

Crystal Field Excitations as Quasi-Particles

M.S.S.Brooks, O.Eriksson,¹ J.M.Wills², M.Colarieti-Tosti¹ and B.Johansson¹

*European Commission, Joint Research Centre, Institute for Transuranium Elements,
Postfach 2340, D-76125 Karlsruhe, Federal Republic of Germany*

¹*Condensed Matter Theory Group, Institute of Physics, University of Uppsala,
BOX 530, S-75121, Uppsala, Sweden*

²*Center for Materials Science and Theoretical Division, Los Alamos National Laboratory,
Los Alamos, NM, 87545 USA*

The splitting of localised atomic energy levels by the crystalline electric field in solids affects many areas of physics and chemistry. The crystal field energy levels of rare earth atoms are particularly important in intermetallic compounds containing Fe, Co and Ni which have both high Curie temperatures and large magnetic anisotropy. The strong magnetic coupling governing the Curie temperature is provided by the 3d element whereas the strong orientational dependence of the magnetism is due to the energy differences between the crystal field levels of the rare earth. Models which attempt to explain the crystal field energy level differences in terms of electrostatic interactions between the 4*f* and conduction electrons exist but computed values for the energies have been poor. The measured crystal field excitation energies with which theory has been compared have been assumed to be bare 4*f* excitations in the static electric field of the ions and conduction electrons. We show here that crystal field excitations in metals are quasi-particles composed of a 4*f* excitation plus an associated cloud of shielding conduction electrons.

The ability to calculate the 4*f* crystal field energies accurately from first principles is not only a prerequisite for the computation of low temperature thermal and magnetic properties, but would also be a considerable aid to the development of rare earth transition metal permanent magnets and other magnetic devices. It is therefore desirable to have a theoretical framework from which the energies of the crystal field levels in solids may be calculated accurately from first principles. Such a framework must, however, combine the merits of the two very successful, but apparently incompatible, models that have been used to describe the localized atomic 4*f* electrons and the metallic conduction electrons, respectively. The standard model [1] for the 4*f*

states is based upon the theory of the free atom and properly includes the effects of electron-electron interactions within the $4f$ shell, leading to Russell-Saunders coupling of the individual electronic angular momenta to a conserved value of the total angular momentum of the atom. A direct consequence of Russell-Saunders coupling, which is preserved in the solid since the $4f$ states are localized is that the $4f$ levels are degenerate in a spherical environment. The energy differences between the crystal field states are then entirely due to the non-spherical environment in the crystal [2]. Calculations based upon this model attribute these energy differences to the average interaction between the non-spherical $4f$ and conduction electron densities [3, 4, 5, 6, 7]. The strengths of the model are that the internal dynamics of the $4f$ shell are handled very well and that only the crystal field energies, which are of the order of meV, enter the calculation. Its weakness is the assumption that the conduction electron density remains unchanged when the $4f$ electron density changes in a transition from one crystal field state to another.

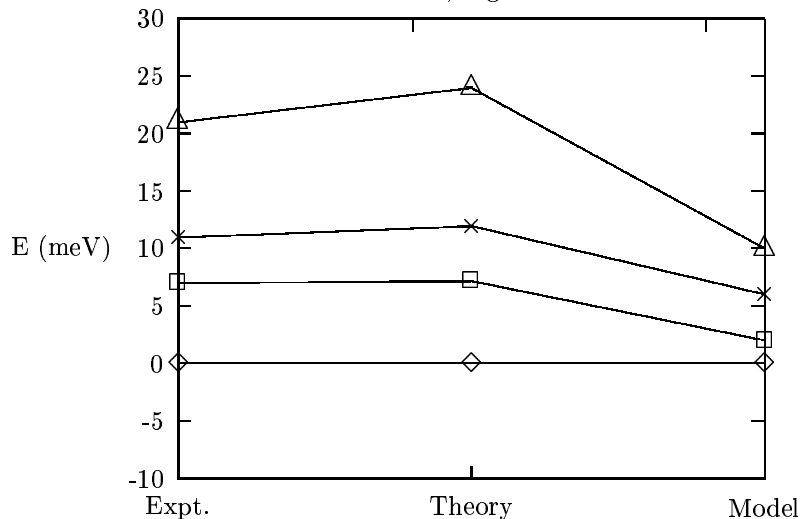
In other areas of physics and chemistry energy differences in solids are obtained from the local density approximation [8] to density functional theory [9] as the difference in the *total* energy, typically of the order of 10^5 eV, of the solid in different states. The strength of this method, which has become the standard model for first principle calculations of ground state properties of metals, is that the entire electron density is allowed to relax since it is calculated self-consistently by iteration. It should in principle be possible to calculate crystal field excitation energies as total energy differences in the same way, removing any assumptions concerning relaxation of the conduction electron density, but adding the requirement that the calculation of the total energy be numerically accurate to at least 10^{-2} meV in 10^5 eV.

However, we have found that such an approach fails in calculations of crystal field excitations and the ultimate evidence for its breakdown is that it does not yield degenerate $4f$ energy levels for the free atom. Density functional theory is based upon a variational principle for the total energy of the entire electron density (which is why the entire electron density is allowed to relax iteratively) and the total energy is a functional [9, 8] of the total electron density, n ,

$$E[n] = T_s[n] + E_N[n] + E_H[n] + E_{xc}[n], \quad (1)$$

where the contributions are the kinetic energy, $T_s[n]$, electron-nuclei interaction energy, $E_N[n]$, Hartree electron-electron interaction energy, $E_H[n]$, and exchange-correlation energy, $E_{xc}[n]$. In the limit of the free atom the Hartree contribution differs for different $4f$ charge densities corresponding to different crystal field states. If the exchange-correlation functional were known exactly its contribution for the different $4f$ densities would cancel the corresponding energy differences from the Hartree contribution and the Russell-Saunders degeneracy would be reproduced. However the exchange correlation functional for such highly correlated localized $4f$ states is not known and the one used in practice is more appropriate for itinerant conduction electrons in metals. This lack of exact cancellation leads to finite energy differences between crystal field levels even in the atomic limit. Since direct application of the local density approximation to localized $4f$ states is flawed but we require it to calculate the total energy of the solid, we have explicitly removed the pertinent $4f-4f$ interactions in both $E_H[n]$ and $E_{xc}[n]$. The total energy of the solid is then slightly incorrect, but by the same amount for each crystal field level and the errors in the transition energies cancel rigorously.

We have imposed a control on the applicability and numerical integrity of the method by verifying



that the calculated crystal field levels become degenerate in the atomic limit for some selected rare earth compounds. This criterion was found to be satisfied for all of the calculations reported here. We have made self-consistent calculations[10] for two experimentally well studied rare earth compounds, PrSb and TmSb [11, 12] with no shape restriction on either the valence electron density or potential. The $4f$ occupation number was constrained 2 and 12 for PrSb and TmSb, respectively. The shape of the $4f$ density was constrained to correspond to the symmetry of each crystal field level whereas the rest of the electron density was obtained self-consistently, being allowed to relax to shield the change in $4f$ density.

In Figs. 1a and 1b we compare the results with measurements. Typically the calculated levels differ from the measurements by less than a few meV, with the largest error being some 30% for the Γ_5 level of PrSb. This level of agreement is much better than that obtained by earlier theories. Whereas previously the crystal field excitation energy was assumed to be the change in energy due to a change in $4f$ density in an unchanged conduction electron density - a bare excitation - we find that there is an important change in conduction electron density in response to the bare crystal field excitation of the $4f$ shell. Therefore the crystal field excitations in metals are composed of the change of density within the $4f$ shell plus the concomitant screening charge of the conduction electrons. The combination is a quasi-particle involving the degrees of freedom of many electrons. The interaction between the $4f$ charge density and the conduction electrons is strong but the interactions between the quasi-particles should be relatively weak.

The importance of the change in valence electron screening is illustrated in Fig.2 by the difference between the valence electron densities of PrSb for the Γ_1 and the Γ_3 crystal field levels. The lobes elongated vertically and horizontally represent a surplus of electron charge whereas the lobes which are rotated by 45 degrees represent a charge deficiency. Therefore rearrangements and relaxation effects of the valence electron states are seen to be substantial in crystal field excitations. The change in valence electron density for the free atom is much larger than for the solid and in this case the shielding is complete because the crystal field levels remain degenerate. The valence electrons in the solid are subject to crystalline boundary conditions which reduce their ability to redistribute to shield a change in the $4f$ density and it is precisely this restriction

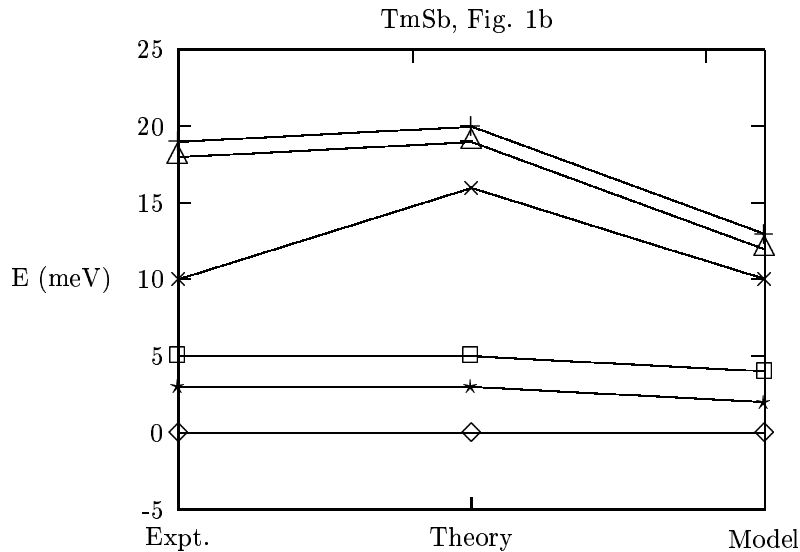


Figure 1: Measured and calculated crystal field energy levels of PrSb and TmSb. For PrSb the diamonds correspond to Γ_1 level, the squares to Γ_4 , the x's refer to Γ_3 , and the triangles correspond to Γ_5 . For TmSb the stars correspond to Γ_4 level, the squares and triangles to Γ_5 , and all the others to Γ .

which splits the crystals field energy levels.

The conventional view that crystal field excitation energies in metals are due to an electrostatic field of the ligands alone is useful for pedagogical purposes but is much too simple to enable computational accuracy. We have shown, however, that it is possible to modify the local density approximation to calculate crystal field excitation energies from first principles and include the effects of relaxation of the conduction electrons. Since shielding by the conduction electrons is strong the crystal field excitations should be viewed as quasi-particle excitations where the change of the localized 4f density is intimately connected with a corresponding change of the valence electron charge.

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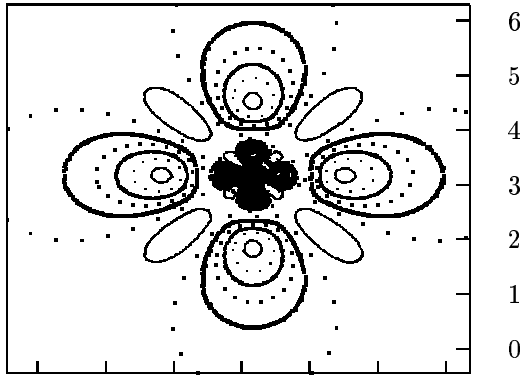


Figure 2: Charge density contour in the 001 plane of the difference in shielding valence electron density of PrSb when there is a transition from the Γ_1 to the Γ_3 crystal field state.

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