Diamagnetic to Paramagnetic Transition in LaCoO$_3$

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Introduction
The diamagnetic to paramagnetic spin state transition in LaCoO$_3$ (LCO) that occurs in the temperature range 30 - 120 K is generally attributed to the small energy gap between the Co$^{3+}$ $t_{2g}$ and $e_g$ states. Evidence for this thermally activated transition has been obtained by a number of workers and interpreted as leading to either the intermediate spin state, $t_{2g}^5 e_g^1$ ($S = 1$), or, alternatively, to the high spin state, $t_{2g}^4 e_g^2$ ($S = 2$) of the Co$^{3+}$ ion, with the issue proving highly controversial. In an effort to obtain a consistent description of the temperature dependence of the magnetic and thermal properties of this system we have carried out a series of experiments on a single crystal sample of LCO involving EPR, magnetization and specific heat measurements. The results have been analyzed using a mean field model allowing for antiferromagnetic (AFM) interactions.

Experimental
Measurements of the magnetization in the range 4 – 200 K were made using a VSM in a resistive magnet at the NHMFL with applied fields up to 33 T. Specific heats were determined as a function of $T$ in fields of 0 and 9 T using the MS&T PPMS facility. In addition, EPR measurements in the frequency range 240 – 406 GHz were made on the same sample using high-field EPR spectrometers (CIMAR, EMR).

Results and Discussion
The Co$^{3+}$ EPR signals appear around 30 K and broaden beyond detection for $T > 70$ K. The spin Hamiltonian parameters obtained from the EPR frequency dependence and rotation patterns collected below 60 K, and given in Fig.1, support the atomic-like energy level description of the Co ion that includes the octahedral crystal field, spin-orbit coupling and the slight trigonal distortion of the lattice.[1] The low-lying first excited state is part of the $^5T_{2g}$ ($^1D$) set and has an effective spin $S_{\text{eff}} = 1$. The magnetization results are analyzed using a mean field model allowing for AFM correlations between the spins. As shown in Fig. 2 the model satisfactorily reproduces the measured susceptibility in applied fields of up to 33 T and allows us to calculate the spin contribution to the specific heat in 0 and 9 T fields.

Conclusions
A consistent description of all the experimental results in the range 4- 200 K has been given using an atomic-like (L=2, S=2) description of the Co$^{3+}$ ion in a mean field model with AFM correlations. The gap between the ground state and the triplet state is 170 K with other states at significantly higher energies.

References