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Orbital polarization in narrow-band systems: Application to volume collapses in light lanthanides

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Energy-band calculations have been performed for Ce, Pr, and Nd. The normal local-spin-density approximation to exchange and correlation for the potential is used but spin-orbit coupling and a newly developed additional contribution to the 4*f* eigenvalue splittings arising from orbital polarization of the 4*f* electrons are also included. This procedure represents the application of all three Hund's rules in the solid state. The observed volume collapses of the light rare-earth metals are correctly described by theory.

Among the metallic elements cerium exhibits an extraordinarily rich pressure-temperature phase diagram.[1] Five distinct solid phases are known to exist, having different magnetic and superconducting properties. A most fascinating phase transition involving an isostructural 14% volume collapse takes place at room temperature and a pressure of 7 kbar.[2] In the low-pressure high-volume fcc phase (γ), cerium has a localized magnetic moment while the magnetic susceptibility in the dense low-volume fcc phase (α) is essentially temperature independent,[3] showing that the moment is quenched. The isostructural nature of the transition indicates that it is electronically driven, therefore, in this paper we shall use a zero-temperature theory applied at the transition pressure of -7 kbar at zero temperature estimated from the phase diagram.[1]

Many attempts have been made to describe this highly unusual behavior.[4] At first it was proposed that the transition involved a promotion of the Ce 4*f* electron to the 5*d* conduction-band state.[5] This promotion transforms the $4f^1$ trivalent (γ) solid to a $4f^0$ tetravalent one and simultaneously the magnetic moment is lost. Further extensions of this hypothesis produced models with a sharp 4*f* level very near the Fermi energy and moving from below it to above it during the $\gamma \rightarrow \alpha$ transition.[6] A radically different model[7] was then proposed involving no essential change of the 4*f* occupation during the transition, where instead the nature of the 4*f* state changes from a local nonbonding to itinerant bonding—a Mott transition. Experiments probing the electron density substantiated the assertion that the number of 4*f* electrons remains practically unchanged during the transition.[8] More recently the transition has been described as a Kondo volume collapse,[9] being described in terms of a volume-dependent coupling constant, *J*, between the local moment and the conduction electrons.

Experimentally, it has been found that the next element in the lanthanide series, praseodymium, first undergoes a phase change from double hcp to fcc structure under pressure and then becomes orthorhombic at 200 kbar.[10] The first transition involves practically no volume change but the second is accompanied by a volume collapse of about 10%. Similarly the following element, neodymium,[11] also changes structure from double hcp to fcc under pressure and then at about 390 kbar there is a transition to an orthorhombic phase, also presumably involving a substantial volume reduction. The fact that there are transitions accompanied by a volume collapse occurring at progressively increasing pressures across the lanthanide series suggests that they all have the same electronic origin. The main difference is that the collapse in Pr and Nd is accompanied by a crystallographic change. It is highly significant in this connection that at high pressure cerium is also orthorhombic.[12]

For certain systems, band theory has successfully described the transition from itineracy to localization. The reason for this is that a filled, unhybridized, band is equivalent to a set of localized states.[13] Therefore, if for some reason, a band or group of bands become filled and split off from the main band structure in a self-consistent calculation, the resulting electronic structure will correspond quite closely to the situation in which such a set of bands are core states—or localized.[14] Since the calculated electronic pressure[15] will be approximately zero for this group of states, they may also be described as nonbonding. Hence our use of the terminology—localized and nonbonding—interchangeably. Reasonable criteria for the merit of the band-structure description of the transition are that it should yield the correct volume on both sides of the transition without parameter adjustment.

Examples are the transitions in the 3*d* monoxides[16] and the actinide elements.[17] Experimentally TiO and VO are metallic compounds, whereas MnO has localized 3*d* states and is a semiconductor. There is also large volume increase when proceeding from TiO and VO to MnO. For the earlier monoxides the paramagnetic metallic solution is stable, while for MnO a fully spin-polarized solution is found where five 3*d* electrons fill the majority band and leave the minority band empty and accordingly there is no bonding contribution from the 3*d* electrons. Similarly, for the earlier actinide metals one finds a stable paramagnetic solution for the 5*f* electrons, while for americium one obtains a fully spin-polarized state. With an essentially filled majority and an empty minority 5*f* band, the 5*f* electrons are almost nonbonding. This explains very accurately the enormous volume increase between plutonium and americium (40%). In both of these examples it is spin polarization that splits off almost the entire group of spin-up bands, hence the transition is best described when the shell is half-filled. When the *d* or *f* shell is far from being half-filled, conventional spin-polarized band theory describes the transition less well as it does not split off an entire group of filled bands from the band structure. For example, spin-polarized band calculations have also been reported for cerium.[18] Indeed a 4*f* spin polarization is found for volumes in the vicinity of the $\gamma \rightarrow \alpha$ transition and above. However, both the calculated volume change and the transition pressure are far too low to explain the experimental data. The reason is that in cerium there is only one 4*f* electron and the 4*f* spin polarization gives an insufficient reduction of the 4*f* electronic pressure since all of the spin-up states are partially filled.

The 4*f* electrons in the rare-earth elements are localized in the condensed phase. Among other things this means that Hund's rules for the free atom still apply for the $4f^n$ configuration in the metal. Under sufficient pressure the 4*f* states could surely be delocalized and, close to the transition on the itinerant side, the correlations implicit in Hund's rules must be important. For the localized phase not only should the 4*f* spin be maximized, but the 4*f* angular momentum should also be maximized. This can only be done within energy-band theory by increasing the variational freedom allowing *f* states with different magnetic quantum number to have different densities.[19]

The problem is not simple because the appropriate density functional must be nonlocal. However, we suggest the following approximate method which yields an energy function—and thus eigenvalue shifts—rather than the more accurate but unknown functional and corresponding potential. The ground state of the atomic f^n configuration can be obtained from a vector model[20] involving interactions of type $\mathbf{s}_i \cdot \mathbf{s}_j$ and $\mathbf{l}_i \cdot \mathbf{l}_j$ ($\mathbf{s}_i$ and $\mathbf{l}_i$ are the spin and angular momenta for the *i*th electron in the f^n configuration, respectively). By replacing the interaction energy of the form $-\sum \mathbf{s}_i \cdot \mathbf{s}_j$ with the mean-field approximation $-(\sum_i s_i^z)(\sum_j s_j^z)$, one obtains an energy $-\frac{1}{4} I M_s^2$ (M_s = spin magnetization = $2S_z$ and I = Stoner exchange parameter) which is the Stoner expression for the spin-polarization energy.[21] Hence the Stoner energy is a function of the spin and the spin-up and -down bands are split rigidly. For the orbital polarization we follow an analogous route. We replace $-\frac{1}{2} \sum \mathbf{l}_i \cdot \mathbf{l}_j$, which occurs in the energy of the ground state of an atom as a function of occupation number, with $-\frac{1}{2}(\sum_i l_i^z)(\sum_j l_j^z)$ and obtain a term proportional to $-\frac{1}{2} L^2$ with a proportionality constant E^3 (the Racah parameter), where L is the total angular momentum.[22] From this we obtain the corresponding one-electron eigenvalue shift $(-E^3 L m_l)$ for the state (m_l). Thus the spin-up or -down *f* manifolds are split into seven equidistant levels when the total orbital moment is nonzero. E^3 now plays a role analogous to the Stoner I.[23]

We have recently applied the present theory to a *series* of actinide compounds with *itinerant* 5*f* electrons and shown that it correctly yields the total moments and ground-state magnetization (or neutron form factors).[24] Precisely the same theory is used here to describe the localization-delocalization transition.

The calculations include the effects of spin polarization within the local-spin-density approximation[25] and spin-orbit coupling was included self-consistently in the same way as has been previously reported for heavy elements and compounds.[26] The Racah parameter E^3 was also recalculated at each iteration step via Slater integrals over the atomic spheres and L_z was computed from the partial state densities as described by Brooks and Kelly.[26] Thus at each cerium site orbital polarization is allowed for by means of an eigenvalue shift $\Delta V_{m_l} = -E^3 L_z m_l$ which depends upon quantities obtained from the previous iteration step. The entire process is self-consistent and no parameters are adjusted. This means that the calculations incorporate all three Hund's rules (spin splitting, orbital splitting, and spin-orbit splitting) and, within the stated approximations, were fully self-consistent.

Figure 1 shows the calculated results for cerium metal. At large volumes the system is characterized by an almost fully spin-polarized 4*f* state. The 4*f* orbital polarization is almost complete with a total orbital moment of $L_z = -2.9$. Hence we obtain a solution where the 4*f*

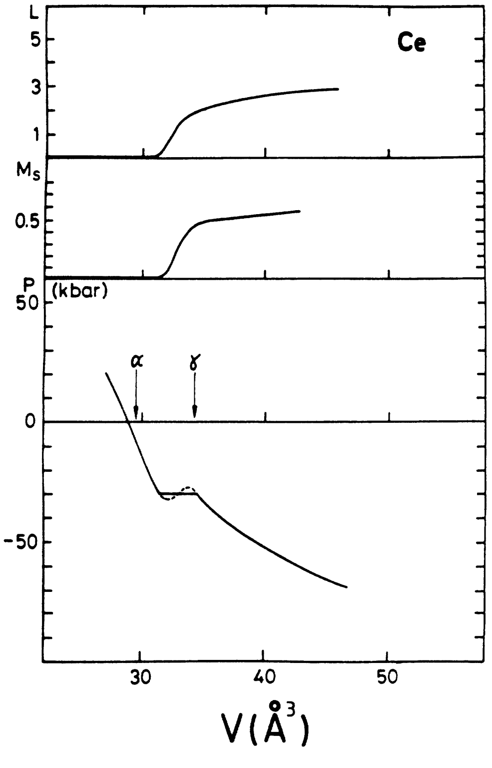

FIG. 1. Self-consistently calculated equation of state for Ce (lower panel). The top panel shows the calculated 4*f* orbital moment and the middle panel shows the 4*f* spin.

($m_l = -3$, $m_s = \frac{1}{2}$) subband is filled leaving all the other $4f$ states practically empty. This reduces the $4f$ partial electronic pressure to nearly zero and the solution can be interpreted as describing a localized $4f$ state. When the volume decreases to 35 Å^3, a first-order transition is calculated with a volume collapse of 10% (obtained from a Maxwell equal-area construction). This is in excellent agreement with experiment since experimentally a 14% volume collapse is found at room temperature for a volume of 35 Å^3. The calculated (zero-temperature) transition pressure is slightly low, $P_{\text{trans}} = -30$ kbar, the estimated value from the phase diagram being -7 kbar.[1] In the collapsed phase both the spin and orbital polarizations are zero, giving a paramagnetic solution with an enhanced susceptibility,[27] also in agreement with experiment.[3] Furthermore, there is now a substantial contribution to the electronic pressure from the occupied $4f$ states. In fact, it is the competition between the $4f$ spin and orbital polarization energies and the $4f$ kinetic energy which drives the transition. The experimental and theoretical results are collected in Table I. The calculated volume for the paramagnetic state agrees well with experiment. In Table I it can also be seen that the calculated values for the bulk moduli are in good agreement with experiment. The calculated $4f$ occupation number does not change during the transition, which reproduces the experimental finding[8] of a negligible change in $4f$ electron density as the system collapses from the γ to the α phase.

For Pr and Nd we find a similar situation as for cerium. At the experimental equilibrium volume for Pr we calculate a $4f$ spin, $S_z = 1.1$, and a $4f$ orbital moment, $L_z = -4.8$, for the ground state. The calculated equilibrium volume and the bulk modulus are in good agreement with experiment (Table I). For Nd the theoretical values also reproduce the equilibrium data very well (Table I). For Nd we find $S_z = 1.5$ and $L_z = -5.6$. Hence for Pr and Nd we obtain an almost complete occupation of the $m_l = -3$ and -2 and $m_l = -3$, -2, and -1 orbital states, respectively, as well as a complete $4f$ spin polarization. This gives rise to a negligible contribution from the $4f$ electrons to the electronic pressure and yields the $4f$ moments for Pr and Nd in agreement with Hund's rules.

Experimentally Pr undergoes a first-order crystallographic transition at $P = 200$ kbar, with an accompanying volume collapse of 10%. This change of crystal structure makes the transition considerably more complex to study theoretically than for cerium. Calculations within the fcc structure show that the $4f$ moment remains rigid from the experimental volume (34.5 Å^3) down to 25 Å^3. Below this volume the moment starts to decrease. However, the decrease is not sufficiently rapid to produce the S-shaped p-V relation obtained for Ce (Fig. 1), and therefore no first-order transition is calculated within the fcc phase. Even for volumes comparable to the collapsed volume there is still a moment in the fcc structure. When the calculations were performed for the orthorhombic structure the solution was found to be paramagnetic with bonding $4f$ states. The paramagnetic solution was actually stable for the entire volume range where the collapsed phase has been experimentally observed. At higher volumes a polarized state was obtained for both the orthorhombic and fcc crystal structure. At 200 kbar we calculated a volume difference between the fcc and orthorhombic phase of 3.0 Å^3 which compares well with the observed value of 2.3 Å^3.[10] From our calculations for the fcc and the orthorhombic structure we conclude that the volume collapse in Pr is driven by a delocalization of the $4f^2$ configuration.

TABLE I. Calculated and experimental volumes for Ce, Pr, and Nd. The computed and experimental values of the bulk modulus, the magnitude of the volume collapse, and the pressure for this collapse, are also given for Ce, Pr, and Nd. The self-consistently calculated values of E^3 (see text) are also given.

	Ce	Pr	Nd
V_{expt} (Å^3)	(γ) 34.3 (α) 29.4	34.5	34.2
V_{theor} (Å^3)	(γ) 34.4 (α) 28.8	34.0	33.5
B_{expt} (kbar)	(γ) 239 (α) 270	305	327
B_{theor} (kbar)	(γ) 220 (α) 260	345	371
ΔV_{expt} (Å^3)	4.8	2.3	
ΔV_{theor} (Å^3)	3.4	3.4	3.2
$P_{\text{crit}}^{\text{expt}}$ (kbar)	-7	200	390
$P_{\text{crit}}^{\text{theor}}$ (kbar)	-30		
E^3 (mRy)	4.9	5.2	5.4

For Nd the experimental situation is very similar to Pr with a change in crystal structure from fcc to orthorhombic at 390 kbar. Exactly the same type of calculations as for Pr yielded a polarized, localized, $4f$ state in the low-density phase and a paramagnetic, itinerant $4f$ state in the high-density orthorhombic region. The calculated volume collapse at 390 kbar is 3.2 Å^3, while experimentally this has not yet been determined.

In conclusion, we have shown that by including orbital polarization of the $4f$ electrons in the solid state (Hund's second rule in free atoms) the isostructural electronic phase transition in cerium can be well described theoretically. The calculated equilibrium properties of praseodymium and neodymium are also in excellent agreement with data and the experimentally observed volume collapses at high pressures can be understood in terms of a Mott transition from localized to itinerant $4f$ states. This emphasizes the fundamental relationship between lanthanide $4f$ and actinide $5f$ states, namely that the light lanthanides at high pressure (of the order of 500 kbar) have several elements with itinerant $4f$ electrons, while the light actinides already have itinerant $5f$ electrons at ambient pressure. The fact that the light lanthanides under pressure have crystal structures which otherwise are only found among the light actinides substantiates these conclusions.

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