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MAGNETIC MEASUREMENTS ON THE HIGH-NUCLEARITY COBALT COMPOUND \( \text{Co}_{55} \left[ \text{P}(\text{CH}_3)_3 \right]_{12} \text{Cl}_{20} \)

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Abstract. — We present the frequency- and magnetic field dependence of the ac-susceptibility on the polynuclear metal cluster compound \( \text{Co}_{55} \left[ \text{P}(\text{CH}_3)_3 \right]_{12} \text{Cl}_{20} \) 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 \( \text{Co}_{55} \left[ \text{P}(\text{CH}_3)_3 \right]_{12} \text{Cl}_{20} \), hereafter denoted by \( \text{Co}_{55} \).

The measurements were carried out with a standard mutual induction bridge operating at frequencies \( f = 100 \text{ Hz} - 40 \text{ kHz} \), 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 \( \text{Co}_{55} \) 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 \( \text{Co}_{55} \) macromolecule is considered to be the same as that proposed [6] for the cluster \( \text{Rh}_{55} \left[ \text{P}(\text{tert-Bu})_3 \right]_{12} \text{Cl}_{20} \), 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 \( \text{P}(\text{CH}_3)_3 \) 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 \( \chi'(\omega) \) and the imaginary \( \chi''(\omega) \) parts of the ac-susceptibility \( \chi(\omega) = \chi'(\omega) + i\chi''(\omega) \), are shown.

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for several values of the dc magnetic field. The temper-
perature 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 ob-
erved 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 de-
gration of our sample, we repeated the experiment us-
ing a 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 $\chi''$ to higher
frequencies were observed. This could be an indica-
tion 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 magneti-
ization curve of this sample, when compared to that
of the fresh sample used in this work (the magneti-
zation 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 ob-
served in superparamagnetic particles [7]. Within such
particles the magnetic moments are ordered, the or-
dering depending on the sign of the exchange inter-
action, and the resultant magnetic moment of the par-
ticle 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 inter-
actions, etc. The axes of the particles are randomly ori-
ented. Relaxation of the total moment of each par-
ticle 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 re-
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 aris-
ing from a broad distribution in relaxation times, as-
associated with a wide distribution in the strengths of
the intercluster interactions. We note that there is
no crystalline order of the Co$_{55}$ macromolecules in
this solid. Instead we may envisage a close pack-
ing 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 ran-
domness and different interactions may lead to a mul-
tivalley 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 or-
ient 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 mo-
ments 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 oth-
erwise masked by the multivalley intercluster process,
becomes possible. At the same time, in going to suc-
cessively higher fields one moves to regions of smaller
d$\text{d}M/\text{d}H$ 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 interclus-
ter couplings should be better defined, e.g. by inves-
tigating possible (intercluster) magnetic ordering phe-
nomena below 1 K, which we plan to do in a near
future.

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