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Supplementary Information

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Magnetic properties of the seven-coordinated nanoporous framework material $Co(bpy)_{1.5}(NO_3)_2$ (bpy=4,4'-bipyridine)

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A. MAGNETIC SUSCEPTIBILITY OF A PAIR OF KRAMERS DOUBLETS

A.1. Formal properties of a Kramers doublet (KD)

The formal properties of a Kramers doublet (KD) are given in[1]. So, a brief notice on them we will be given here.

If T is the time inversion operator ($T^2 = -1$ for a system with Kramers degeneracy), for any state, φ, in the KD a base of the doublet is given by the pair of Kramers conjugates states $\{\varphi, T\varphi\}$. Besides, two bases of pairs of Kramers conjugates states are related by an unitary transformation of the SU(2) group. Any time-even operator, when restricted to a Kramers doublet, results proportional to the identity and the Kramers degeneracy is only lifted by a time-odd operator, V, ($TVT^{-1} = T^{-1}VT = -V$). The general matrix form of a time-odd operator, V, in the pair $\{\varphi, T\varphi\}$ takes the form:

$$V_{\{\varphi,T\varphi\}} = \begin{pmatrix} -V_d & V_n e^{i2\alpha} \\ V_n e^{-i2\alpha} & V_d \end{pmatrix} \tag{A.1}$$

where V_d, V_n and α are real.

By the transformation

$$\varphi' = cos\beta e^{i\alpha}\varphi - sin\beta e^{-i\alpha}T\varphi$$

and, consequently,

$$T\varphi' = sin\beta e^{i\alpha}\varphi + cos\beta e^{-i\alpha}T\varphi \tag{A.2}$$

with

$$cos\,2\beta = \frac{V_d}{\sqrt{V_d^2+V_n^2}} \qquad sin\,2\beta = \frac{V_n}{\sqrt{V_d^2+V_n^2}} \tag{A.3}$$

V is diagonalized and in the $\{\varphi', T\varphi'\}$ base takes the form:

$$V_{\{\varphi',T\varphi'\}} = \begin{pmatrix} -\sqrt{V_d^2+V_n^2} & 0 \\ 0 & \sqrt{V_d^2+V_n^2} \end{pmatrix} \tag{A.4}$$

In summary, given a time-odd perturbation, V, it is possible to choose a base of a KD formed by a pair of Kramers conjugates states in which V is diagonal.

A.2. Magnetic susceptibility of two Kramers doublets. Paramagnetic behavior.

Let us consider now a system with an energy level scheme formed, in the absence of an applied field, by two KDs separated by an energy, Δ. If V is a time-odd perturbation, according to the previous section, there are two bases of Kramers conjugate states, $\{\phi, T\phi\}$ for the ground state and $\{\psi, T\psi\}$ for the excited one, accomplishing that V is diagonal within each doublet. Besides, the elements of the perturbation matrix V connecting wavefunctions of different doublets hold:

$$\langle T\phi|V|T\psi\rangle = \langle T\phi|VT\psi\rangle = -\langle T\phi|TV\psi\rangle = -\langle\phi|V\psi\rangle^* = -\langle\phi|V|\psi\rangle^* \tag{A.5}$$

and
$$\langle\phi|V|T\psi\rangle = -\langle T^2\phi|VT\psi\rangle = \langle T(T\phi)|T(V\psi)\rangle = \langle T\phi|V\psi\rangle^* = \langle T\phi|V|\psi\rangle^* \tag{A.6}$$

In conclusion, denoting:

$$\begin{aligned} \langle\phi|V|\phi\rangle = -\langle T\phi|V|T\phi\rangle = V_\phi \qquad & \langle\phi|V|\psi\rangle = V_1 e^{i\theta_1} \\ \langle\psi|V|\psi\rangle = -\langle T\psi|V|T\psi\rangle = V_\psi \qquad & \langle T\phi|V|\psi\rangle = V_2 e^{i\theta_2} \end{aligned} \tag{A.7}$$

where V_ϕ, V_ψ, V_1, V_2, θ_1 and θ_2 are real, the energy matrix (including the splitting within the KD) is given by:

$$H_0 + V = \begin{pmatrix} -\frac{\Delta}{2}+V_\phi & 0 & V_1 e^{i\theta_1} & V_2 e^{-i\theta_2} \\ 0 & -\frac{\Delta}{2}-V_\phi & V_2 e^{i\theta_2} & -V_1 e^{-i\theta_1} \\ V_1 e^{-i\theta_1} & V_2 e^{-i\theta_2} & \frac{\Delta}{2}+V_\psi & 0 \\ V_2 e^{i\theta_2} & -V_1 e^{i\theta_1} & 0 & \frac{\Delta}{2}-V_\psi \end{pmatrix} \tag{A.8}$$

and the energies, up to a second-order of perturbation, are:

$$\begin{aligned} E_\phi &= -\frac{\Delta}{2}+V_\phi-2\frac{V_1^2+V_2^2}{\Delta} \qquad & E_\psi &= +\frac{\Delta}{2}+V_\psi+2\frac{V_1^2+V_2^2}{\Delta} \\ E_{T\phi} &= -\frac{\Delta}{2}-V_\phi-2\frac{V_1^2+V_2^2}{\Delta} \qquad & E_{T\psi} &= +\frac{\Delta}{2}-V_\psi+2\frac{V_1^2+V_2^2}{\Delta} \end{aligned} \tag{A.9}$$

Consider now that the perturbation represents the coupling with a magnetic field (Zeeman interaction), and that our system could be described as isotropic from a magnetic point of view. Then we can write:

$$V = G\cdot B \tag{A.10}$$

where B is the intensity of the applied field and G is an operator acting on the states.

Then, defining the values of G_ϕ, G_ψ, G_{12}, as $V_k = G_k B$, the energies of the states can be expanded in powers of B up to a second order and, using the Van Vleck's formula[2], the paramagnetic susceptibility (a scalar in this case) is given by:

$$\chi = N \frac{\left(\frac{G_\phi^2}{k_B T} + 2\frac{G_{12}^2}{\Delta}\right) e^{\frac{\Delta}{2k_B T}} + \left(\frac{G_\psi^2}{k_B T} - 2\frac{G_{12}^2}{\Delta}\right) e^{\frac{-\Delta}{2k_B T}}}{e^{\frac{\Delta}{2k_B T}} + e^{\frac{-\Delta}{2k_B T}}} \tag{A.11}$$

where N is the number of paramagnetic entities (N_A for the molar susceptibility). Equation (A.11) can be conveniently written as:

$$\chi = \frac{N}{k_B T}\left\{C_0 + C_1\left(\frac{2k_B T}{\Delta}\right) th\left(\frac{\Delta}{2k_B T}\right) + C_2 th\left(\frac{\Delta}{2k_B T}\right)\right\} \tag{A.12}$$

with:

$$C_0 = \frac{1}{2}\left(G_\phi^2 + G_\psi^2\right) \qquad C_1 = G_{12}^2 \qquad C_2 = \frac{1}{2}\left(G_\phi^2 - G_\psi^2\right) \tag{A.13}$$

These constants depend on the specific electronic structure of the Kramer doublets involved.

The most general case is a little bit more complicated, since the magnetic susceptibility is a second range (symmetric) tensor. In consequence, when a magnetic field is applied in an arbitrary direction, the magnetization is not oriented, in general, parallel to the field. Nevertheless, since the susceptibility tensor is symmetric, there will be three directions mutually orthogonal to each other, (principal directions) such that when a magnetic field is applied parallel to one of them, the magnetization will be parallel to the field. We shall denote these directions as $\hat{u}_r$, $r = X, Y, Z$. The susceptibility tensor expressed in this system of axes is diagonal and its principal values will be denoted as χ_X, χ_Y, χ_Z. In order to determine the susceptibility it is enough to measure the magnetization with the field applied along each one of the principal directions. In such a case it is possible to apply the previously described formalism for the isotropic case, where the values of G_ϕ, G_ψ, and G_{12}, and the wavefunctions $\{\phi, T\phi, \psi, T\psi\}$, will depend now on the specific principal direction. The notation $G_\phi(r)$, $G_\psi(r)$ and $G_{12}(r)$ ($r = X, Y, Z$) will be used to make this dependence more explicitly and, the quantities $C_i(r)$, $i = 0, 1, 2$, are defined in a similar way as (A.13). Then, the principal values of the paramagnetic susceptibility are given as:

$$\chi_r = \frac{N}{k_B T}\left\{ C_0(r) + C_1(r)\left(\frac{2k_B T}{\Delta}\right) th\left(\frac{\Delta}{2k_B T}\right) + C_2(r)\, th\left(\frac{\Delta}{2k_B T}\right)\right\} \qquad (r = X, Y, Z) \qquad \text{(A.14)}$$

and, consequently, the temperature dependence of the susceptibility tensor results to be:

$$\widetilde{\chi} = \frac{N}{k_B T}\left\{ \widetilde{C}_0 + \widetilde{C}_1\left(\frac{2k_B T}{\Delta}\right) th\left(\frac{\Delta}{2k_B T}\right) + \widetilde{C}_2\, th\left(\frac{\Delta}{2k_B T}\right)\right\} \qquad \text{(A.15)}$$

where $\widetilde{C}_i$ (i =0, 1, 2) are symmetric tensors whose principal axes coincide with the susceptibility principal axes being $C_i(r)$, ($r = X, Y, Z$) their principal values.

On the other hand, if a macroscopic sample consisting of randomly oriented polycrystalline powder is measured, it behaves isotropically, and its susceptibility is given by:

$$\chi_{pol} = \frac{1}{3} tr(\widetilde{\chi}) = \frac{1}{3}(\chi_X + \chi_Y + \chi_Z) \qquad \text{(A.16)}$$

and its temperature dependence is also given by (A.12), but in this case

$$C_0 = \frac{1}{6}\sum_{r=X,Y,Z}\left\{G_\phi^2(r) + G_\psi^2(r)\right\} \quad C_1 = \frac{1}{3}\sum_{r=X,Y,Z} G_{12}^2(r) \quad C_2 = \frac{1}{6}\sum_{r=X,Y,Z}\left\{G_\phi^2(r) - G_\psi^2(r)\right\} \qquad \text{(A.17)}$$

Finally, we shall analyze some properties of expression (A.12), which can be more conveniently written as:

$$T\chi = \frac{N}{k_B}\left\{ C_0 + C_1\left(\frac{2k_B T}{\Delta}\right) th\left(\frac{\Delta}{2k_B T}\right) + C_2\, th\left(\frac{\Delta}{2k_B T}\right)\right\} \qquad \text{(A.18)}$$

The low temperature behavior is given by

$$T\chi \xrightarrow[T\to 0]{} \frac{N}{k_B}(C_0 + C_2) = \frac{N}{3k_B}\sum_{r=X,Y,Z} G_\phi^2(r) \qquad \text{(A.19)}$$

which only depends on the electronic properties of the ground state, whereas the high temperature behavior is given by:

$$T\chi \xrightarrow[T\to \infty]{} \frac{N}{k_B}(C_0 + C_1) = \frac{N}{6k_B}\sum_{r=X,Y,Z}\left\{ G_\phi^2(r) + G_\psi^2(r) + 2G_{12}^2(r)\right\} \qquad \text{(A.20)}$$

On the other hand, it is interesting to compare these results with those obtained by an EPR experiment, in a common situation where the energy gap between the two KD, Δ, is larger than the microwave frequency so that only transitions within each doublet are observed. The description of the EPR spectra in this case corresponds to that of the two independent

KD, i.e, it is equivalent to take (A.8) to a first-order. So, we can associate to each doublet an effective spin, S'_ϕ and S'_ψ (= ½) by defining the effective giromagnetic tensors; we shall denote $g_{s\phi}$ ($s\phi = x\phi, y\phi, z\phi$) and $g_{s\psi}$ ($s\psi = x\psi, y\psi, z\psi$) the principal values of the giromagnetic tensors corresponding to the ground $\{\phi, T\phi\}$ and excited $\{\psi, T\psi\}$ states, respectively, being (x_ϕ, y_ϕ, z_ϕ) and (x_ψ, y_ψ, z_ψ) the corresponding principal directions. Note that, in general, these directions do not need to coincide with the principal directions of the susceptibility tensor (X, Y, Z).

If $l_{r,s\phi}$ and $l_{r,s\phi}$ are the director cosines of the r direction (r = X, Y, Z, principal directions of χ) with respect to the axes (x_ϕ, y_ϕ, z_ϕ) and (x_ψ, y_ψ, z_ψ), respectively, it holds:

$$\begin{aligned} G_\phi^2(r) &= \frac{1}{4}\mu_B^2\left(l_{r,x\phi}^2 g_{x\phi}^2 + l_{r,y\phi}^2 g_{y\phi}^2 + l_{r,z\phi}^2 g_{z\phi}^2\right) \\ G_\psi^2(r) &= \frac{1}{4}\mu_B^2\left(l_{r,x\psi}^2 g_{x\psi}^2 + l_{r,y\psi}^2 g_{y\psi}^2 + l_{r,z\psi}^2 g_{z\psi}^2\right) \end{aligned} \qquad (r = X, Y, Z) \qquad \text{(A.21)}$$

and, taking into account the normalization properties of $l_{r,s\phi}$ and $l_{r,s\phi}$, it is followed:

$$\begin{aligned} \frac{1}{3}\sum_{r=X,Y,Z} G_\phi^2(r) &= \frac{1}{4}\mu_B^2\,\frac{g_{x\phi}^2 + g_{y\phi}^2 + g_{z\phi}^2}{3} = \frac{1}{4}\mu_B^2 g_\phi^2 \\ \frac{1}{3}\sum_{r=X,Y,Z} G_\psi^2(r) &= \frac{1}{4}\mu_B^2\,\frac{g_{x\psi}^2 + g_{y\psi}^2 + g_{z\psi}^2}{3} = \frac{1}{4}\mu_B^2 g_\psi^2 \end{aligned} \qquad \text{(A.22)}$$

where we have introduced the (quadratic) average g values of the ground, g_ϕ, and excited states, g_ψ, given by:

$$g_\phi^2 = \frac{1}{3}\left(g_{x\phi}^2 + g_{y\phi}^2 + g_{z\phi}^2\right) \quad \text{and} \quad g_\psi^2 = \frac{1}{3}\left(g_{x\psi}^2 + g_{y\psi}^2 + g_{z\psi}^2\right) \qquad \text{(A.23)}$$

Finally

$$T\chi \xrightarrow[T\to 0]{} \frac{N}{3k_B}\sum_{r=X,Y,Z} G_\phi^2(r) = \frac{N\mu_B^2 g_\phi^2}{4k_B} = \frac{NS'_\phi\left(S'_\phi + 1\right)\mu_B^2 g_\phi^2}{3k_B} \qquad \text{(A.24)}$$

i.e., in the low temperature limit, the susceptibility follows a Curie law with an effective spin S'_ϕ = ½ and with the effective g factors of the ground state.

A.3 A particular case: the S = 3/2 quartet.

Frequently, the description of two Kramers doublet is given in terms of an effective spin S = 3/2 by including a zero field term, H_{ZFS}, which accounts for the splitting among the doublet. The magnetic properties are determined by using the following spin-Hamiltonian:

$$H = \underbrace{D\left\{\left[S_Z^2 - \frac{1}{3}S\left(S+1\right)\right] + \eta\left[S_X^2 - S_Y^2\right]\right\}}_{H_{ZFS}} - \underbrace{\mu_B \vec{H}\cdot\tilde{g}\cdot\vec{S}}_{H_{Ze}} \qquad (A.25)$$

with $S = 3/2$. $\hat{g}$ stands for the g-tensor, which describes the electronic Zeeman interaction, H_{Ze}, and the D and η account for the zero field contribution, resulting $\Delta = 2D(1 + 3\eta^2)^{½}$. The magnetic susceptibility of a system described by (A.25) have been calculated by several authors in the particular case of axial symmetry, $\eta = 0$[3-6]. Before, Ganguli *et al.*[7] calculated the principal values of the paramagnetic susceptibility tensor in a case of orthorhombic symmetry where the principal directions of the g-tensor coincide with the principal directions of the ZFS contribution (X, Y, Z). In this particular situation these directions are also the principal directions of the paramagnetic susceptibility tensor and the thermal evolution of the principal values obtained by those authors coincides with that given by (A.14) but an explicit dependence of the $C_i(r)$ constants on the "true" principal g-values, g_X, g_Y, g_Z, and on the parameter η was obtained. In summary, for a polycrystalline, randomly oriented sample, the paramagnetic susceptibility is given by equation (A.12) with:

$$C_0 = \frac{\mu_B^2}{12\left(1+3\eta^2\right)}\left\{\left(2g_X^2 + 2g_Y^2 + 5g_Z^2\right) - 6\left(g_X^2 - g_Y^2\right)\eta + 3\left(4g_X^2 + 4g_Y^2 + g_Z^2\right)\eta^2\right\}$$

$$C_1 = \frac{\mu_B^2}{12\left(1+3\eta^2\right)}\left\{3\left(g_X^2 + g_Y^2\right) + 6\left(g_X^2 - g_Y^2\right)\eta + 3\left(g_X^2 + g_Y^2 + 4g_Z^2\right)\eta^2\right\} \qquad (A.26)$$

$$C_2 = \frac{\mu_B^2}{6\sqrt{1+3\eta^2}}\left\{\left(g_X^2 + g_Y^2 - 2g_Z^2\right) - 3\left(g_X^2 - g_Y^2\right)\eta\right\}$$

From the EPR point of view, if $\Delta >> h\nu$, ν being the microwave frequency, the system can be described as two systems S = ½ (Kramers doublets) with effective g tensors[8]. Their principal values are given by

$$
\begin{aligned}
g_x^{1)} &= g_X\left(1+\frac{1-3\eta}{\sqrt{1+3\eta^2}}\right) & g_x^{2)} &= g_X\left(1-\frac{1-3\eta}{\sqrt{1+3\eta^2}}\right) \\
g_y^{1)} &= g_Y\left(1+\frac{1+3\eta}{\sqrt{1+3\eta^2}}\right) & g_y^{2)} &= g_Y\left(-1+\frac{1+3\eta}{\sqrt{1+3\eta^2}}\right) \\
g_z^{1)} &= g_Z\left(\frac{2}{\sqrt{1+3\eta^2}}-1\right) & g_z^{2)} &= g_Z\left(\frac{2}{\sqrt{1+3\eta^2}}+1\right)
\end{aligned}
\qquad \text{(A.27)}
$$

where the superscript stands for each of the two doublets.

Usually only the signal corresponding to the transition within a doublet (that labeled by 1 in A.27) are observed. So, if the temperature evolution of the susceptibility is known, using these last equations with (A.26), the principal values of the "true" *g*-tensor (g_X, g_Y, g_Z) and the ZFS parameters (D, η) can be estimated.

A.4. Magnetic susceptibility of two KD. A phenomenological description of weak magnetic interactions.

Let us consider now the existence of weak magnetic interactions. So, the temperature dependence of the paramagnetic susceptibility should depart from that predicted by equation (A.15). This question was studied by Carlin and Burriel[9]; these authors modified the Ganguli *et al.* expression[7] by introducing a molecular field correction[6] and asymptotic expressions were obtained in the high temperature regime.

Our case is quite different. The temperature dependence shown in figure 3 of the main text clearly indicate that the evolution of χ follows that predicted by (A.12) at temperatures higher than 15 K. As $\Delta \approx 200$ K, in our case the ZFS contribution is higher than the exchange interactions. On the other hand, at low enough temperature ($k_BT << \Delta$) the system could be described as a S = ½ one and a Curie-Weiss law could account for the temperature dependence of magnetic susceptibility in the paramagnetic phase when exchange interactions are present. Then (A.24) should be modified and then:

$$
T\chi \underset{T\to 0}{\longrightarrow} \frac{N}{3k_B}\frac{T}{T-T_0}\sum_{r=X,Y,Z} G_\phi^2(r) \qquad \text{(A.28)}
$$

As $T/(T\text{-}T_0) \approx 1$ for $T >> T_0$, the expression:

$$
\chi = \frac{N}{k_B(T-T_0)}\left\{C_0 + C_1\left(\frac{2k_BT}{\Delta}\right)th\left(\frac{\Delta}{2k_BT}\right) + C_2 th\left(\frac{\Delta}{2k_BT}\right)\right\} \qquad \text{(A.29)}
$$

instead of (A.12) results useful to describe the temperature evolution of the susceptibility when some weak exchange interactions are present. Equation (3) in the main paper corresponds to add to (A.29) a temperature independent contribution, χ_0.

A.5. References

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B. MAGNETIZATION VERSUS MAGNETIC FIELD AND MAGNETIC HEAT CAPACITY IN A RANDOMLY ORIENTED POWDERED SAMPLE OF AN ORTHORHOMBIC S = ½ SYSTEM.

Let us consider an S =1/2 system with an orthorhombic g-tensor. Its principal values will be denoted as g_X, g_Y, g_Z and its principal axes as (X, Y, Z). The question now is determining, beyond the linear region, the magnetization, of a randomly oriented powdered sample, as a function of the applied magnetic field at a given temperature.

Firstly consider a single crystal and an orientation of the magnetic field given by the unitary vector $\hat{u}$, (u_X, u_Y, u_Z). Defining the effective g-factor, which depends on the magnetic field orientation, $g(\hat{u})$.

$$g^2(\hat{u}) = g^2(u_X, u_Y, u_Z) = g_X^2 u_X^2 + g_Y^2 u_Y^2 + g_Z^2 u_Z^2 , \tag{B.1}$$

the magnetic field induced splitting of the two spin level, which also depends on the magnetic field orientation, is given by:

$$E(\hat{u}) = g(\hat{u})\mu_B H , \tag{B.2}$$

where H is the intensity of the magnetic field.

On the other hand, as a consequence of the g-tensor anisotropy, the magnetization is not parallel to the magnetic field. Its components in the (X, Y, Z) frame are:

$$M_\alpha(\hat{u}) = N\mu_B\, g^{-1}(\hat{u})\, g_\alpha^2 u_\alpha \frac{1}{2} th\left(\frac{g(\hat{u})\mu_B H}{2k_B T}\right) \quad (\alpha = X, Y, Z) . \tag{B.3}$$

Then the magnetization along a direction fixed by and unitary vector $\hat{w}$ is:

$$M_{\hat{w}}(\hat{u}) = \vec{M}(\hat{u}) \cdot \hat{w} = N\mu_B\, g^{-1}(\hat{u})\left(g_X^2 u_X w_X + g_Y^2 u_Y w_Y + g_Z^2 u_Z w_Z\right)\frac{1}{2} th\left(\frac{g(\hat{u})\mu_B H}{2k_B T}\right), \tag{B.4}$$

where (w_X, w_Y, w_Z,) are the components of $\hat{w}$ in the (X, Y, Z) frame.

In particular, the component parallel to the applied field, $M_0(\hat{u})$, results to be:

$$M_0(\hat{u}) = \vec{M}(\hat{u}) \cdot \hat{u} = N\mu_B g(\hat{u})\ \frac{1}{2} th\left(\frac{g(\hat{u})\mu_B H}{2k_B T}\right) . \tag{B.5}$$

On the other hand, the magnetic contribution to the molar heat capacity also depends of the magnetic field orientation, $C_m(\hat{u}, T/H)$ and is given by a Schottky contribution:

$$C_m\left(\hat{u},\frac{T}{H}\right)=R\left(\frac{g(\hat{u})\mu_B H}{k_B T}\right)^2 sec\,h^2\left(\frac{g(\hat{u})\mu_B H}{k_B T}\right) \tag{B.6}$$

A randomly oriented powdered sample macroscopically behaves as isotropic and the observed magnetization is parallel to the applied field. It can be obtained by adding the former expression for all possible orientations taking into account that now *N* corresponds to the number of crystallite with an orientation of the magnetic field given by *û*; then it has to be substituted by *Np*(*û*), where *p*(*û*) accounts for the probability of finding a crystalline oriented with the applied magnetic field along *û*.

By the normalization condition u_X, u_Y, u_Z are not independent and an specific orientation is given by the colatitude, θ, and azimuth, ϕ, angles. For computational convenience it commonly introduce the variable $u = cos\theta$ is introduced which, for a randomly oriented sample is uniformly distributed in the [-1, 1] interval; ϕ is uniformly distributed in the [0, 2π] interval. In practice, taking into account the symmetry (B.1) the computational task is performed by considering only an octant: $0 \leq u < 1$ and $0 \leq \phi < \pi/2$.

The effective *g* factor, as a function of *u* and ϕ, results:

$$g(u,\phi)=\sqrt{(1-u^2)(g_X^2 cos^2\phi+g_Y^2 sin^2\phi)+g_Z^2 u^2} \tag{B.7}$$

and

$$M_0(u,\varphi)=N\mu_B\, g(u,\varphi)\,\frac{1}{2}th\left(\frac{g(u,\varphi)\,\mu_B H}{2k_B T}\right) \tag{B.8}$$

Then, the magnetization of a randomly oriented powdered sample is given by:

$$M\left(\frac{H}{T}\right)=\frac{2}{\pi}\int_0^1\left\{\int_0^{\pi/2}M_0(u,\phi)d\phi\right\}du \tag{B.9}$$

In the same way, the magnetic contribution to the molar heat capacity of a powdered randomly oriented sample is obtained by averaging (B.6) resulting:

$$C_m\left(\frac{T}{H}\right)=\frac{2}{\pi}\int_0^1\left\{\int_0^{\pi/2}C_m\left(u,\phi,\frac{T}{H}\right)d\phi\right\}du \tag{B.10}$$

with

$$C_m\left(u,\phi,\frac{T}{H}\right)=R\left(\frac{g(u,\phi)\mu_B H}{k_B T}\right)^2 sec\,h^2\left(\frac{g(u,\phi)\mu_B H}{k_B T}\right) \tag{B.11}$$