

DENSITY FUNCTIONAL CALCULATIONS OF THE CRYSTAL FIELD
IN UPD₃, UGA₂, AND UPD₂Al₃¹

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1. Introduction

Atoms with incompletely filled shells not involved in the chemical bonding may exhibit a class of low-energy excitations responsible for a multitude of physical phenomena and peculiarities: the crystal field (CF) excitations. These excitations originate from the splitting of degenerate $|J \neq 0\rangle$ states into crystal field levels $|JT \tau\rangle$ in a non-spherical environment, described by the CF Hamiltonian [1],

$$H_{CF} = \sum_{lm} B_{lm} O_{lm}. \quad (1)$$

The Stevens operator equivalents O_{lm} are polynomials in \hat{j}_x , \hat{j}_y , and \hat{j}_z , and the CF parameters B_{lm} can be obtained from

$$B_{lm} \propto \int dr r^2 Y_{lm}(r) \rho^*(r), \quad (2)$$

where $Y_{lm}(r)$ is the lm -component in a spherical harmonics representation of the potential and $\rho^*(r)$ is the spherically averaged charge density of the incompletely filled shell.

In many metallic $4f$ systems, there is direct (inelastic neutron scattering) or indirect (magnetic, thermodynamic and transport properties) experimental evidence for CF splitting [2]. There are many $5f$ intermetallic compounds, too, where the CF model was used to explain indirect effects, but up to now UPd₃ is the only example where CF excitations [3] and inter-multiplet transitions [4] have been directly measured. The rare occurrence of CF excitations in $5f$ intermetallics can be understood from the stronger

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tendency of the 5f states in comparison to the 4f states to participate in the chemical bonding. If bands are formed, the occupation number will fluctuate on a much smaller time scale than the lifetime needed for sharp CF excitations ($> 10^{-11}$ s).

In this paper we shall consider, besides the aforementioned clearly localized 5f system UPd₃, two compounds which have been controversially discussed: UGa₂ (Ref. [5] favouring localized behaviour, Ref. [6] favouring a delocalized picture) and the heavy fermion compound UPd₂Al₃ (see Ref. [7] for localized and Ref. [8] for itinerant 5f states).

2. Method

Two ingredients are required to calculate the CF parameters: i) the potential around the atomic site under consideration in a non-spherical representation, excluding the contributions generated by the on-site f charge itself, and ii) the accurate radial f charge density. The first ingredient is obtained from so-called full-potential density functional calculations employing the local density approximation (LDA). Working remarkably well for delocalized (i.e., bonding) states, this approximation fails to describe localized states correctly. In particular, the single particle energies obtained in the mean field like LDA scheme are too high in energy and the related falloff of $\rho^*(r)$ is too small in the 'tail' region. It has been shown recently [9, 10] that this problem can be overcome by the application of the self-interaction correction (SIC, [11]) to the localized states. CF parameters of 4f intermetallics calculated in this way without artificial assumptions deviate from CF parameters obtained from fits to experimental data by factors up to 4. A comparable quality of matching has been obtained in earlier LDA calculations without SIC but employing artificial constraints on the 4f charge density [12]. Up to now there exist, to our knowledge, no 'first principles' calculations of the CF parameters in 5f intermetallic compounds.

In this first attempt we used the SIC-LDA linear combination of atomic orbitals method as in the aforementioned calculations on 4f systems [9]. The band states have been treated in the scalar relativistic approximation. This might be a point to be improved in future calculations, but it is generally accepted to yield fairly accurate valence charge densities and potentials even in actinide systems. On the other hand, core states and, in particular, 5f states are obtained from the solution of the full effective Dirac equation. The inclusion of spin-orbit interaction in the calculation of $\rho^*(r)$ turned out to change the resulting CF parameters up to factors of three if compared with a scalar relativistic calculation of ρ^* .

3. Results and Discussion

In the case of UPd₃, the experimental data point to a singlet ground state for both inequivalent U sites [3], and the measured inter-multiplet excitations demonstrate that the U configuration is 5f² [4]. Assuming this configuration to be valid, the ground state symmetry can be reproduced from our results. The gross intra-multiplet splitting of the ³H₄ state is overestimated, however, by one order of magnitude (360 meV for

the quasi-cubic and 290 meV for the hexagonal U position in the calculation to be compared with 46 meV and 40 meV, respectively, obtained from a CF parameter fit to the two measured transitions [3]). We have also calculated the transition probabilities of the neutron excitations using the CF eigenstates of Hamiltonian (1). Comparing the strongest excitations from the ground state with the only measured excitations, the following values are found: calculated 136 meV (doublet) at the quasi-cubic and 160 meV (doublet) at the hexagonal site in comparison to measured values of 1.5 meV and 15.0 meV, respectively. It should be noted that these results are much more sensitive to technical details of the calculation than in the case of 4f systems. New calculations with these details refined are under preparation. In contrast to the experimental analysis which was restricted to a quasi-cubic approximation for the CF Hamiltonian related to the U-2a position ($B_{43}/B_{40} = -20\sqrt{2}$, [13]), we have found the relation $B_{43}/B_{40} \approx -11$. This points to the necessity of considering the full trigonal symmetry of the U-2a site in future analyses of experimental data based on the CF model.

There do exist experimental data on the hexagonal ferromagnetic compound UGa₂ suggesting a 5f² ground state [5] as in the case of UPd₃. Motivated by this fact and by the difficulty to describe measured magnetization curves by the conventional band theory [14] we have calculated CF parameters related to a localized 5f² configuration and found a much better agreement with experiment for both the total moment and the magneto-crystalline anisotropy, if an interatomic exchange-coupling of appropriate magnitude is assumed. Details of these calculations will be published elsewhere [14].

A more subtle example is the heavy fermion compound UPd₂Al₃. Very recently, de Haas - van Alphen data on this compound have been explained in terms of conventional LDA band structure results [8]. On the other hand, the specific heat in the paramagnetic phase and the highly anisotropic magnetic susceptibility with easy direction in the hexagonal plane have been interpreted in terms of a localized 5f² configuration [7]. Assuming this interpretation to be correct we have calculated the related CF parameters. It is found that the second order parameter B_{20} is not consistent with the measured easy axis of magnetization. This parameter, however, is extremely sensitive to the shape of $\rho^*(r)$ due to the large charge density of the nearest neighbor Pd atoms forming a hexagon around U. The question whether a localized or a delocalized description of the 5f states is more appropriate for this peculiar compound remains open.

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