MAGNETIC MEASUREMENTS ON THE HIGH-NUCLEARITY COBALT COMPOUND Co55[P(CH3)3]12Cl20

J. Albino O. de Aguiar, M. Jurgens, G. Schmidt, L. De Jongh

To cite this version:

HAL Id: jpa-00228933
https://hal.archives-ouvertes.fr/jpa-00228933
Submitted on 1 Jan 1988

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
MAGNETIC MEASUREMENTS ON THE HIGH-NUCLEARITY COBALT COMPOUND Co55 [P(CH₃)₃]₁₂Cl₂₀

J. Albino O. de Aguiar (¹), M. J. G. M. Jurgens (¹), G. Schmidt (²) and L. J. de Jongh (¹)

(¹) Kamerlingh Onnes Laboratorium der Rijksuniversiteit Leiden, Postbus 9506, 2300 RA Leiden, The Netherlands
(²) Institut für Anorganische Chemie, Universität Essen, Universitätstrasse 5-7, 4300 Essen 1, F.R.G.

Abstract. - We present the frequency- and magnetic field dependence of the ac-susceptibility on the polynuclear metal cluster compound Co₅₅ [P(CH₃)₃]₁₂Cl₂₀ at helium temperatures (1.05 K < T < 4.2 K). Relaxation effects, characteristic of superparamagnetic particles, which are observed in the absence of an applied dc magnetic field become suppressed in low fields of 0.1 tesla. The frequency dependence of the ac-susceptibility shows features ascribable to intra- and intercluster relaxation effects.

Polynuclear metal cluster compounds [1] formed by a metal core surrounded by a shell of ligands provide a model system of small, identical metal particles embedded in a dielectric solid [2]. In these molecular clusters the number n of atoms in the core can be varied in a systematic way, and thus one can study the important physical and chemical properties as a function of cluster size [2, 3]. The interest in studying these compounds is to unravel the electronic structure of these molecules, and also to draw comparisons with surface effects for metals, as well as the problem of adsorption of molecules at metal surfaces. As part of a systematic study [4, 5] of the physical properties of polynuclear metal cluster compounds, we present here preliminary results of the frequency- and dc magnetic field dependence of the ac-susceptibility on the polynuclear metal cluster compound Co₅₅ [P(CH₃)₃]₁₂Cl₂₀, hereafter denoted by Co₅₅. The measurements were carried out with a standard mutual induction bridge operating at frequencies f = 100 Hz - 40 kHz, and in the temperature range of 4.2 K to 1.05 K. A resistive solenoid provided the external dc magnetic fields (up to 0.4 tesla) which were applied parallel to the ac driving field. A freshly prepared Co₅₅ sample in the form of black polycrystalline powder was introduced under a nitrogen atmosphere in a teflon tube that was subsequently sealed. These precautions were necessary in view of the extreme sensitivity to oxygen of the materials. Manganese-tutton salt was used as a calibration sample for the susceptibility.

The structure of the Co₅₅ macromolecule is considered to be the same as that proposed [6] for the cluster Rh₅₅ [P(tert-Bu)₃]₁₂Cl₂₀, and is shown in figure 1. It consists of a metal core of 55 cuboctahedrally packed Co-atoms, with a diameter of about 15 Å, that is surrounded by the ligand shell. In this metal core the central Co atom is surrounded by a shell of 12 Co atoms, followed by another surface metal shell of 42 atoms. Twelve of these surface Co atoms, namely those located at the vertices of the cuboctahedron are coordinated to P(CH₃)₃ groups. Another ten are unbonded, whereas the remaining twenty are coordinated by Cl atoms. The 55 atom metal cores are thus encapsulated by these ligand shells, and we can therefore consider our sample as an assembly of identical Co particles in a dielectric matrix.

In figure 2 the frequency dependence of both the real (χ'(ω)) and the imaginary (χ''(ω)) parts of the ac-susceptibility χ(ω) = χ'(ω) + iχ''(ω), are shown...
for several values of the dc magnetic field. The temperature is 1.2 K. In the absence of a dc magnetic field an almost constant absorption $\chi''(\omega)$ is observed. By applying an external dc magnetic field of 0.1 tesla this constant contribution appears to become suppressed, and a peak in $\chi''(\omega)$ is clearly revealed around 12 kHz. Increasing the dc magnetic field to 0.4 tesla this peak becomes broadened. Very similar behavior was observed at 1.05 K, except that the peak in $\chi''(\omega)$ appeared at slightly lower frequencies ($\approx 10$ kHz). At 4.2 K we could find no peak in $\chi'(\omega)$ in the frequency range of our experiment.

In order to check a possible contamination or degradation of our sample, we repeated the experiment using a $\text{Co}_{55}$ sample that had been stored for about six months. Although the results were qualitatively the same, substantially higher values of both $\chi'(\omega)$ and $\chi''(\omega)$ as well as a shift of the peak in $\chi''(\omega)$ to higher frequencies were observed. This could be an indication of partial deterioration of the sample, with the formation of free Co particles. Indeed, evidence for this was also found from the behavior of the magnetization curve of this sample, when compared to that of the fresh sample used in this work (the magnetization was measured at 4.2 K in fields up to 30 tesla [2]). Due to the observed partial deterioration of the long term stored sample we shall restrict ourselves to a qualitative discussion of the results only.

The frequency dependency of the ac-susceptibility shown in figure 2 is qualitatively similar to that observed in superparamagnetic particles [7]. Within such particles the magnetic moments are ordered, the ordering depending on the sign of the exchange interaction, and the resultant magnetic moment of the particle is aligned along the local anisotropy axis. These axes are the result of anisotropy energy barriers which may arise from various contributions such as shape or surface-effects, crystal-field effects, exchange interactions, etc. The axes of the particles are randomly oriented. Relaxation of the total moment of each particle between the two magnetization directions along the local easy axis will give rise to a maximum in the frequency dependence of $\chi''(\omega)$. This has been seen for example in some magnetic colloids [8]. If for some reason or the other, e.g. due to a distribution of anisotropy energies, there exists a distribution of relaxation times, one will get a correspondingly flattened maximum in the frequency dependence of $\chi''(\omega)$.

The nearly constant absorption at zero applied dc magnetic field in figure 2 can be interpreted as arising from a broad distribution in relaxation times, associated with a wide distribution in the strengths of the intercluster interactions. We note that there is no crystalline order of the $\text{Co}_{55}$ macromolecules in this solid. Instead we may envisage a close packing of spheres with substantial short-range order, as in a glass. Assuming the intercluster interactions to be dominated by magnetic dipolar couplings, this will lead to a broad range of interactions strengths. In fact the situation is very reminiscent to the spin-glasses, for which it is known that the combined effects of randomness and different interactions may lead to a multivalley energy structure, which in turn is responsible for a broad spectrum of relaxation times. In this picture we would consider the net magnetic moments within each cluster molecule to be relatively free to orient itself, which would agree with the high symmetry of the macromolecule (Fig. 1). Then, the application of even a small dc magnetic field will align the moments of the clusters and thus destroy the disorder. Consequently, this intercluster relaxation mechanism becomes progressively suppressed and the observation of the intracluster relaxation mechanism, that is otherwise masked by the multivalley intercluster process, becomes possible. At the same time, in going to successively higher fields one moves to regions of smaller $\text{dM}/\text{dH}$ along the magnetization curve, and both $\chi'$ and $\chi''$ will decrease, as indeed is seen in figure 2.

Although we can therefore qualitatively understand the experimental results, a quantitative analysis is as yet not meaningful. First, the nature of the intercluster couplings should be better defined, e.g. by investigating possible (intercluster) magnetic ordering phenomena below 1 K, which we plan to do in a near future.

**Acknowledgments**

This work is part of the research program of the Leiden Materials Science Center (WFMo), and is sponsored by the "Stimulation Action" program of the Commission of the European Communities. One of us (JAO de A) thanks the Brazilian agency CNPq for financial support during his stay in Leiden, and J. C. Verstelle for stimulating discussions.