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Temperature dependent properties of metallic clusters containing magnetic impurities

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Abstract. The properties of magnetic impurities in small metallic clusters are investigated in the framework of the Anderson model by using exact diagonalization methods. Parameters representative of the Kondo limit are considered. The spin gap $\Delta E = E(S{=}1,3/2) - E(S{=}0,1/2)$ shows a remarkable band-filling dependence that can be interpreted in terms of the cluster-specific conduction-electron spectrum. Finite-temperature properties such as the magnetic susceptibility and specific heat are calculated exactly in the canonical and grand canonical ensembles. The structural dependence is illustrated.

PACS. 73.22.-f Electronic structure of nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 75.20.Hr Local moment in compounds and alloys; Kondo effect, valence fluctuations, heavy fermions – 71.27.+a Strongly correlated electron systems; heavy fermions

1 Introduction

In past years, itinerant magnetism in $3d$ transition-metal clusters has been the subject of numerous systematic experimental and theoretical studies [1,2]. In contrast, very little is still known about clusters involving rare-earth atoms, where the magnetic moments have a strongly localized character [3–5]. In solids, the rare-earth compounds show remarkable magnetic phenomena, which are intrinsically related to the localized f electrons and to their interactions with the conduction-band electrons [6–8]. It would be therefore very interesting from the point of view of cluster physics to understand how these interactions are affected by finite size effects and how the resulting magnetic properties depend on the size, structure and composition of the cluster.

A single rare-earth impurity in a metallic cluster is probably the simplest physical situation for studying the magnetic behaviour of localized magnetic moments in finite systems. In solids, valence fluctuations and magnetic screening lead to the Kondo effect which is characterized by the formation of a singlet ground-state between the localized magnetic moment of the impurity and the delocalized conduction electrons [7,8]. At low temperatures the local moment is masked by the spins of the conduction electrons, that build a polarization cloud which couples antiferromagnetically with the impurity moment. At temperatures higher than the Kondo temperature T_K, in other words, when $k_B T_K$ is of the order of the singlet-triplet gap ΔE, the singlet state is broken and the local moment may be observed directly in a susceptibility measurement. Physically, one expects to observe a cluster-specific behaviour when the radius of the cluster is comparable or smaller than the spatial extension ξ_K of the screening cloud (Kondo length). Interesting size and structural dependences should be observed, since the binding energy ΔE of the Kondo singlet is expected to depend crucially on the hybridizations between the f-orbitals and the delocalized valence states close to the Fermi energy. The purpose of the present paper is to discuss this problem by reporting a few first results on small clusters, that were obtained using the Anderson impurity model [9] and exact diagonalization methods. A more detailed account of our investigations will be published elsewhere.

2 Theory

We consider an N-atom cluster containing $N-1$ simple-metal atoms and one magnetic impurity. The model Hamiltonian is given by

$$\hat{H} = \hat{H}_s + \hat{H}_f + \hat{H}_{sf}. \tag{1}$$

The first term,

$$\hat{H}_s = -t_{ss} \sum_{\langle i,j\rangle,\sigma} \hat{c}^{\dagger}_{i\sigma} \hat{c}_{j\sigma}, \tag{2}$$

describes the s-like valence-electron states of the simple-metal atoms and of the impurity atom using a single-band tight-binding model. As usual, $\hat{c}^{\dagger}_{i\sigma}$ ($\hat{c}_{i\sigma}$) refers to the creation (annihilation) operator of an electron with spin σ

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at the s orbital of atom i, and t_{ss} to the nearest-neighbor (NN) s-electron hopping integral. Possible differences between the s levels ε_s in different atoms are disregarded by setting $\varepsilon_s = 0$ at both the impurity ($i = 0$) and the metal-host sites ($1 \leq i \leq N-1$). The second term,

$$\hat{H}_f = \varepsilon_f \sum_\sigma \hat{n}_{f\sigma} + U_{ff}\, \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}, \tag{3}$$

concerns the magnetic degrees of freedom of the impurity[9]. Here $\hat{n}_{f\sigma} = \hat{f}^\dagger_\sigma \hat{f}_\sigma$ is the electron number operator, ε_f the energy, and U_{ff} the Coulomb-repulsion integral of the localized f-like level. The orbital degeneracy of the f-level is neglected for simplicity. Finally, the third term,

$$\hat{H}_{sf} = V_{sf} \sum_\sigma \left(\hat{f}^\dagger_\sigma\, \hat{c}_{0\sigma} + \hat{c}^\dagger_{0\sigma} \hat{f}_\sigma \right), \tag{4}$$

takes into account the coupling between the f level and the delocalized electrons by means of an intra-atomic $s-f$ hybridization at the impurity atom $i = 0$.

$\hat{H}$ may be written in terms of the single-particle eigenstates $\hat{a}^\dagger_k = \sum_i \alpha_{ik} \hat{c}^\dagger_i$ of $\hat{H}_s$ as

$$\hat{H} = \sum_{k\sigma} \varepsilon_k\, \hat{n}_{k\sigma} + \sum_\sigma \varepsilon_f\, \hat{n}_{f\sigma} + U_{ff}\, \hat{n}_{f\uparrow}\hat{n}_{f\downarrow} + \sum_{k\sigma} V_{kf} \left(\hat{f}^\dagger_\sigma \hat{a}_{k\sigma} + \hat{a}^\dagger_{k\sigma} \hat{f}_\sigma \right). \tag{5}$$

The s-electron eigenenergies are denoted by ε_k ($[\hat{H}, a^\dagger_{k\sigma}] = \varepsilon_k\, a^\dagger_{k\sigma}$) and the $k-f$ hybridizations by $V_{kf} = \alpha_{0k} V_{sf}$. Notice that ε_k and V_{kf} depend strongly on the size and structure of the cluster. As we shall see, this form of the Hamiltonian is particularly useful in cases where symmetry considerations allow to reduce the number of conduction electron states that couple to the impurity.

The model is solved numerically by expanding its eigenfunctions $|\Psi_l\rangle$ in a complete set of basis states $|\Phi_m\rangle$ which have definite occupation numbers $n^m_{i\sigma}$ at all orbitals $i\sigma$, *i.e.*, $\hat{n}_{i\sigma}|\Phi_m\rangle = n^m_{i\sigma}|\Phi_m\rangle$ with $n^m_{i\sigma} = 0$ or 1. The values of $n^m_{i\sigma}$ satisfy the usual conservation of the number of electrons $\nu = \nu_\uparrow + \nu_\downarrow$ and of the z component of the total spin $S_z = (\nu_\uparrow - \nu_\downarrow)/2$, where $\nu_\sigma = \sum_i n^m_{i\sigma}$. Ground-state and excited-state properties are calculated exactly by using standard diagonalization procedures [10]. In particular, the spin gap is given by

$$\Delta E = E(S = 1, 3/2) - E(S = 0, 1/2), \tag{6}$$

where $E(S)$ stands for the lowest eigenenergy of spin S. Relevant finite-temperature properties, like the magnetic susceptibility of the impurity

$$\chi_f = \left(\langle S^2_{zf} \rangle - \langle S_{zf} \rangle^2 \right) / (k_B T), \tag{7}$$

and the specific heat

$$C = \left(\langle E^2 \rangle - \langle E \rangle^2 \right) / \left(k_B T^2 \right), \tag{8}$$

are determined in the canonical and grand-canonical ensembles. T refers to the temperature of the cluster source that defines the macroscopic thermal bath with which the clusters are in equilibrium before expansion in the beam. Average is applied then to the ensemble of clusters in the beam.

For clusters having a high point group symmetry (*e.g.*, face-centered cubic clusters of nearly spherical shape) a decoupling scheme is introduced that permits the calculation of finite-temperature properties of relatively large clusters containing of the order of 80 atoms. For example, when the impurity is located at the center of symmetry of the cluster only the fully symmetric (s-like) single-particle conduction states have a non-vanishing V_{kf}. Thus, only these k states couple with the magnetic degrees of freedom. The other conduction states may be solved independently and need not be included in the many-body diagonalization. The grand partition function is then given by

$$\Omega = \Omega_f\, \Omega_0, \tag{9}$$

where

$$\Omega_f = \sum_{\nu_f} \sum_\alpha e^{-\beta[\varepsilon_\alpha(\nu_f) - \mu\, \nu_f]} \tag{10}$$

refers to the states that couple to the impurity, and

$$\Omega_0 = \prod_{k\sigma} \left[1 + e^{-\beta(\varepsilon_k - \mu)} \right] \tag{11}$$

to the remaining conduction-electron states having $V_{kf} = 0$.

In Eq. (10), $\varepsilon_\alpha(\nu_f)$ denotes the eigenenergy of the αth many-body state having ν_f electrons in the subspace that couples with the impurity f level. In Eq. (11), ε_k refers to the single-particle states that do not hybridize with the f level. Notice that both subsystems share the same chemical potential μ. The properties of physical interest (magnetic susceptibility χ, specific heat C, etc.) are then obtained from the derivatives of $G = k_B \ln \Omega$ [11].

3 Results and discussion

The parameters used in the calculations are representative of the Kondo limit: $\varepsilon_f/t_{ss} = -10$, $V_{sf}/t_{ss} = -0.1$, and $U_{ff} \to \infty$. The resulting singlet-triplet gap in the case of a two-level system is $\Delta E_0 = 2V^2_{sf}/|\varepsilon_f| = 2 \times 10^{-3}$ eV.

Fig. 1 shows results for the band-filling dependence of the spin gap $\Delta E = E(S{=}1, 3/2) - E(S{=}0, 1/2)$ in a seven-atom cluster with a magnetic impurity at the apical site $i{=}1$ (see Fig. 2). For $\nu = 2, 8$, and 14 the ground state is a singlet, and ΔE is of the order of the singlet-triplet gap ΔE_0 in the two-level system. For $\nu = 4{-}6$ and $\nu = 10{-}12$ the singlet-triplet splitting vanishes since the ground state is degenerate ($\Delta E = 0$). In contrast, for $\nu = 3, 7, 9$, and 13, ΔE is of the order of the s-electron hopping parameter t_{ss}, which indicates that here we are dealing essentially with an electron-hole excitation within the conduction band.

In metallic solids the behaviour of magnetic impurities and in particular the Kondo temperature depend crucially

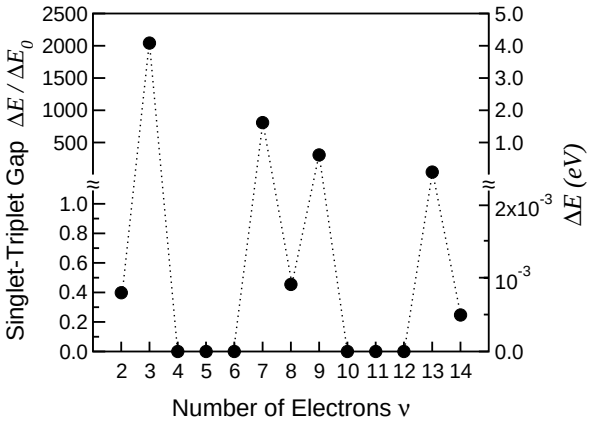

Fig. 1. Singlet-triplet gap ΔE of a seven-atom icosahedron (see Fig. 2) with a magnetic impurity in an apical site (*e.g.*, i=1) as a function of the total number of electrons ν. Notice that ΔE is of the order of the two-level gap $\Delta E_0 = 2V_{sf}^2/|\varepsilon_f| = 2\times10^{-3}$ eV for $\nu = 2, 8$, and 14, and that ΔE is of the order of t_{ss} for ν=3, 7, 9, and 13.

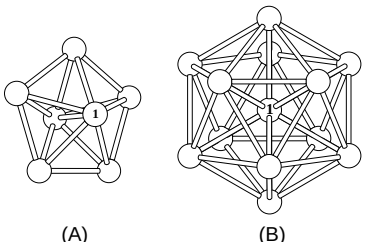

Fig. 2. Illustration of the structures considered in the calculations: for $N = 7$ (A) and $N = 13$ (B).

on the value of the density of states at the Fermi level. It is therefore very interesting to investigate to which extent the finite-size counterpart of this phenomenon share such characteristics. In fact, the band filling dependence of ΔE may be qualitatively understood in terms of the cluster-specific single-particle spectrum ε_k and $k-f$ hybridizations V_{kf} shown in Table 1. Let us first note that in the considered parameter regime (Kondo limit) the f-level occupation is always very close to 1 ($\nu - 1$ electrons in delocalized s states). When the total number of valence electrons (s and f) in the cluster is $\nu = 2$, the low-lying many-body states can be approximately described by considering only the impurity level ε_f and the lowest s-electron state ($k = 1$ in Table 1), this is a consequence of the fact that the gaps in the single-particle spectrum are large (for example, $\varepsilon_2 - \varepsilon_1 \sim 4t_{ss}$). Thus, the singlet-triplet gap can be obtained accurately by solving this two-level problem. One obtains $\Delta E^1 = 2V_{1f}/(\varepsilon_1 - \varepsilon_f)$ which is very close to the exact result shown in Fig. 1. The situation changes for $\nu = 3$ since the $k = 1$ level is fully occupied in the lowest energy configurations. The $s-f$ hybridization may only promote an electron to the levels having $k \geq 2$, which are empty for both spin directions, leaving the impurity spin essentially frozen ($S = 1/2$). The first $S = 3/2$ state corresponds to the creation of an electron-hole pair in the conduction-band spectrum, and consequently the excitation energy is of the order of $\varepsilon_2 - \varepsilon_1 \sim 4t_{ss}$. Furthermore, the fact that $V_{2f} = V_{3f} = 0$ leads to a ground-state spin degeneracy for $\nu = 4-6$, this explains that $\Delta E = 0$ for $\nu = 4-6$. The same effect occurs for $\nu = 10-12$. The rest of the band filling dependence may be understood in an analogous way. For example, for $\nu = 7, 9$, and 13, we recover the same situation as for $\nu = 3$. Here we find a closed-shell configuration for the conduction electrons and the first spin excitation corresponds to the formation of an electron-hole pair in the conduction band. The most interesting cases are for $\nu = 2, 8$, and 14, where very small singlet-triplet gaps are obtained, that, as we shall see later, can be interpreted as a finite-size equivalent of the Kondo effect.

Table 1. Single-particle energies ε_k, local component α_{0k} of state k at the impurity site, and kf hybridizations V_{kf} for a seven-atom icosahedral cluster (see Fig. 2). $V_{sf}/t_{ss} = -0.1$.

k	ε_k/t_{ss}	α_{0k}^2	$(V_{kf}/t_{ss})^2$
1	−4.702	0.212	0.0021
2	−0.618	0.000	0.0000
3	−0.618	0.000	0.0000
4	1.000	0.500	0.0050
5	1.618	0.000	0.0000
6	1.618	0.000	0.0000
7	1.702	0.289	0.0029

The finite-temperature properties in the presence of low-energy Kondo-like excitations are shown Fig. 3. Here, results are given for the impurity magnetic susceptibility $\chi_f(T)$ and the specific heat $C(T)$ for a seven-atom icosahedral cluster with the magnetic impurity at site $i = 1$ (see Fig. 2). Statistical averages were calculated in the canonical ensemble with $\nu = 8$ (dashed line) and in the grand canonical ensemble with a temperature-dependent chemical potential $\mu(T)$ that yields $\langle\nu\rangle = 8$ for all T (full line). The singlet ground state for $\nu = 8$ is responsible for the vanishing magnetic susceptibility $\chi_f(T)$ at low temperatures ($T > 0$). With increasing T, χ_f increases very rapidly as the triplet state is populated. A maximum is obtained at the temperature T_K of the order the singlet-triplet gap $\Delta E/k_B \simeq 10$ K. Finally for $T > T_K$, χ decreases following a Curie-like law ($\chi_f \propto 1/T$) as in the case of free magnetic impurities or of magnetic impurities in insulators.

Another consequence of the singlet-triplet excitation ΔE is the maximum in the specific heat $C(T)$ at approximately the same temperature for which $\chi_f(T)$ is maximum. In fact, $C(T)$ is very close to that of a two-level Schottky anomaly. Only at much higher temperatures (of the order of $T_{ss}/k_B \simeq 10^4$) one observes a further exponential increase of $C(T)$ due to electron-hole excitations within the s band. The position of the peaks in $\chi_f(T)$ and $C(T)$ scale with ΔE. As an example we also show in Fig. 3 the results for a thirteen-atom icosahedron with a magnetic impurity at the center and $\langle\nu\rangle = 20$ (dotted line). In this case we calculated the partition function in

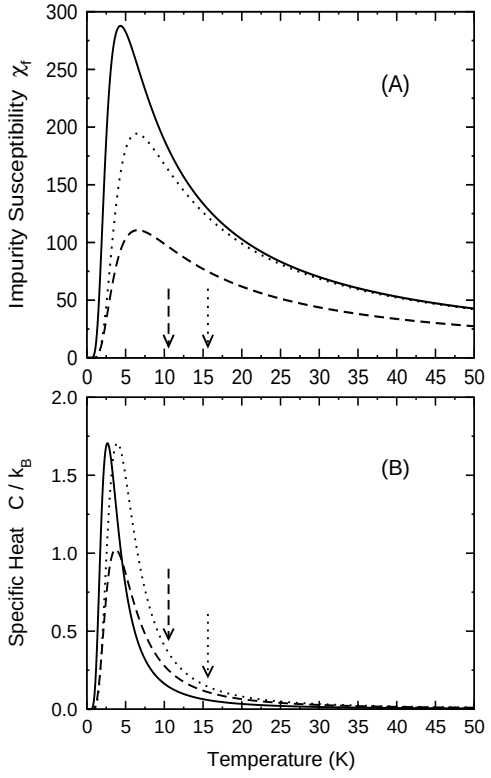

Fig. 3. Temperature-dependence of (A) impurity susceptibility $\chi_f(T)$ and (B) specific heat $C(T)$. Results are given for a 7-atom cluster with the impurity at an apical site (i=1, see Fig. 2) in the canonical ensemble (ν=8, dashed curve) and in the grand canonical ensemble ($\langle\nu\rangle$=8, full curve), as well as for a 13-atom icosahedron with the impurity at the center ($\langle\nu\rangle$=20, dotted curve). The vertical arrows indicate the corresponding Kondo temperatures $T_K = \Delta E/k_B$.

the grand canonical ensemble using the decoupling scheme given by Eqs. (10, 11). In order to illustrate how the impurity magnetic moment is screened at temperatures below $T_K = \Delta E/k_B$, we show in Fig. 4 the temperature dependence of the spin compensation cloud $S_c(T)$, which is defined as

$$S_c(T) = \sum_{i=1}^{N} \langle \hat{S}_f^z \cdot \hat{s}_i^z \rangle. \qquad (12)$$

$\langle \hat{S}_f^z \cdot \hat{s}_i^z \rangle$ is the spin correlation function between the impurity spin $\hat{S}_f$ and the conduction-electron spin $\hat{s}_i$ at site i. Strong antiferromagnetic correlations at temperatures well below $T_K = \Delta E/k_B$ lead to a complete compensation of the impurity magnetic moment by the delocalized electrons ($S_c = -1/4$ for $T = 0$), while at temperatures higher than T_K these correlations are strongly suppressed ($S_c \to 0$ for $T > T_K$).

Further studies are needed in order to extend the results presented in this article, for example, by performing calculations on larger clusters as a function of size and structure. Research in these directions is currently in progress.

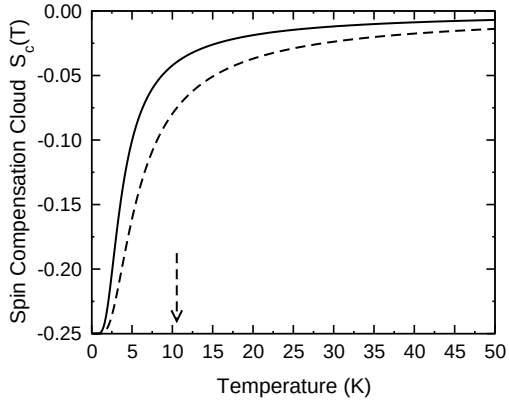

Fig. 4. Temperature dependence of the spin compensation cloud. Results are given for the seven-atom cluster illustrated in Fig. 2 with a magnetic impurity at site $i = 1$. The dashed curve corresponds to the canonical ensemble with $\nu = 8$ and the full curve to the grand-canonical ensemble for $\langle\nu\rangle = 8$. The Kondo temperature $T_K = \Delta E/k_B$ is indicated by the arrow.

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References

1. I.M.L. Billas, A. Châtelain, W.A. de Heer, Science **265**, 1682 (1994); S.E. Apsel, J.W. Emert, J. Deng, L.A. Bloomfield, Phys. Rev. Lett. **76**, 1441 (1996).
2. G.M. Pastor, K.H. Bennemann, in *Metal Clusters*, edited by W. Ekardt (Wiley & sons, New York, 1999).
3. D.C. Douglass, J.P. Bucher, L.A. Bloomfield, Phys. Rev. Lett. **68**, 1774 (1992); D.P. Pappas, A.P. Popov, A.N. Anisimov, B. Reddy, S.N. Khanna, Phys. Rev. Lett. **76**, 4332 (1996); D. Gerion, A. Hirt, A. Châtelain, Phys. Rev. Lett. **83**, 532 (1999).
4. M. Lübcke, B. Sonntag, W. Niemann, P. Rabe, Phys. Rev. B **34**, 5184 (1986); R.-J. Tarento, P. Joyes, Phys. Rev. B **41**, 4547 (1990); C. Bréchignac *et al.*, Z. Phys. D **28**, 67 (1993).
5. C.-S. Neumann, P. Fulde, Z. Phys. B **74**, 277 (1989); M. Koga, W. Liu, M. Dolg, P. Fulde, Phys. Rev. B **57**, 10648 (1998).
6. *Valence Instabilities*, edited by P. Wachter, H. Boppart (North-Holland, Amsterdam, 1982), and references therein.
7. C.M. Varma, Y. Yafet, Phys. Rev. B **13**, 2950 (1976).
8. P. Fulde, *Electron correlations in molecules and solids*, (Springer, Berlin, 1993).
9. P.W. Anderson, Phys. Rev. **124**, 41 (1961).
10. See, for instance, G.M. Pastor, R. Hirsch, B. Mühlschlegel, Phys. Rev. B **53**, 10382 (1996).
11. Further details will be published elsewhere.