Electron correlations in transition metal-telluride cluster compounds

Palstra, Thomas; Steigerwald, M.L.; Ramirez, A.P.; Zaanen, J.

Published in:
Physica B: Condensed Matter

DOI:
10.1016/0921-4526(94)91924-0

Publication date:
1994

ELSEVIER

Physica B 199&200 (1994) 619–621

PHYSICA B

Electron correlations in transition metal-telluride cluster compounds

T.T.M. Palstra*, M.L. Steigerwald, A.P. Ramirez, J. Zaanen[1]

AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, NJ 07974, USA

Abstract

We report the magnetic properties of a new class of materials: $Ni_9Te_6^{n+}$ and $Co_6Te_8^{n+}$ with $n = 0, 1, 2$. These cluster compounds, which can be charged by chemical means from neutral to 2 +, provide a unique and novel way to change the Fermi level. For most charge states, we observe quenching of the spin and orbital moments at low temperatures, accompanied by a large value for the temperature-independent susceptibility of the ground state. The magnitude and universality of these results among different charge states can be explained neither by local moments in a finite size system nor by the molecular orbital approximation. The generic presence of low-energy magnetic excitations in these compounds indicates that these systems exhibit strong electron correlations and form mesoscopic analogues of the mixed valence/heavy fermion compounds.

The problem of strongly correlated electrons has been extensively studied in bulk systems. Little is known about electronic correlations at small length scales. In order to study these phenomena, we have synthesized a new class of cluster compounds: $Ni_9Te_6^{n+}$ and $Co_8Te_6^{n+}$ with $n = 0, 1, 2$. These materials offer some unique properties: (1) the clusters are completely identical, order in a regular lattice, and large single crystals can be grown, (2) the passivating ligands form a weak bond to the cluster (different from, e.g., the metal-carbonyl clusters), and (3) the clusters can be obtained in various charge states, without changing the structure significantly.

Our results [1] indicate that the magnetic properties are unparalleled in either bulk or molecular magnetism [2,3]. The high-temperature moments are large and vary strongly with cluster and charge state, as is usual for small complexes containing d or f ions. However, we find as a generic feature that the effective moment is strongly reduced in the ground state. Moreover, we identify a large paramagnetic contribution to the low-temperature susceptibility, additionally indicating low-lying magnetic excitations. At the same time, we expect that charge excitations are pushed to high energies, at least by finite size effects. We argue, following ideas by Fulde et al. [4], that these clusters form mesoscopic analogues of the mixed valence/heavy fermion materials.

In Fig. 1 we show one of the two cluster compounds under discussion. Each structure is completed by a passivating layer of neutral ligands of triethylphosphine (L). The ligands form a weak bond to the surface of the cluster and provide a gentle barrier between neighboring clusters. (These materials are electrically insulating.) Electrons can be chemically removed from the cluster sequentially.

* Corresponding author.

[1] Present address: Lorentz Instituut, University of Leiden, The Netherlands.

SSDI 0921-4526(93)E0435-J

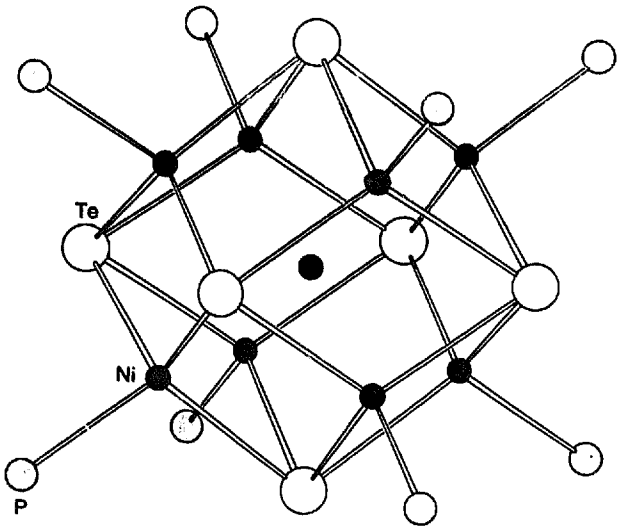

Fig. 1. Crystallographically determined structure of $Ni_9Te_6(PEt_3)_8$. The large circles represent Te atoms, the small circles Ni atoms and the intermediate-sized circles represent P atoms of the passivating ligands. The C and H atoms have been omitted for clarity. Upon oxidation the cluster contracts slightly (< 1%). Complete structural details are described elsewhere [6].

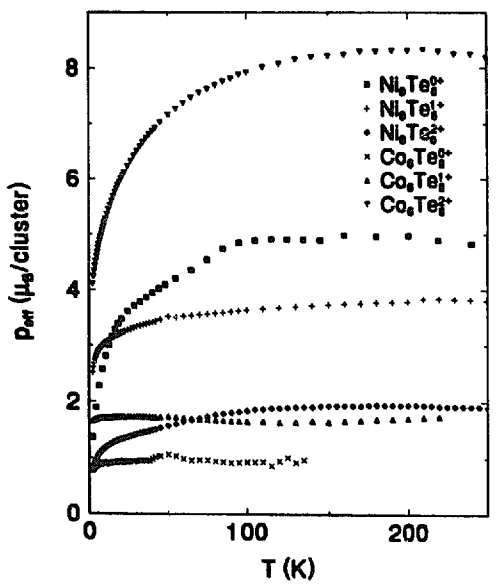

Fig. 2. Temperature dependence of the effective magnetic moment $p_{eff} = \sqrt{8\chi T}$ of $Ni_9Te_6^{n+}$ and $Co_6Te_8^{n+}$ with $n = 0, 1, 2$ measured in a field of 0.1 T.

In Fig. 2 we show the effective magnetic moment p_{eff} (defined as $\sqrt{8\chi T}$) versus temperature. This figure shows that the high-temperature effective moments per cluster are comparable to the value of a *single* metal ion. This indicates that the magnetic properties are related to the electronic structure of the cluster as a whole, and not

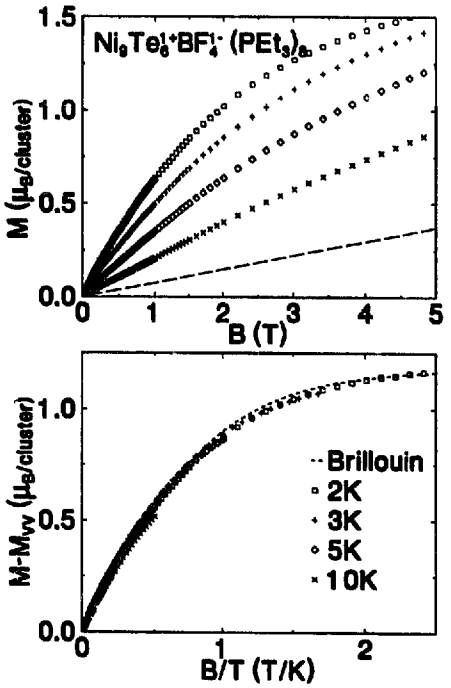

Fig. 3. Magnetic field dependence of the magnetization of $Ni_9Te_6^{1+}$ at 2, 3, 5, and 10 K. Panel (a) shows the raw data. Panel (b) shows the same data replotted as $M - \chi_{vv} H$ versus B/T, and compares the data with the theoretically expected Brillouin curve, using $M_{sat} = 1.18\mu_B$/cluster.

to the magnetism of the individual atoms. At low temperature, the moments decrease rapidly for four of the six compounds. It is difficult to obtain ground state moments from these measurements. We have used another method to study the ground state properties.

In Fig. 3 we show the magnetization versus magnetic field at 2, 3, 5 and 10 K for $Ni_9Te_6^{1+}$. We can separate the magnetization in a Curie term, that fits the Brillouin function, and a temperature-independent Van Vleck term, as shown in Fig. 3. This shows that the magnetic ground state consists of a single spin-only electron per cluster and no interactions between the clusters. Turning now to the uncharged and the doubly charged Ni_9Te_6 clusters, a similar analysis shows that these clusters have a nonmagnetic ground state, exhibiting a small, noninteracting moment of only $0.15\mu_B$ and $0.32\mu_B$, respectively. For the Co Te compounds, we find a nonmagnetic ground state ($M_{sat} = 0.02\mu_B$) for the uncharged cluster, $\sim 1\mu_B$ for the singly charge cluster, and $\sim 2\mu_B$/cluster for the doubly charged cluster. We note that this ground state moment is reduced enormously from the effective moment at room temperature.

The unconventional character of the magnetism in these clusters is emphasized by the paramagnetic contribution to the low-temperature susceptibility, showing up

in all cases where the moment is strongly temperature dependent. Such a contribution signals the mixing in by the magnetic field of excited terms into the ground state and, according to Van Vleck, $\chi_{vv} = 2\mu_B^2 T/\Delta$, with T the matrix element between the ground state and the excited state and Δ the energy difference. The Van Vleck susceptibility in the clusters appears to be anomalously large. Thus, we find in these clusters a small energy scale governing the magnetic properties. It seems unlikely that this is due to an accidental near-degeneracy of low-spin and high-spin terms. In fact, strong parallels exist with the magnetic phenomenology of heavy fermion/mixed valence metals [5]. These materials are characterized by local moments (Ni) immersed in a sea of weakly correlated conduction electrons (Te). The interaction between the local moments and the conduction electrons leads to an energy scale for spin excitations which is exponentially smaller than single particle bandwidths, manifesting itself in the susceptibility as a cross-over between free local moments at high temperatures and quenched moments at low temperatures. Moreover, a large paramagnetic susceptibility is found at low temperatures which is now associated with the Pauli susceptibility, coming from quasiparticles whose (heavy) mass scale is set essentially by the spin dynamics. Recently, Fulde et al. suggested that similar effects might occur in molecular systems [4]. They pointed out that the scale for the spin dynamics is only indirectly related to the finite-size splittings between the single-particle states, and the splittings between spin states can be exponentially smaller than the finite-size splittings.

In conclusion, we have studied the cluster compounds $Ni_9Te_6^{n+}$ and $Co_6Te_8^{n+}$, with $n = 0, 1, 2$. We observe moment reduction in the various charge states, accompanied by a large value for the temperature-independent susceptibility in the ground state. This indicates a nonaccidental low-energy scale for magnetic excitations in these materials. These results are similar to the magnetic properties of mixed valence/heavy fermion materials.

References

[1] For more details see: T.T.M. Palstra, M.L. Steigerwald, A.P. Ramirez, Y.-U. Kwon, S.M. Stuczynski, L.F. Schneemeyer, J.V. Waszczak and J. Zaanen, Phys. Rev. Lett. 71 (1993) 1768.

[2] J.S. Griffith, in: The Theory of Transition Metal Ions (Cambridge University Press, London, 1961).

[3] E.A. Boudreaux and L.N. Mulay, in: Theory and Applications of Molecular Paramagnetism (Wiley, New York, 1976).

[4] P. Fulde, in: Strong Electron Correlations (Springer, Berlin, 1992); C.-S. Neumann and P. Fulde, Z. Phys. B 74 (1989) 277.

[5] G.R. Stewart, Rev. Mod. Phys. 56 (1984) 755; P.A. Lee, T.M. Rice, J.W. Serene, L.J. Shaw and J.W. Wilkins, Commun. Condens. Matter Phys. 12 (1986) 99.

[6] J.G. Brennan, T. Siegrist, S.M. Stuczynski and M.L. Steigerwald, J. Amer. Chem. Soc. 111 (1990) 9240.