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CRYSTALLOGRAPHIC TEXTURE DETERMINATIONS FROM INVERSE SUSCEPTIBILITY MEASUREMENTS

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Abstract:

Determination of the quantitative relationship between crystallographic texture and magnetic properties in advanced permanent magnets may be hampered by complex microstructures, which complicate methods that rely on diffraction, or by interparticulate interactions, which adversely affect methods based on magnetic remanence measurements. To this end, new techniques in the determination of texture of bulk permanent magnets are being explored to overcome these inherent experimental difficulties. The analysis of inverse paramagnetic susceptibility measurements constitutes a new method to investigate crystallographic texture. Such measurements also provide Curie temperature data, which is sensitive to chemical changes that may have occurred in the magnetic phase during processing.

The mathematical formalism underlying the analysis of inverse susceptibility measurements is outlined, and is used to evaluate magnetic measurements taken from a series of $Nd_2Fe_{14}B$ magnets that have been processed by different means, and thus contain different degrees of texture. While

this method does provide qualitative information concerning the relative crystallographic alignment of magnet samples, it needs calibration to obtain an explicit value for a texture order parameter.

Introduction:

Improvements in processing to approach an ideal degree of crystallographic texture are desired for the engineering of increasingly higher $(BH)_{max}$ magnets. Unfortunately, the degree of crystallographic alignment in bulk magnets is sometimes difficult to determine. A number of methods based on a variety of techniques, such as magnetic measurements, x-ray diffraction and microscopy methods exist to evaluate texture, but there are limitations to the application of each technique. By way of example, the anticipated début of two-phase anisotropic "exchange-spring" magnets consisting of a magnetically soft phase intimately mixed with an aligned hard phase (1) presents significant challenges in the determination of the degree of orientation of the ensemble of crystallites. In this case the exchange interactions amongst the constituent phases nullify the use of techniques that utilize measurements of the remanence B_r, such as the angular dependence of B_r (2) or the remanence ratio B_r/M_s (3).

The analysis of the temperature dependence of the inverse paramagnetic susceptibility $1/\chi_p$ provides an alternative method to obtain information concerning crystallographic texture. Because the material is probed while it is in a paramagnetic state there are no interphase or intergranular interactions to affect the data. This method also allows an examination of the samples' paramagnetic Curie temperatures, allowing one to easily monitor any chemical changes that may have occurred in the paramagnetic phase during

processing. We present here the mathematical formalism used to examine the inverse susceptibility, and then apply the results to a series of $Nd_2Fe_{14}B$ magnets that have been fabricated by different processes.

Theoretical Framework:

The paramagnetic susceptibility χ of a material of uniaxial symmetry is a second-rank tensor with two distinct elements: the susceptibilities for magnetic field parallel and perpendicular to the symmetry axis (4). Thus, in principle, if one has a suitable single crystal with which to establish these two tensor elements, it is possible to use a measurement of the susceptibility of a textured polycrystal to estimate the degree of texture present. This work will address only the case of measurements made at temperatures high enough such that a Curie-Weiss-type temperature dependence is observed. Practically speaking, the data must be taken at elevated temperatures that are at least 50 K above the Curie temperature of the phase of interest. In such cases the distinct elements of the susceptibility tensor of each crystallite have the form:

$$\chi_{i=}\frac{C_i}{(T-\theta_i)} \qquad (1)$$

where i denotes either the basal (ab) or the axial (c) component. In principle, both the Curie constant C_i and the paramagnetic Curie temperature θ_i depend on the direction of

the magnetic field with respect to the crystallite axis. Bowden *et al.* (5) have considered the case of anisotropy in the paramagnetic Curie temperature θ_i that arises from crystal field effects, while Niira and Oguchi (6) have discussed the anisotropy of the Curie constant C_i which can arise from anisotropic g-factors. Anisotropy of C_i can also arise from anisotropic exchange. If it is assumed that both θ_i and C_i are anisotropic, then the transformation properties of second rank tensors (4) show that the paramagnetic susceptibility of an ensemble of independent crystallites, a good approximation to a polycrystal in the Curie-Weiss regime of paramagnetism, even for exchange-coupled two-phase materials, is given by:

$$\chi_p = \frac{C_c}{T-\theta_c} + \langle n^2 \rangle \cdot \left[\frac{C_{ab}}{T-\theta_{ab}} - \frac{C_c}{T-\theta_c} \right] \qquad (2)$$

where $\langle n^2 \rangle$ is an ensemble average of the square of the cosine n_i of the angle between the symmetry axis of each crystallite and the applied field. The texture dependence of $\langle n^2 \rangle$ is the key to using the paramagnetic susceptibility as a measure of crystallographic texture: for a random polycrystal $\langle n^2 \rangle = \frac{1}{3}$, while for a perfectly axially-textured polycrystal $\langle n^2 \rangle = 1$. It is convenient to introduce a texture order parameter Σ which lies in the range $0 \leq \Sigma \leq 1$ for these cases as a measure of the axial texture:

$$\Sigma = \frac{\langle n^2 \rangle - \frac{1}{3}}{1 - \frac{1}{3}} \qquad (3)$$

Thus Σ is valid in the range $-1/2 \leq \Sigma \leq 1$, where $\Sigma=1/2$ describes the isotropic two-dimensional case with all symmetry axes in a plane, $\Sigma=0$ describes the random alignment case, and $\Sigma=1$ is the uniaxially-aligned case. In terms of the texture order parameter Σ, the susceptibility of the polycrystal is

$$\chi_p = \frac{1}{3} \cdot \left\{ \frac{2C_{ab}}{T - \theta_{ab}} + \frac{C_c}{T - \theta_c} \right\} + \frac{2\Sigma}{3} \cdot \left\{ \frac{C_c}{T - \theta_c} - \frac{C_{ab}}{T - \theta_{ab}} \right\} \qquad (4)$$

If the single crystal parameters C_{ab}, C_c, θ_{ab} and θ_c are known, then a measurement of the polycrystalline susceptibility yields the texture order parameter Σ for the polycrystal. This, however, is not always the case, since processing may alter the values of C_i and θ_i as well as the texture. Thus it is of value to simplify and approximate Eq. (4). The experimental data of Burzo *et al.* (8) and Liu *et al.* (9) show that the deviation of the paramagnetic Curie temperature θ_p from the thermodynamic Curie temperature T_C is small compared with T_C for both polycrystals (8) and single crystals (9). Furthermore, these data plus our own work show that the anisotropy of θ_p, $\frac{(\theta_c - \theta_{ab})}{T_c}$, is also small. To first order in this anisotropy and in the anisotropy of the Curie constant, $\frac{(C_c - C_{ab})}{C_c}$, Eq. (4) becomes:

$$\chi_p^{-1} \cong \left(\frac{T}{\theta_p} - 1\right) \cdot \left\{\frac{T_c}{C_c} \cdot \left[1 - \frac{2}{3} \cdot \left(\frac{\Delta C}{C_c} - \frac{\Delta\theta}{T_c}\right) \cdot \Sigma\right]\right\} = \left(\frac{T}{\theta_p} - 1\right) \cdot \Omega \qquad (5)$$

where θ_p and T_C are the paramagnetic and thermodynamic Curie temperatures, respectively, of the polycrystal and $\Delta C \equiv C_c - C_{ab}$, $\Delta\theta \equiv \theta_c - \theta_{ab}$. In the derivation of Eq. (5) it was assumed that the deviation of θ_p from T_C arises from crystal field effects only, and that, following the use of experimental crystal field coefficients of Boltich and Wallace (7) in the theory of Bowden *et al* (5), $\theta_c > \theta_{ab}$..

From Eq. (5) we see that a plot of the inverse susceptibility χ_p^{-1} versus the scaled temperature $\frac{T}{\theta_p}$ yields a straight line with a slope Ω that varies linearly with the texture order parameter Σ. The condition that this slope increases with decreasing texture, as is observed experimentally and discussed in the next section, is simply that $\frac{C_c - C_{ab}}{C_c} > \frac{\theta_c - \theta_{ab}}{T_c}$, *i.e.*, that the fractional anisotropy of the Curie constant be dominant over the fractional anisotropy of the paramagnetic Curie temperature.

Experimental Procedures and Results:

Magnetic measurements were made on a series of samples with nominally the same composition but processed in different manners. The nominal compositions and processing details of the samples are listed in Table I. The samples were cut with a slow-speed wire saw to the appropriate dimensions to fit inside quartz capillary tubes. The tubes were

evacuated to a base pressure of 5.6×10^{-5} torr and sealed with Zr turnings to avoid oxidation during measurement (10). Prior to each high-temperature hysteresis loop measurement the magnets were brought to temperature and then saturated in an applied field of +5.0 T. The resultant hysteresis loops were adjusted for demagnetization with a geometric correction.

In every case the magnets were confirmed to consist mainly of $Nd_2Fe_{14}B$ with a small amount, on the order of 0.1 vol%, of an unknown ferromagnetic phase that has a Curie temperature T_C in the vicinity of 950 °C (11). Additionally, room-temperature saturation magnetization measurements indicate that the sintered sample contains only 86% of the $Nd_2Fe_{14}B$ phase, the remainder presumably being the 1-4-4 phase; the slope of the paramagnetic signal was adjusted for this deficiency. The paramagnetic signal from the 2-14-1 matrix phase and the ferromagnetic signal of the unknown phase were separated from one another (11). Fig. 1 shows the inverse of the susceptibility of the paramagnetic portion of the signal graphed as a function of reduced temperature, T/θ_P, where θ_P was determined experimentally to be the linear extrapolation of the inverse susceptibility to the temperature axis. The paramagnetic Curie temperatures θ_P for each sample are included in the legend of Fig. 1. Fig. 1 also displays the susceptibilities taken from the literature of isotropic single-phase $Nd_2Fe_{14}B$ powder (8) and a $Nd_2Fe_{14}B$ single crystal (9), measured along the easy-axis *c*-direction. It

should be noted that Liu *et al.* (9) determined the single crystal to possess a Curie temperature of 574 K, approximately 20 degrees lower than the accepted literature values of 595 K - 600 K. In accordance with the formalism outlined above, the experimental inverse susceptibilities *vs.* reduced temperature curves exhibit slopes that increase with decreasing sample alignment. The inverse susceptibility slopes increase from the single crystal and MQ-3 sample to the sintered sample and are highest for the powder and hot-pressed samples.

It is reassuring that the two isotropic samples, the powder and the hot-pressed samples, both exhibit very similar slopes. However, it is not expected that the single crystal and the MQ-3 sample would have exactly the same slope; it appears that the slope of the inverse susceptibility curve is not sensitive to small misorientation angles. This empirical observation may be understood by way of the analysis of the construction of a simple "box distribution" to describe the distribution of misorientation angles between the symmetry axes of the constituent crystals and the overall deformation direction. For the box distribution the population of crystal axes is uniform over a solid angle for misorientation angles less than Φ, whereas there are no crystals with such misorientation for angles greater than Φ. If the "box distribution" is chosen so as to match its variance with that of the true distribution, the cutoff parameter Φ is approximately 2.7 times the half-width at half-maximum (HWHM) of the rocking

curve. The texture order parameter Σ of Eq. 5 may be related to the box-distribution cut-off angle Φ as:

$$\Sigma \cong \frac{\cos\Phi \sin^2\Phi}{2\cdot[1-\cos\Phi]} \tag{6}$$

This expression is graphed in Fig. 2. Note that for good textures, with only small deviations from uniaxial alignment, the texture order parameter may be approximated as $\Sigma \approx \left[1-\left(\frac{\Phi^2}{2}\right)\right]$. This result means that small misorientation deviations from ideal alignment do not significantly affect the paramagnetic susceptibility because of the quadratic variation in Φ; this situation appears verified experimentally, as noted above.

Summary:

The methodology and underlying rationale for a new technique that may be used to probe the crystallographic texture distribution in a polycrystalline magnetic material have been presented. The use of paramagnetic susceptibility measurements, while preliminary, may prove to be useful in circumstances that preclude the use of the more standard determinations of magnetic remanence, B_r, such as in the case of novel exchange-spring magnets. The trend of the inverse paramagnetic susceptibility *vs.* temperature data collected from a selection of $Nd_2Fe_{14}B$-based magnetic materials fabricated by different methods agrees with that predicted from a

simple linearization of the Curie-Weiss law for textured polycrystals that has been rewritten to take into account both anisotropic paramagnetic Curie temperatures and anisotropic Curie constants. While this method does provide qualitative information concerning the relative crystallographic alignment of magnet samples, it needs calibration to obtain an explicit value for the texture order parameter.

Acknowledgments

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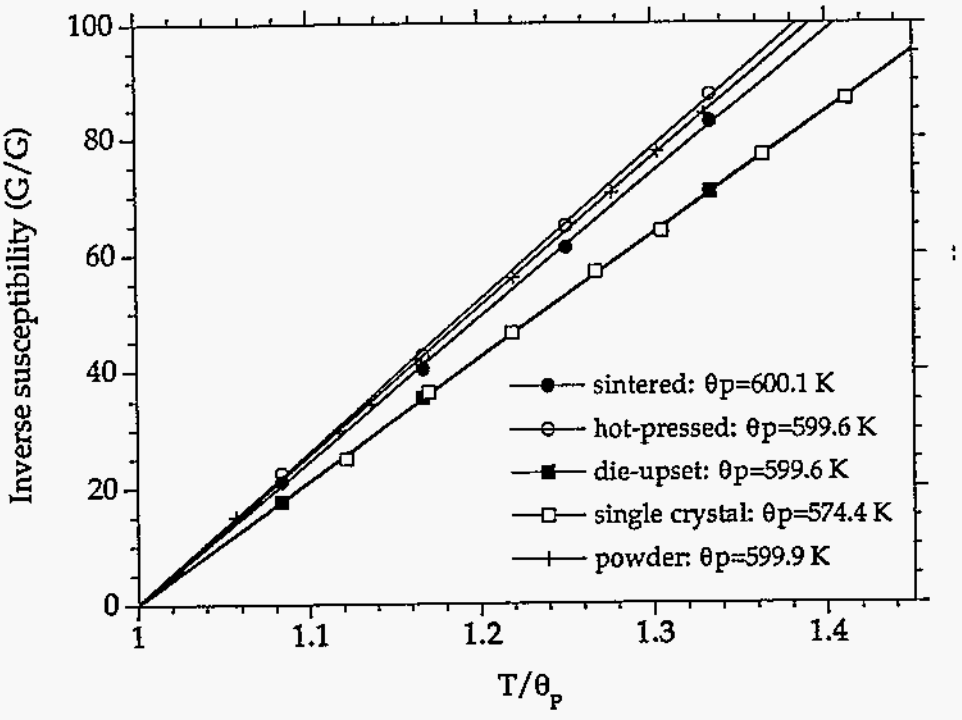
Table I: Descriptions of $Nd_2Fe_{14}B$-based samples:

Processing	*Bulk Composition*
Die-upset (MQ-3)	$Nd_{13.75}Fe_{80.25}B_6$
Sintered	$Nd_{15}Fe_{78.5}B_{6.5}$
Hot-pressed (MQ-2)	$Nd_{13.75}Fe_{80.25}B_6$

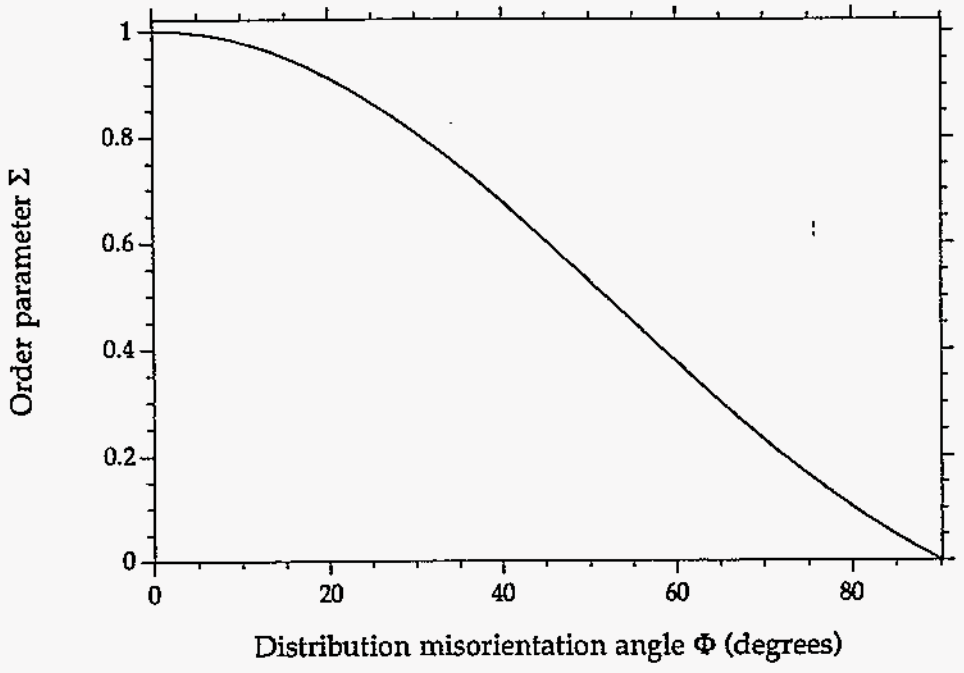
Figure Captions:

1. Inverse susceptibilities of $Nd_2Fe_{14}B$ magnetic materials processed in various manners.

2. The order parameter Σ, based on the "box distribution" as defined in the text, as a function of crystallite misorientation angle.



L. H. Lewis, et al., FE-13, MMM'96 Fig. 1



L. H. Lewis, et al., FE-13, MMM'96 Fig. 2