Electronic correlation strength of Pu

A. Svane,[1,*] R. C. Albers,[2] N. E. Christensen,[1] M. van Schilfgaarde,[3] A. N. Chantis,[4] and Jian-Xin Zhu[2]
[1]*Department of Physics and Astronomy, Aarhus University, DK 8000 Aarhus C, Denmark*
[2]*Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*
[3]*Department of Physics, King's College London, The Strand, London WC2R 2LS, UK*
[4]*American Physical Society, 1 Research Road, Ridge, New York 11961, USA*
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An electronic quantity, the correlation strength, is defined as a necessary step for understanding the properties and trends in strongly correlated electronic materials. As a test case, this is applied to the different phases of elemental Pu. Within the *GW* approximation we have surprisingly found a "universal" scaling relationship, where the *f*-electron bandwidth reduction due to correlation effects is shown to depend only on the local density approximation bandwidth and is otherwise independent of crystal structure and lattice constant.

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I. INTRODUCTION

Many technologically important materials have strong electron-electron correlation effects. They exhibit large anomalies in their physical properties when compared with materials that are weakly correlated, and have significant deviations in their electronic structure from that predicted by conventional band-structure theory based on the local-density approximation (LDA). Because the anomalies and deviations are caused by electronic correlation effects, which often dominate the physics of these materials, in this paper we define a quantity that we call the "correlation strength," or C, as a necessary step in order to be able to describe trends and bring order into our understanding of correlated materials. We emphasize the word "quantity" since a quantitative measure is needed to answer the question, "How strong are the electronic correlations?" Without some understanding of how big this is, it is not possible to make sense of the properties of these materials. In this context, "correlation" is defined in a way somewhat different from how it is sometimes used (e.g., in the term "exchange-correlation potential"). By "correlation" we specifically mean "correlation beyond LDA theory." This usage reflects the way the term is often loosely used in common terminology in the area of strongly correlated electronic systems.

To create a new quantity requires determining a "scale" by which to measure its size. In principle, any experimental or theoretical property (e.g., specific heat) that monotonically increases or decreases over the full range of correlation effects, where we define correlation strength to lie between zero for none and one for full correlation, can be used as a measure of this quantity. Hence correlation strength is an indeterminant quantity and depends on the property used to define it. However, this does not matter since only relative rather than any absolute strength is important for characterizing these materials and for predicting trends in their properties. Any measure based on one property can easily be converted to that based on another property. In this paper we develop a theoretical correlation strength based on the *GW* approximation[1–4] to electronic-structure theory and apply it to plutonium,[5,6] which is known to have significant correlation effects. The *GW* approximation is named for the correction term in this theory, which is a Green's function G times a screened Coulomb interaction W. We also demonstrate a scaling relationship that is universal in that it is independent of crystal structure and atomic volume. The ideas in this paper could certainly be modified and generalized to be able to treat other types of correlated materials (e.g., spin-fluctuation or high-temperature superconducting materials) by using other electronic properties to determine a correlation strength and by using more sophisticated theoretical techniques than are considered here.

Of course, there is a long history in physics and chemistry of using various quantities to predict materials trends. For example, with respect to the actinides, in 1970 Hill[7] plotted the magnetic and superconducting transition temperatures of actinide compounds as a function of the actinide-actinide nearest-neighbor distance. These "Hill plots" brought some sensible order into what had previously been seen as a somewhat random occurrence of these various ground states, and also provided some degree of predictability, in that superconducting compounds tended to occur for short actinide spacings and magnetic compounds at large spacings.[8] The plots were intuitively based on the idea that f-wave-function overlap was the key factor determining the stability of the relative ground states. These plots failed for heavy-fermion compounds[8] and our understanding of electronic structure has now advanced to the point where we realize that at large actinide nearest-neighbor distances the f electrons tend to hop predominantly through hybridizations with other orbitals on nearby atoms rather than through a direct f-f hybridization.

Another important actinide trend was developed by Smith and Kmetko.[9] They showed that the crystal structures of the actinides can be plotted as a continuous function of atomic number (Z), with alloys filling in between the atomic numbers of the pure elements. When plotted in this way, one obtains "connected binary alloy phase diagrams for the light actinides," which provide a clear picture of the trends and relationships between the crystal structures of all the light actinides "at a glance."

More generally, in materials science, many different variables have been used in an attempt to understand systematic trends in crystal structures among classes of different compounds. Such variables have included electronegativity differences, covalent and ionic contribution to the average spectroscopic energy gap, and various types of core, ionic, and metallic radii. These have been reviewed in a review article on "Structure Mapping" by Pettifor;[10] see also Refs. 11–15. However, these methods are not relevant for our purposes, since, as we shall show below, correlation effects are more important than crystal structure for determining the properties of many actinide metals.

Among different classes of correlated materials, superconducting transition pressures have often been plotted versus either specific structural properties or some characteristic correlated quantity. These are too numerous to report in full. A typical example are trends in superconducting transition temperatures[16,17] with numbers of planar (layered or two-dimensional) structural units (e.g., CuO_2 or FeAs planes), and similarly for representative classes of some heavy-fermion superconductors (e.g., Ce*M*In5 and Pu*M*Ga5 for $M =$ Co, Rh, Ir, also including c/a structural anisotropies[18]). Closer in spirit to this paper are trends in superconducting transition temperature versus characteristic spin-fluctuation energies, except that the trends were all based on experimental measurements rather than theoretical input.[18–20]

Perhaps the closest analog to the ideas of our paper is the correlation between crystal structure and d-occupation numbers in rare-earth systems (including under pressure).[21,22] In this case theoretical calculations are required to determine the number of occupied d electrons as a function of d element and volume per atom (which can be equated to pressure). Given this input, however, the correct crystal structure can then usually be predicted. What is different about our approach is that we believe that not just one property such as crystal structure or transition temperature but many properties of actinide metals will follow trends based on our correlation scale (see below).

The outline of the paper is as follows: In Sec. II, a theoretical definition of the correlation scale is presented. It is expressed in terms of the effective bandwidth based on the parameter-free LDA and *GW* approaches. In Sec. III, we apply the scenario to determine the correlation strength in elemental Pu solids. A universal scaling relationship is obtained, where the f-electron bandwidth reduction due to correlation effects is shown to depend only upon the LDA bandwidth and is otherwise independent of crystal structure and lattice constant. The same type of trend is also found for the d-electron systems. A concluding summary is given in Sec. IV.

II. THEORETICAL METHOD

Our meaning of correlation makes it necessary to use a theory that includes correlation effects that go beyond those included by the LDA approximation in order to determine a theoretical correlation strength. This is challenging, since the most sophisticated treatments of correlation effects have historically been mainly confined to abstract theoretical models, and have parameterized the electronic structure in such an oversimplified manner that the connection with actual materials examined experimentally was often somewhat vague.[23] In the last decade, however, great progress has been made in this area, especially those involving dynamical mean-field theory (DMFT)[24–27] techniques, and strong correlation effects are beginning to be integrated into true first-principles methods. To achieve this, instead of using *ad hoc* Hubbard Hamiltonians that were essentially added without derivation to local density approximation calculations, more recent methods have been attempting to explicitly calculate screened Coulomb interactions directly in the random phase approximation (RPA) and related approximations. These techniques have been recently reviewed by Imada and Miyake.[28] One direction that has been particularly fruitful recently is the construction of low-energy effective models involving a downfolding of the electronic states and using localized Wannier orbitals and *ab initio* real-space tight-binding models. States far from the Fermi energy can be treated with conventional LDA-like techniques, while correlation effects are taken explicitly into account for the important states around the Fermi energy. Usually constrained RPA (or cRPA) methods are used to screen the Coulomb interactions. Such methods have achieved a fair degree of success for semiconductors, $3d$ transition-metal oxides, iron-based superconductors, and organic superconductors.

However, these methods rely upon being able to separate the electronic structure into some electrons belonging to fairly isolated bands near the Fermi level and the rest to band degrees of freedom far from the Fermi level. For metals, as we are considering, such methods therefore appear to be unlikely to be successful. Another approach,[29,30] which seems more suitable to our case, is $GW+$DMFT. This has also been reviewed in Ref. 28. Such a method involves *GW* (or RPA-like) methods for calculating the Coulomb interactions that are then integrated with DMFT techniques. In the full implementation the entire scheme would be made self-consistent and would be independent of the initial *GW* calculations used to initiate the method. In the initial description of the method[30] only a simplified one-shot approach was applied to nickel. Since the initial papers outlining the methodology, almost no progress has been made, perhaps indicating the difficulty of this approach. Very recently, however, a more sophisticated implementation[31] has been applied to $SrVO_3$. While these calculations are not yet fully self-consistent, they may stimulate more interest in pushing through the technical issues involved in implementing this method.

Since there is not yet widely available a suitable code that involves these more sophisticated treatments of correlation for the metallic systems that we are interested in, we have used the *GW* method[1,3,4] as a theoretical method for estimating correlation effects. Although this is a low-order approximation that definitely fails for very strong correlation effects, it is sufficient for our purposes as a way to estimate correlation deviations from LDA band-structure theory, and in particular for the main purpose of our work, which is to show that it is possible and useful to define a new quantity, which we call correlation strength, in order to be able to place new materials in their proper physics context and hence to be able to observe important trends in their properties.

Among the available *GW* codes, we have used the quasiparticle self-consistent *GW* approximation (QSGW).[32–34] The *GW* approximation, itself, can be viewed as the first term in the expansion of the nonlocal energy-dependent self-energy $\Sigma(\mathbf{r},\mathbf{r}',\omega)$ in the screened Coulomb interaction W. From a more physical point of view it can also be interpreted as a dynamically screened Hartree-Fock approximation plus a

Coulomb hole contribution.[3,4] Therefore, *GW* is a well defined perturbation theory. In its usual implemention, sometimes called the "one-shot" approximation, it depends on the one-electron Green's functions which use LDA eigenvalues and eigenfunctions, and hence the results can depend on this choice. Unfortunately, as correlations become stronger serious practical and formal problems can arise in this approximation.[33] However, Kotani *et al.*[34] have provided a way to surmount this difficulty, by using a self-consistent one-electron Green's function that is derived from the self-energy (the quasiparticle eigenvalues and eigenfunctions) instead of LDA as the starting point. In the literature, it has been demonstrated that the QSGW form of *GW* theory reliably describes a wide range of semiconductors,[32,35–37] *spd*,[32,38,39] and rare-earth systems.[40] It should be noted that the energy eigenvalues of the QSGW method are the same as the quasiparticle spectra of the GW method. This captures the many-body shifts in the quasiparticle energies. However, when presenting the quasiparticle DOS, this ignores the smearing by the imaginary part of the self-energy of the spectra due to quasiparticle lifetime effects, which should increase as quasiparticle energies become farther away from the Fermi energy.

To define a theoretical correlation strength some electronic-structure quantity that scales with an intuitive notion of correlation strength is needed. In our application to Pu, we propose to consider the f bandwidth, W_f, and use the relative bandwidth reduction in QSGW compared to LDA,

$$w_{\text{rel}} = W_f(\text{GW})/W_f(\text{LDA}), \qquad (1)$$

as the key quantity, where $W_f(\text{GW})$ and $W_f(\text{LDA})$ are the f bandwidths as obtained from QSGW and LDA calculations, respectively. This is consistent with the correlation-induced QSGW f-bandwidth reduction in Pu that was demonstrated in Ref. 5.

Using a quasiparticle calculation is important since lifetime effects, which are absent in the LDA calculations, would obscure the band narrowing in *GW* relative to LDA. We also need a measure that is robust at the high temperatures of the strongly correlated phases of Pu, where any low-energy features in the electronic structure are likely to be thermally averaged away.[41] In this regard, it should be noted that although temperature certainly plays an important role in predicting the correct equilibrium crystal structure, we believe that it is the resulting volume per atom of any Pu phase that determines the amount of correlation, since this is an electronic property. In particular, we do not expect that the bandwidth predicted by our zero-temperature *GW* calculations will be sensitive to any temperature in the range set by the Pu solid phases.

The choice of bandwidth narrowing as a measure of correlation strength is consistent with ideas of correlation going back almost to the beginning of modern electronic structure theory. Quasiparticle descriptions of electronic structure have been standard since Landau developed Fermi liquid theory and have been derived from standard many-body approaches (see, for example, the discussion in Refs. 2, 42, and 43). They have since been extended to strongly correlated electronic materials (see, for example, the review in Ref. 44). Much of our modern understanding of correlation effects has been developed using simple model Hamiltonians, especially the Hubbard model.[45] For metals, most of these approaches for strong correlations have focused on low temperatures,[44] where the electronic structure at the Fermi energy can yield a rich and diverse set of phenomena at low-energy scales. In such a case, for example, specific heat or effective mass enhancements at the Fermi energy have often been used to characterize the strength of correlations. As we describe below, pure elemental plutonium forms correlated states at very high temperatures, and therefore electronic states are sampled that are far from the Fermi energy. Although it is an interesting question how far away from the Fermi energy correlations effects extend (see, e.g., Ref. 46), it is nonetheless important to include correlation effects for all the quasiparticle states of the f electrons in Pu. By including the real part of the self-energy for all of these states, which are involved in the band narrowing, our *GW* approach is thus more relevant for these high-temperature correlated phases than more traditional measures of correlation that focus exclusively on effects at or near the Fermi energy. In addition, the bandwidth is closely related to the bonding strength of the $5f$ states (see Ref. 51 for more details about this), and hence is highly relevant for tracking any property involving bonding.

To set an appropriate correlation scale, we define our theoretical C by

$$C = 1 - w_{\text{rel}}, \qquad (2)$$

which ranges from $C = 0$ (no bandwidth reduction) in the LDA limit to $C = 1$ in the fully localized or atomic limit (the bandwidth becomes zero).

As mentioned above, our test case for correlation is elemental Pu, an actinide metal, which exhibits large volume changes compared to predictions from band structure theory that are clearly due to correlation effects.[47–51] The large variation in volumes is controlled by the amount of strong f bonding, which is due to direct f-f wave-function overlap. The f bonding for many of the different phases is greatly reduced leading to anomalous volume expansions due to the narrowing of the f bands that results from correlation effects.[51] If no correlation were present, the f bonds would have their full strength and a relatively small volume per atom for all phases would be accurately predicted by LDA band-structure methods. In the limit of extremely strong correlation the bands would have narrowed so much that the f electrons would be fully localized, and they would not contribute to the bonding. The volume per atom would then be much larger and close to that of Am, which has fully localized f electrons that do not extend outside the atomic core.

Using the QSGW approximation we have calculated[52] the quasiparticle band structures of the fcc, bcc, simple cubic (sc), γ, and pseudo-α phases of Pu as a function of volume. The pseudo-α is a two-atom per unit cell approximation[53] to the true α structure of Pu that preserves the approximate nearest-neighbor distances and other essential features needed for the electronic structure. In this way we avoid performing an extremely large and expensive 16-atom per unit cell calculation for the α structure. We are unfortunately unable to present *GW* results for the β structure, which is even more complex than the α structure, since no pseudostructure for this crystal structure is available and a QSGW calculation is presently not feasible for so many atoms per unit cell.

To calculate the f-electron bandwidths from the f-electron projected density of states (DOS), $D_f(E)$, an algorithm is needed to determine the width of the main peak in this DOS. A simple first guess is to choose a rectangular DOS and to use a least-squares fit to the GW or LDA f-DOS to determine the best height and width of the rectangle. A drawback of this method is that an artificial broadening of the effective f bandwidth appears, which is due to a significant d-f hybridization at the bottom of the f-DOS that creates an extra peak at low energies. This masks the correlation-induced band narrowing. Since this peak has relatively lower height than the main f peak, we may avoid this complication by generating an algorithm that emphasizes the "high-peak" part of the f DOS. The algorithm we have used is therefore the second moment of the f DOS

$$W = 2(\langle E^2\rangle - \langle E\rangle^2)^{1/2}. \quad (3)$$

The factor of two is needed because the bandwidth extends above and below the mean energy and is not just the average deviation from the mean energy. To emphasize the main part of the f-DOS peak, the square of the f DOS is used as weight function:[54]

$$\langle f(E)\rangle \equiv \int dE f(E) D_f^2(E) \Big/ \int dE D_f^2(E). \quad (4)$$

III. NUMERICAL RESULTS AND DISCUSSION

In Fig. 1 we illustrate how $w_{\rm rel}$ varies with volume for the five different phases considered here.[55] Large volume variations ranging between about 14–28 Å^3 per atom are considered, with bandwidths that span almost an order of magnitude, from about 0.5 eV to 2.5 eV. Although the LDA bandwidth decreases with increased volume due to reduction in f-f overlap of the wave functions, the QSGW bandwidth decreases even faster illustrating increased correlation effects

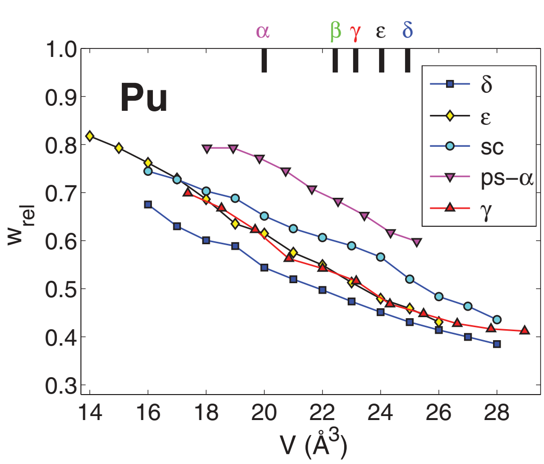

FIG. 1. (Color online) Plot of $w_{\rm rel} = W_f(GW)/W_f(\rm LDA)$ versus volume, V, per atom, for the γ, fcc, bcc, sc, and ps-α [pseudo-α, an approximate α phase (Ref. 53)] crystal phases of Pu. Note that the sc (simple cubic) is a hypothetical structure for Pu. The small, vertical bars at the top of the figure mark the experimentally observed atomic volumes (Ref. 54).

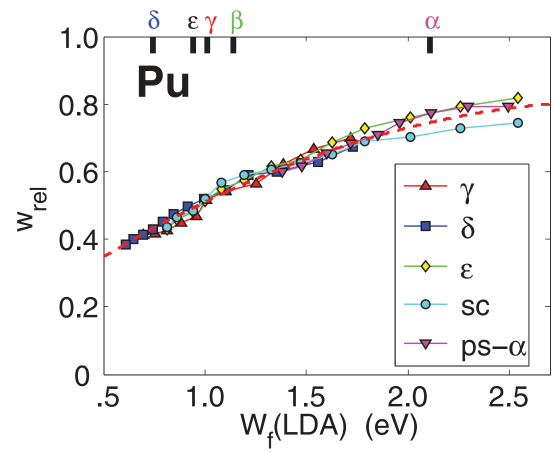

FIG. 2. (Color online) Plot of $w_{\rm rel} = W_f(GW)/W_f(\rm LDA)$ versus $W_f(\rm LDA)$ for the γ, fcc, bcc, sc, and ps-α. The dashed red line represents the fit of Eq. (5). The small, vertical bars at the top of the figure mark the values of $W_f(\rm LDA)$ calculated at the experimental volumes of the five Pu phases (Ref. 54).

with lattice expansion. The bandwidth at a specific volume depends on crystal structure (due to differences in coordination and bond lengths), as does also the correlation strength.

Although we expect electronic-structure calculations to strongly depend on the crystal structure and lattice constant, we surprisingly found that correlation effects were approximately independent of these. Indeed, Fig. 2 shows that all of our different calculations for our measure of correlation strength, the reduced bandwidth, collapse to a single "universal" curve when plotted as a function of the LDA bandwidth. In making this plot, it is likely that the effective screened Coulomb interaction between the $5f$ electrons is approximately constant and that the correlation effects are being tuned by the effective average kinetic energy of these electrons as reflected in their LDA bandwidth. In the range of W_f values considered here the curve is approximately quadratic, i.e.,

$$w_{\rm rel}(x) = 0.15 + 0.43x - 0.07x^2, \quad (5)$$

where $x = W_f(\rm LDA)$ in eV. From Eq. (2) we can use these results to determine a correlation strength C. It is remarkable that the many-body properties of a strongly correlated system can be tuned with what is normally considered to be a one-electron property.

In Fig. 3 we show[56] that our definition of theoretical correlation strength does indeed fulfill our expectations and can be used to bring order into the trends for various experimental properties, including volume, sound velocity, and resistivity. These properties exhibit an approximately 25%, 50%, and 35% change over the correlation range (about 0.2 to 0.6) between the α and δ phases of Pu and, with some scatter that might partially depend on sample quality, fall on smooth curves when plotted as a function of our theoretical correlation strength. It is remarkable that all of these data should collapse to a single curve for each property that is independent of any explicit consideration of temperature, crystal structure, or other variable. However, more generally, we would only expect this to be true for a property that was predominantly affected by correlation effects.

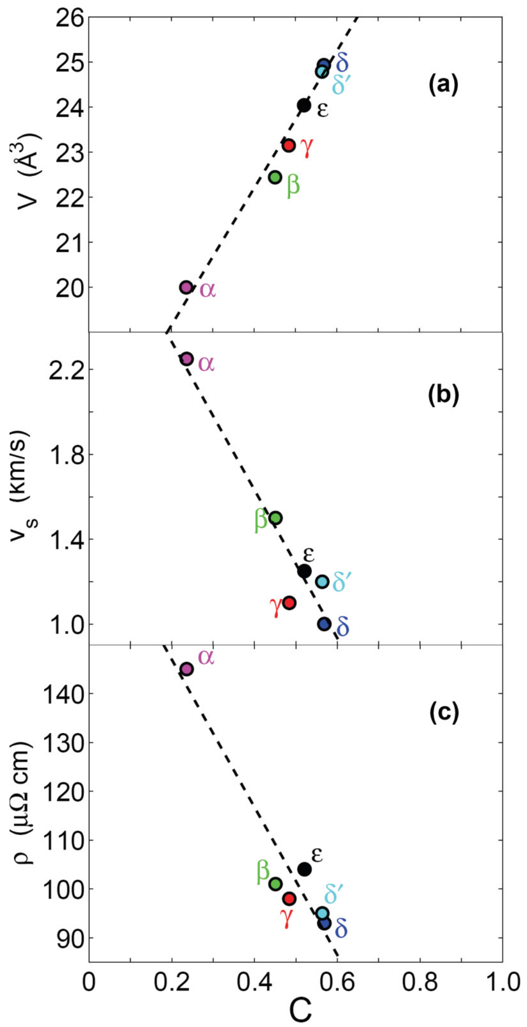

FIG. 3. (Color online) Trends in Pu properties as a function of correlation strength C, including (a) volume per atom (Ref. 54), (b) sound velocity (Ref. 57), and (c) resistivity (Ref. 57).

In terms of theoretical trends, various theories have often attempted to estimate the amount of correlation in terms of the Z factor,

$$Z_{n\mathbf{k}} = \left(1 - \langle \Psi_{n\mathbf{k}} | \frac{\partial \Sigma(\epsilon_{n\mathbf{k}})}{\partial \omega} | \Psi_{n\mathbf{k}} \rangle \right)^{-1}, \tag{6}$$

where $\Psi_{n\mathbf{k}}$ are the (LDA) electronic eigenfunctions with energies $\epsilon_{n\mathbf{k}}$, and Σ denotes the self-energy. We have found that the volume dependence of the Z factors follows the trend of the f-bandwidth reduction in Fig. 1, i.e., our measure of correlation strength, albeit with variations due to **k**- and hybridization-dependence. However, it should be noted that the relation between Z and bandwidth reduction is not the same in all materials, especially for weakly correlated broadband systems, which seem very different from strongly correlated materials such as Pu.

The simplest Hubbard-like Hamiltonian[45] to describe strongly correlated electron systems has a form

$$H = \sum_{ij,\sigma} t_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} \tag{7}$$

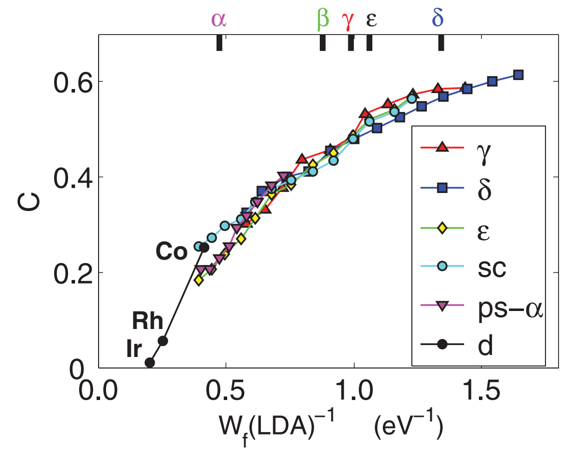

FIG. 4. (Color online) C from GW theory versus $1/W_f$(LDA). The data for Co, Rh, and Ir are for the $3d$, $4d$, and $5d$ bandwidths, respectively. The small, vertical bars at the top of the figure mark the values of $W_f(\mathrm{LDA})^{-1}$ calculated at the experimental volumes of the five Pu phases (Ref. 54).

with two parameters: the Hubbard parameter U which induces correlation, and an effective t, which can be related to the *uncorrelated* bandwidth W. When W dominates, the system is in a weakly correlated limit and, when U dominates, the system is in a strongly correlated regime. Hence, one can study the solutions as a function of U/W to go from one limit to another. In more realistic electronic-structure calculations, the same physics is intuitively expected to carry over. The Hubbard U can then be thought of as a screened on-site Coulomb interaction and the bandwidth as due to the normal band-structure hybridization. In our context, this suggests that the correlation strength C should also be a function of U/W. To test this, in Fig. 4 we plot C versus $1/W_f$(LDA). If the effective U were approximately constant, we had hoped to observe some approximate linear behavior at weak correlations, but any such behavior is unclear in Fig. 4. To show what might happen at weaker correlation strengths we have also included in Fig. 4 the equilibrium-volume results for Co, Rh, and Ir for the d-electron projected DOS. Interestingly enough, the d-electron results seem to follow the same overall trend to large bandwidths (small correlation). Among the transition metals included in the plot, Co ($3d$) has the most narrow d band, and the correlation value is close to the lowest values for Pu in the figure.

IV. CONCLUSION

In summary, we have introduced the idea of a "correlation strength" quantity C, which must be taken into account in order to explain the properties of strongly correlated electronic materials. As an example, we have shown how to use the GW method to define a theoretical C for metallic Pu, and that various experimental physical properties, including anomalous volume expansion, sound velocity, and resistivity, for the different phases of Pu follow well-defined trends when plotted versus our theoretical correlation strength. We have also demonstrated a universal scaling relationship for the correlation-reduced bandwidth as a function of the LDA bandwidth.

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*svane@phys.au.dk

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[56]For the volumes of the different phases of Pu, we have followed the same method used to generate Fig. 1. We have also used the same volumes of the different phases for the sound velocity and resistivity needed to determine the correlation strength from the *GW* calculations plotted in Fig. 1. Note that since we have not directly calculated the value of w_{rel} for the β phase, we instead used the availability of the bandwidth reduction of Eq. (5) together with the calculated LDA bandwidth for the correct crystal structure of β Pu to determine $w_{\rm rel}(\beta) = 0.55$.

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