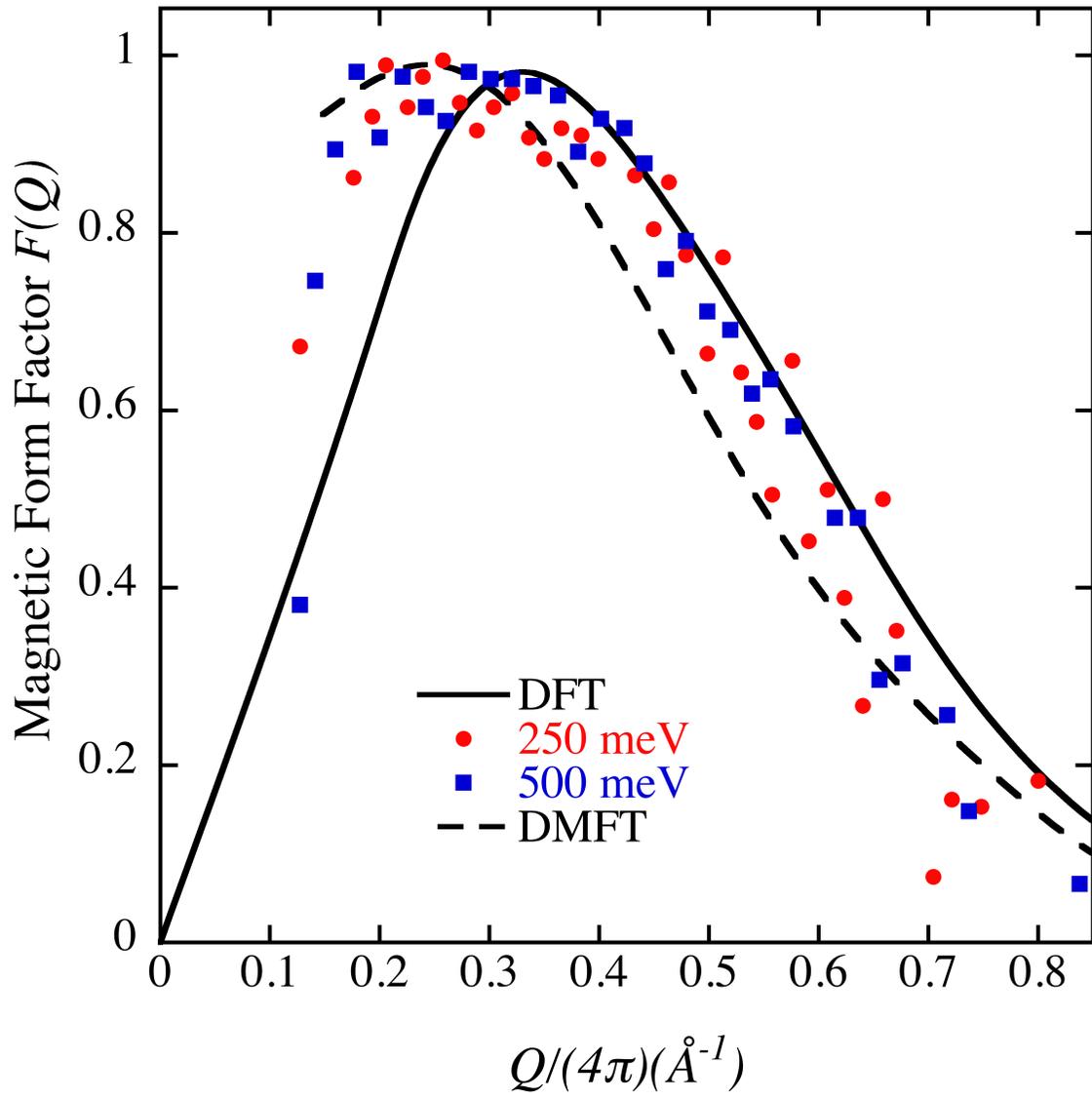


Fig. 4