

Average g -Factors of Anisotropic Polycrystalline SamplesRandy S. Fishman^{*,†} and Joel S. Miller[‡]*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6071, and Department of Chemistry, University of Utah, Salt Lake City, Utah 84112-0850**Received: May 3, 2010; Revised Manuscript Received: May 20, 2010*

Due to the lack of suitable single crystals, the average g -factor of anisotropic polycrystalline samples are commonly estimated from either the Curie–Weiss susceptibility or the saturation magnetization. We show that the average g -factor obtained from the Curie constant is always greater than or equal to the average g -factor obtained from the saturation magnetization. The average g -factors are equal only for a single crystal or an isotropic polycrystal. We review experimental results for several compounds containing the anisotropic cation $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+$ and propose an experiment to test this inequality using a compound with a spinless anion.

I. Introduction

Many orbitally nondegenerate magnetic molecules are highly anisotropic with different g -factors parallel and perpendicular to some local axis.¹ The g -factors of an anisotropic molecule can be measured by performing electron paramagnetic resonance^{2,3} on an oriented single crystal. However, suitable single crystals of anisotropic materials are frequently unavailable. Consequently, the average g -factors of polycrystalline materials are commonly estimated from either the Curie–Weiss (CW) susceptibility or the saturation magnetization. In this paper, we demonstrate that the average g -factors $g_{\text{av}}^{\text{CW}}$ and $g_{\text{av}}^{\text{sat}}$ obtained by these two techniques are different.

We show that $g_{\text{av}}^{\text{CW}} \geq g_{\text{av}}^{\text{sat}}$, where the equality only holds for single crystals or isotropic polycrystals. Depending on the distribution of polycrystalline axis, $g_{\text{av}}^{\text{sat}}/g_{\text{av}}^{\text{CW}}$ can be substantially smaller than 1. For polycrystalline samples that favor alignment along one axis, $g_{\text{av}}^{\text{CW}}$ will typically overestimate the degree of alignment along that axis compared to $g_{\text{av}}^{\text{sat}}$. In practice, our results apply either to spin-1/2 molecules or to higher-spin molecules with single-ion anisotropy that is not too strong.

This paper is divided into five sections. Results for the average g -factors are derived in section II. Section III demonstrates the inequality $g_{\text{av}}^{\text{CW}} \geq g_{\text{av}}^{\text{sat}}$ by using two simple distribution functions for the polycrystalline axis with a simplified g -tensor. Section IV reviews experimental results for several compounds containing the highly anisotropic cation $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+$. Section V proposes an experiment to rigorously test the inequality $g_{\text{av}}^{\text{CW}} \geq g_{\text{av}}^{\text{sat}}$ and contains a brief summary.

II. Average g -Factors

In a magnetic field H along the \mathbf{n} direction, the effective Hamiltonian of an anisotropic molecule with spin S and an orbitally nondegenerate ground state (so that the expectation value of the orbital angular momentum vanishes) is given by⁴

$$H_{\text{eff}} = \mu_{\text{B}}H \sum_{\mu,\nu} g_{\mu\nu} n_{\mu} S_{\nu} + DS_z^2 \quad (1)$$

where μ_{B} is the Bohr magneton, D is the single-ion anisotropy, and $g_{\mu\nu} = (g)_{\mu\nu}$ are the components of the g -tensor, which is real and symmetric. The quantization axis m is introduced by rewriting $\mu_{\text{B}}H \sum_{\mu,\nu} g_{\mu\nu} n_{\mu} S_{\nu} = K\mathbf{m} \cdot \mathbf{S}$, where

$$Km_{\mu} = \mu_{\text{B}}H \sum_{\nu} g_{\mu\nu} n_{\nu} \quad (2)$$

defines both the unit vector \mathbf{m} and the constant K .

With energy $E_{\text{eff}} = \langle H_{\text{eff}} \rangle$, the magnetization \mathbf{M} per ion is obtained from

$$M_{\nu} = -\frac{\partial E_{\text{eff}}}{\partial H_{\nu}} = -\mu_{\text{B}} \sum_{\mu} g_{\mu\nu} \langle S_{\mu} \rangle \quad (3)$$

The thermal expectation values of the spin components are defined by

$$\langle S_{\alpha} \rangle = \frac{1}{Z} \text{Tr}\{S_{\alpha} \exp(-H_{\text{eff}}/k_{\text{B}}T)\} \quad (4)$$

$$Z = \text{Tr}\{\exp(-H_{\text{eff}}/k_{\text{B}}T)\} \quad (5)$$

where Tr is a trace over all diagonal matrix elements. Although $\langle \mathbf{S} \rangle$ is always parallel to the quantization axis \mathbf{m} , \mathbf{M} is not generally parallel to $\langle \mathbf{S} \rangle$ due to the anisotropic g -tensor.

From this point on, we shall neglect the single-ion anisotropy energy D . Of course, D has no effect for spin-1/2 molecules because $S_x^2 = S_y^2 = S_z^2 = 1/4$. For higher-spin molecules, D can be neglected at very high temperatures $k_{\text{B}}T \gg DS^2$ or in very high fields $\mu_{\text{B}}H \gg DS$. Since measurements of the CW susceptibility typically range in temperature from 50 to 300 K, our theory applies to higher-spin molecules with $DS^2 \ll 5$ meV. By contrast, the restriction to high fields can be ignored because

* To whom correspondence should be addressed.

† Oak Ridge National Laboratory.

‡ University of Utah.

single-ion anisotropy always lowers the estimated value of the saturation magnetization, leaving the inequality $g_{av}^{CW} \geq g_{av}^{sat}$ unaffected.

When $k_B T$ is much larger than the exchange interactions, the Curie constant C sums the contributions from each magnetic ion. Expanding the exponentials in eqs 4 and 5 for high temperatures, we obtain the spin and magnetization components

$$\langle S_\alpha \rangle = -\frac{S(S+1)}{3k_B T} \mu_B H \sum_\nu g_{\alpha\nu} n_\nu \quad (6)$$

$$M_\alpha = \frac{S(S+1)}{3k_B T} \mu_B^2 H \sum_{\mu,\gamma} g_{\mu\alpha} g_{\mu\gamma} n_\alpha \quad (7)$$

The generalized susceptibility is then given by

$$\chi_{\mu\nu} = \frac{\partial M_\mu}{\partial H_\nu} = \frac{\mu_B^2 S(S+1)}{3k_B T} (g^2)_{\mu\nu} \quad (8)$$

which utilizes the symmetry of the g -tensor.

For a partially aligned polycrystalline sample, $\rho(\cos \theta, \phi)$ is the distribution function of the anisotropy axis \mathbf{z} of the crystallites with respect to the direction

$$\mathbf{n} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \quad (9)$$

of the magnetic field. Integrated over all solid angles, $\rho(\cos \theta, \phi)$ is normalized to 1

$$\int \frac{d\Omega}{4\pi} \rho(\cos \theta, \phi) \equiv \int_0^{2\pi} \frac{d\phi}{2\pi} \int_0^1 d(\cos \theta) \rho(\cos \theta, \phi) = 1 \quad (10)$$

For a single crystal oriented along the field direction, $\mathbf{n} = \mathbf{z}$ and $\rho(\cos \theta, \phi) = \delta(\cos \theta - 1)$. For a nonaligned polycrystalline sample, $\rho(\cos \theta, \phi) = 1$ for all values of ϕ and for $\cos \theta$ between 1 (crystal axis along the field direction) and 0 (crystal axis perpendicular to the field direction). As a polycrystal becomes progressively more aligned parallel to the field, $\rho(\cos \theta, \phi)$ becomes more heavily weighted toward $\cos \theta = 1$. For the purposes of this paper, many “single crystals” behave like polycrystals due to the misalignment of the anisotropy axis for the individual magnetic ions.

The average magnetic susceptibility of a polycrystalline sample is obtained by integrating the projection of the magnetization \mathbf{M} along the field direction \mathbf{n} over all solid angles:

$$\mathbf{M} \cdot \mathbf{n} = \frac{\mu_B^2 H}{3k_B T} S(S+1) [\mathbf{n}^T g^2 \mathbf{n}] \quad (11)$$

$$\chi_{av} = \frac{\mu_B^2}{3k_B T} S(S+1) \int \frac{d\Omega}{4\pi} \rho(\cos \theta, \phi) [\mathbf{n}^T g^2 \mathbf{n}] \quad (12)$$

where

$$[\mathbf{n}^T g^2 \mathbf{n}] \equiv \sum_{\mu,\gamma} n_\mu g_{\mu\gamma} g_{\gamma\nu} n_\nu \quad (13)$$

Defining the average Curie constant by $\chi_{av} \equiv C_{av}/k_B T$ with $C_{av} = (\mu_B g_{av}^{CW})^2 S(S+1)/3$, we obtain the average g -factor

$$g_{av}^{CW} = \left(\int \frac{d\Omega}{4\pi} \rho(\cos \theta, \phi) [\mathbf{n}^T g^2 \mathbf{n}] \right)^{1/2} \quad (14)$$

For a nonaligned polycrystalline sample with a diagonal g -tensor $g_{\mu\nu} = \delta_{\mu\nu} g_{\mu\mu}$, this reduces to the well-known result^{1,5} $g_{av}^{CW} = (g_{xx}^2/3 + g_{yy}^2/3 + g_{zz}^2/3)^{1/2}$.

To evaluate the saturation magnetization \mathbf{M}^{sat} , we must keep in mind that \mathbf{M}^{sat} is not parallel to $\langle \mathbf{S} \rangle$. For large fields, eqs 4 and 5 imply that

$$\langle S_\alpha \rangle = -S m_\alpha = -\frac{S \mu_B H}{K} \sum_\nu g_{\alpha\nu} n_\nu \quad (15)$$

Combining this relation with eq 2 yields

$$K = \mu_B H \sum_{\mu,\nu} m_\mu g_{\mu\nu} n_\nu = \mu_B H \sqrt{[\mathbf{n}^T g^2 \mathbf{n}]} \quad (16)$$

Since the projection of \mathbf{M}^{sat} along \mathbf{n} is given by

$$\mathbf{M}^{sat} \cdot \mathbf{n} = \frac{HS \mu_B^2}{K} [\mathbf{n}^T g^2 \mathbf{n}] = \mu_B S \sqrt{[\mathbf{n}^T g^2 \mathbf{n}]} \quad (17)$$

$$g_{av}^{sat} \equiv \frac{M_{av}^{sat}}{\mu_B S} = \int \frac{d\Omega}{4\pi} \rho(\cos \theta, \phi) \sqrt{[\mathbf{n}^T g^2 \mathbf{n}]} \quad (18)$$

is the average g -factor obtained from the average saturation magnetization M_{av}^{sat} .

Comparing eqs 14 and 18, we obtain the ratio

$$\frac{g_{av}^{CW}}{g_{av}^{sat}} = \frac{\left(\int \frac{d\Omega}{4\pi} \rho(\cos \theta, \phi) [\mathbf{n}^T g^2 \mathbf{n}] \right)^{1/2}}{\int \frac{d\Omega}{4\pi} \rho(\cos \theta, \phi) \sqrt{[\mathbf{n}^T g^2 \mathbf{n}]}} \quad (19)$$

The Appendix provides a proof that $g_{av}^{CW} \geq g_{av}^{sat}$ for any distribution $\rho(\cos \theta, \phi)$ of crystal axis and for any magnitude of the anisotropy. The equality $g_{av}^{CW} = g_{av}^{sat}$ holds under one of two conditions: for an anisotropic single crystal with $\rho(\cos \theta, \phi) = \delta(\cos \theta - \cos \theta_0) \delta(\phi - \phi_0)$ or for an isotropic polycrystal with $[\mathbf{n}^T g^2 \mathbf{n}]$ equal to a constant independent of angle.

III. Polycrystalline Distribution Functions

In order to simplify the following discussion, we consider the common case where the g -tensor is diagonal with perpendicular $g_{xx} = g_{yy} = g_\perp$ and parallel $g_{zz} = g_\parallel$ components. In terms of the ratio $r \equiv g_\perp/g_\parallel$,

$$[\mathbf{n}^T g^2 \mathbf{n}] = g_\parallel^2 ((1-r^2)\cos^2 \theta + r^2) \quad (20)$$

is independent of ϕ . Two simple distribution functions $\rho(\cos \theta)$ (both independent of ϕ) will be used to demonstrate our results.

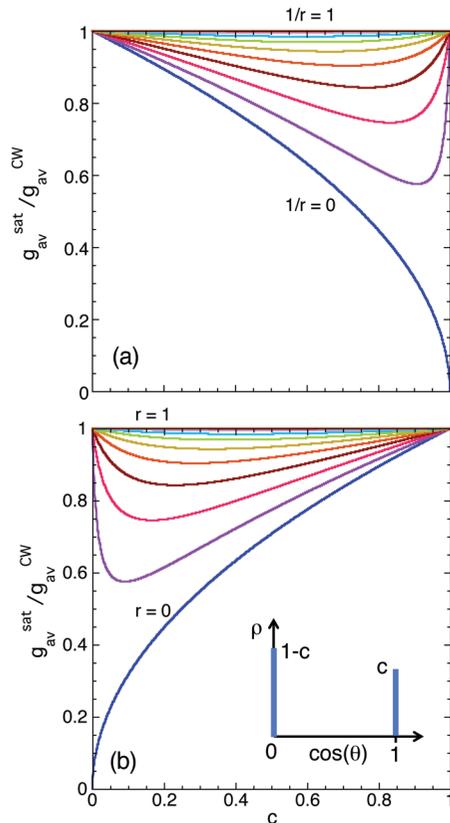


Figure 1. Ratio of average g -factors g_{av}^{sat}/g_{av}^{CW} with (a) $1/r$ and (b) r between 1 and 0 in increments of 0.1 for a bimodal distribution $\rho(\cos(\theta))$ of crystal axis with fraction c aligned along the z axis (parallel to the field) and fraction $1 - c$ aligned in the xy plane.

Figure 1 uses the bimodal distribution function

$$\rho(x) = c\delta(x - 1) + (1 - c)\delta(x) \quad (21)$$

where $x \equiv \cos \theta$. This distribution describes a polycrystalline sample with fraction c aligned along the field direction and fraction $1 - c$ aligned perpendicular to the field. For $c = 0$, $g_{av}^{CW} = g_{av}^{sat} = g_{\perp}$ and for $c = 1$, $g_{av}^{CW} = g_{av}^{sat} = g_{\parallel}$. For $0 < c < 1$, $g_{av}^{sat}/g_{av}^{CW} < 1$. In the limit $c \rightarrow 0$ for $r = 0$, $g_{av}^{sat}/g_{av}^{CW} \rightarrow 0$ because $g_{av}^{sat} \propto c$ while $g_{av}^{CW} \propto \sqrt{c}$. Results for $1/r = g_{\parallel}/g_{\perp}$ (Figure 1a) can be mapped onto the results for $r = g_{\perp}/g_{\parallel}$ (Figure 1b) with $c \rightarrow 1 - c$.

Figure 2 uses a step-function distribution with $\rho(\cos \theta)$ constant for $\theta < \theta_0$ and 0 otherwise so that the crystal axis form a cone around the field direction. The distribution with $\theta_0 < \pi/2$ may describe a sample that was partially aligned in an eicosane matrix by a high magnetic field. With $\theta_0 = \pi/2$ and $\rho(\cos \theta) = 1$, this distribution describes a nonaligned polycrystalline sample, in which case $g_{av}^{sat}/g_{av}^{CW} \rightarrow \sqrt{3}/2 \approx 0.866$ as $r \rightarrow 0$. Results for $1/r \leq 1$ and $r \leq 1$ are not simply related.

Clearly, the ratio g_{av}^{sat}/g_{av}^{CW} can be smaller for the bimodal than for the conical distribution. Since the actual distribution of polycrystalline axis may differ from one sample to another of the same compound, it is not possible to provide a definitive estimate for the ratio g_{av}^{sat}/g_{av}^{CW} . This type of variation can be seen in Table 1, where different groups obtain different estimates of g_{av}^{CW} and g_{av}^{sat} for the same compound.

As mentioned in section II, incomplete saturation of the magnetization will not affect the inequality $g_{av}^{CW} > g_{av}^{sat}$ for a polycrystalline sample. But there are several experimental factors that can lead to its violation. The strong magnetic field applied

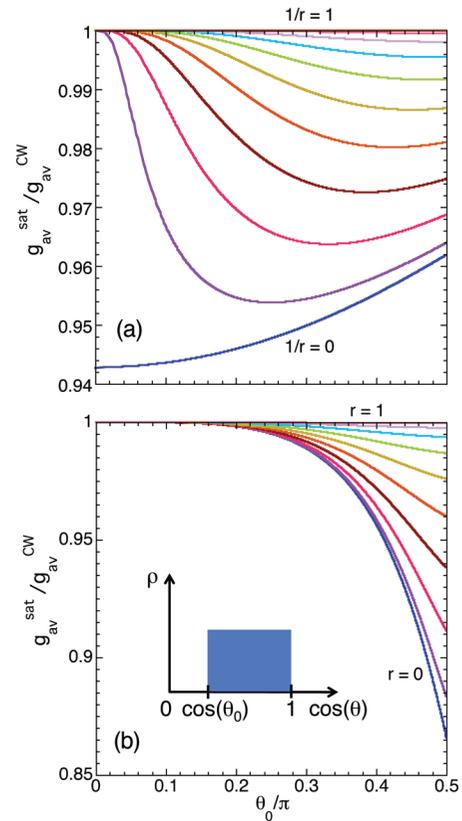


Figure 2. Ratio of average g -factors for a conical distribution $\rho(\cos(\theta))$ of crystal axis that is uniform between 1 ($\theta = 0$) and $\cos(\theta_0)$ with (a) $1/r$ and (b) r between 0 and 1 in increments of 0.1. The end point $\theta_0 = \pi/2$ describes a nonaligned polycrystalline sample.

TABLE 1: Average g -Factors Obtained from the CW Susceptibility and the Saturation Magnetization for Eight Compounds with the Anisotropic Cation $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+$

anion	g_{av}^{CW}	g_{av}^{sat}	g_{av}^{sat}/g_{av}^{CW}	ref
HDDQ ⁻	3.83	3.96	1.03	5
[HFeW ₁₂ O ₄₀] ⁻⁴	2.65	2.54	0.96	7
TCNE ⁻ (poly)	2.97	1.94	0.65	8
TCNE ⁻ ()	4.07	3.87	0.95	9
TCNE ⁻ (⊥)	1.25	1.15	0.92	9
TCNQ ⁻ (1FO)	3.07	2.15	0.70	10
TCNQ ⁻ (1FO)	3.64	3.99	1.10	11
[C ₄ (CN) ₆] ⁻	4.61	4.34	0.94	12 and 13

^a The contributions of the anion to the g -factors have been removed.

to obtain the saturation magnetization may also partially align the polycrystalline axis, thereby enhancing M_{av}^{sat} and g_{av}^{sat} . The magnetic susceptibility may not be measured at a sufficiently high temperature to eliminate the coupling between the magnetic constituents. This will depress g_{av}^{CW} for antiferromagnetic coupling and enhance g_{av}^{CW} for ferromagnetic coupling. Also keep in mind that g_{av}^{CW} and g_{av}^{sat} must be evaluated for the same polycrystalline sample with the same distribution of polycrystalline axis in order for the inequality $g_{av}^{CW} > g_{av}^{sat}$ to hold.

IV. Experimental Results for a Highly Anisotropic Cation

To apply these ideas, we consider one of the most anisotropic classes of molecule-based magnets: quasi-one-dimensional electron-transfer salts with the $S = 1/2$ cation $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+$. Sketched in Figure 3 this cation is characterized by strong anisotropy with $g_{\perp} \approx 1.25$ and $g_{\parallel} \approx 4.4$ so that the Fe spin

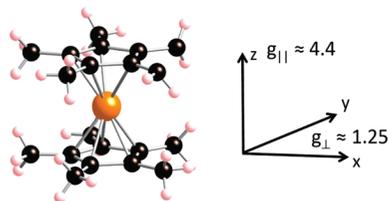


Figure 3. $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+$ cation showing two pentagons of carbon atoms, each with five methyl (Me) groups, above and below a Fe(III) ion in a low-spin $S = 1/2$ state with anisotropic g -factors g_{\perp} and g_{\parallel} .

preferentially aligns along the chain axis perpendicular to the C_5Me_5 pentagons.³ But g_{\perp} and g_{\parallel} may vary slightly from one compound to another due to the distortion of the cation induced by the neighboring anions.

For this spin-1/2 cation, the single-ion anisotropy D neglected in our earlier derivation has no effect. The intrachain exchange interaction in quasi-one-dimensional compounds with magnetic anions is of order 6 meV or 60 K.⁶ Hence, measurements of the magnetic susceptibility at room temperature should provide fairly good estimates for the average g -factor $g_{\text{av}}^{\text{CW}}$ of the $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+$ cation. Because the strong intrachain interactions can only suppress the estimated values of $M_{\text{av}}^{\text{sat}}$ and $g_{\text{av}}^{\text{sat}}$, they will not affect the inequality $g_{\text{av}}^{\text{CW}} \geq g_{\text{av}}^{\text{sat}}$.

In order to isolate the contribution of the anisotropic cation, we subtract the contribution of the anion, if any. For the average Curie constant and saturation magnetization

$$C_{\text{av}} = C(\text{anion}) + C_{\text{av}}(\text{cation}) \quad (22)$$

$$M_{\text{av}}^{\text{sat}} = M_{\text{av}}^{\text{sat}}(\text{anion}) + M_{\text{av}}^{\text{sat}}(\text{cation}) \quad (23)$$

where the anion is assumed to be isotropic. Recall that $C_{\text{av}}(\text{cation}) \propto (g_{\text{av}}^{\text{CW}})^2$ and $M_{\text{av}}^{\text{sat}}(\text{cation}) \propto g_{\text{av}}^{\text{sat}}$, where $g_{\text{av}}^{\text{CW}}$ and $g_{\text{av}}^{\text{sat}}$ are the cation contributions to the average g -factors.

Table 1 compares $g_{\text{av}}^{\text{CW}}$ and $g_{\text{av}}^{\text{sat}}$ for several $[\text{Fe}(\text{C}_5\text{Me}_5)_2]$ -based compounds with different anions or distributions $\rho(x)$. The inequality $g_{\text{av}}^{\text{CW}} > g_{\text{av}}^{\text{sat}}$ is satisfied in six of eight cases, including for the three-dimensional compound $[\text{Fe}(\text{C}_5\text{Me}_5)_2]_4[\text{HfFeW}_{12}\text{O}_{40}]$.⁷ Notice that $g_{\text{av}}^{\text{sat}}/g_{\text{av}}^{\text{CW}}$ lies between 0.92 and 0.95 for two polycrystalline samples containing the spin-1/2 TCNE⁻ anion,⁹ one primarily aligned along the field direction and the other primarily aligned in the plane perpendicular to the field.

There are two puzzling exceptions where $g_{\text{av}}^{\text{sat}} > g_{\text{av}}^{\text{CW}}$, most notably for a sample containing the spinless HDDQ⁻ anion.⁵ Although the absence of intrachain exchange interactions for the $[\text{Fe}(\text{C}_5\text{Me}_5)_2]\text{HDDQ}$ compound would seem to increase the reliability of both susceptibility and saturation measurements, the measured value for the ratio $g_{\text{av}}^{\text{sat}}/g_{\text{av}}^{\text{CW}}$ is slightly greater than 1. While the ferromagnetic (1FO) phase of the second compound with the spin-1/2 TCNQ⁻ anion¹¹ also fails to satisfy the inequality $g_{\text{av}}^{\text{sat}} < g_{\text{av}}^{\text{CW}}$, the estimated value for the ratio $g_{\text{av}}^{\text{sat}}/g_{\text{av}}^{\text{CW}} = 1.10$ may contain an experimental error greater than 10%.

V. Conclusion

One way of testing the inequality $g_{\text{av}}^{\text{CW}} \geq g_{\text{av}}^{\text{sat}}$ would be to prepare a polycrystalline HDDQ⁻ compound in an eicosane matrix¹¹ that fixes the polycrystalline axis. The high magnetic fields used to evaluate the saturation magnetization would not disturb the distribution $\rho(x)$ of polycrystalline axis and exchange within each chain would not contaminate the high-temperature magnetic susceptibility.

To summarize, this paper has demonstrated a systematic difference between the average g -factors evaluated from the Curie constant and saturation magnetization. Due to the general inequality $g_{\text{av}}^{\text{CW}} \geq g_{\text{av}}^{\text{sat}}$, the saturation magnetization and CW susceptibility will provide different estimates for the anisotropy and alignment of a polycrystalline sample. For a diagonal g -tensor with $g_{\parallel} > g_{\perp}$, $g_{\text{av}}^{\text{CW}}$ will overestimate the degree of alignment along the easy axis compared to $g_{\text{av}}^{\text{sat}}$. The inequality proven in this paper can be used to check experimental results and to guide estimates for the alignment of polycrystalline samples.

Acknowledgment. We would like to thank Prof. Janice Musfeldt for her helpful comments. This research was sponsored by the Division of Materials Sciences and Engineering of the U.S. Department of Energy (RSF) and by the U.S. National Science Foundation (Grant No. 0553573) (JSM).

Appendix: Proof of Inequality

This appendix demonstrates the inequality

$$\left(\int_0^1 dy \rho(y) f(y)\right)^{1/2} \geq \int_0^1 dy \rho(y) \sqrt{f(y)} \quad (\text{A1})$$

where $\rho(y) \geq 0$ and $f(y) \geq 0$ for any y and $\rho(y)$ is normalized to 1. It is easily shown that

$$\begin{aligned} F &\equiv \int_0^1 dy \rho(y) f(y) - \left(\int_0^1 dy \rho(y) \sqrt{f(y)}\right)^2 \\ &= \int_0^1 dy \rho(y) \left\{ \sqrt{f(y)} - \int_0^1 dz \rho(z) \sqrt{f(z)} \right\}^2 \\ &\geq 0 \end{aligned} \quad (\text{A2})$$

Since both sides of eq A1 are positive, the desired inequality follows. By converting the integral over y into a double integral over solid angles, this proof is readily generalized to show that $g_{\text{av}}^{\text{CW}} \geq g_{\text{av}}^{\text{sat}}$.

References and Notes

- (1) Kahn, O. *Molecular Magnetism*; VCH: New York, 1994.
- (2) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Ions*; Dover: New York, 1970.
- (3) (a) Dugan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 955. (b) Ammeter, J. H. *J. Magn. Reson.* **1978**, *30*, 299. (c) Miller, J. S.; Glatzhofer, D. T.; O'Hare, D. M.; Reiff, W. M.; Chakraborty, A.; Epstein, A. J. *Inorg. Chem.* **1989**, *28*, 2930.
- (4) White, R. M. *Quantum Theory of Magnetism*; Springer: Berlin, 2007.
- (5) Gebert, E.; Reis, A. H., Jr.; Miller, J. S.; Rommelmann, H.; Epstein, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 4403.
- (6) Her, J.-H.; Stephens, P. W.; Ribas-Arino, J.; Novoa, J. J.; Shum, W. W.; Miller, J. S. *Inorg. Chem.* **2009**, *48*, 3296.
- (7) Le Magueres, P.; Ouahab, L.; Golhen, S.; Grandjean, D.; Pena, O.; Jegaden, J.-C.; Gomez-Garcia, C. J.; Delhaes, P. *Inorg. Chem.* **1994**, *33*, 5180.
- (8) Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Chittipeddi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769.
- (9) Chittipeddi, S.; Selover, M. A.; Epstein, A. J.; O'Hare, D. M.; Manriquez, J.; Miller, J. S. *Synth. Met.* **1987**, *27*, B417.
- (10) Broderick, W. E.; Eichhorn, D. M.; Liu, S.; Toscano, P. J.; Owens, S. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1995**, *117*, 3641.
- (11) Taliaferro, M. L.; Palacio, F.; Miller, J. S. *J. Mat. Chem.* **2006**, *16*, 2677.
- (12) Miller, J. S.; Zhang, J. H.; Reiff, W. M. *J. Am. Chem. Soc.* **1987**, *109*, 4584.
- (13) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201.