Materials Research Express

PAPER

Structural and magnetic properties of RE-Al substituted nanocrystalline hexaferrites (Sr$_{1-x}$RE$_x$Al$_2$Fe$_{10}$O$_{19}$)

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Keywords: hexaferrite, rare-earth substitution, aluminum substitution, ball milling, structural properties, magnetic properties

Abstract

We describe the synthesis and characterization of magnetic materials with improved magnetic properties for permanent magnet applications. Sr$_{1-x}$RE$_x$Al$_2$Fe$_{10}$O$_{19}$ (RE = La, Ce, Tb, and Dy; $x = 0.0$ and $0.1$) were prepared by ball milling and sintering at $1200$ °C for 6 h. The effects of (Al$^{3+}$–RE$^{3+}$) substitution on the structural and magnetic properties of SrM hexaferrites were investigated by x-ray diffraction, scanning electron microscopy, and magnetic measurements at low (5 K), and high temperatures (from room temperature to above Curie temperature). The sample with $x = 0$, and that with La substitution, consisted of a single SrM phase. The rest of the samples contained traces of secondary oxide phases, and exhibited a small reduction in lattice parameters compared with the unsubstituted SrFe$_{12}$O$_{19}$. The coercivity of the samples ($8800 \leq H_C \leq 9750$ Oe) was more than double the standard value of the unsubstituted compound, and the Curie temperatures was $>300$ °C for all samples. Also, the saturation magnetization ($32.5–46.4$ emu g$^{-1}$) was high enough to make the overall magnetic properties of these compounds potentially important for the permanent magnet industry.

1. Introduction

The permanent magnet (PM) industry faces real challenges in producing high performance magnets with high operating temperature and chemical and thermal stability at a reasonably low cost. The first generation of rare-earth (RE) Sm–Co high performance PM, the (1–5) with composition (SmCo$_5$), was discovered in the mid-1960s, and introduced to the market in 1970. Further improvements led to the development of the second generation, the (2–17) family with the nominal commercial composition Sm(Fe, Co, Cu, Zr)$_{6–7}$, which was introduced to the market in 1980 as a PM far superior to pre-existing ones ([1, 2] and references therein).

Commercial Sm–Co PMs were produced with a remnant magnetization of $\sim 60–110$ emu g$^{-1}$, and high intrinsic coercivity of $4.5–25$ kOe. However, due to the high market price of Sm and Co, huge efforts were made to produce a new generation of RE magnets, free of Sm and Co. These efforts culminated in the discovery of the first new Nd–Fe–B magnet in the 1980s, with remnant magnetization of $137$ emu g$^{-1}$ and intrinsic coercivity of $33$ kOe. Nevertheless, the high production cost balanced the reduction of the raw material cost, and the market price of Nd–Fe–B magnets remained relatively high. Further, the low operating temperature ($\sim 100$ °C) of the first generation of Nd–Fe–B magnets limited their use in motors and generators [3]. Better thermal stability at higher temperatures ($\sim 200$ °C) was achieved by adding a RE element such as Dy. Unfortunately, the market price of Dy is extremely volatile, which imposes a new challenge to the PM industry. Under these considerations, M-type hexaferrite permanent magnets, although exhibiting lower performance, emerged as the most cost effective materials as extrapolations to the year 2022 indicated [4].

Hexaferrite materials were discovered and characterized in the early 1950s [5–7], and received exponentially increasing interest since then due to their practical importance [8, 9]. In addition to cost effectiveness, BaM hexaferrites (BaFe$_{12}$O$_{19}$) are easy to produce with a wide range of tunable magnetic properties [10–12], and
chemical stability required for a wide range of applications [8, 13–21]. The magnetic properties of BaM hexaferrites can be effectively modified by different substitutions for Ba2+ or Fe3+ ions. The Sr2+ substitution for Ba2+ resulted in improvement of the magnetic properties of M-type hexaferrite ([11] and references therein). Also, Al3+ was long recognized as an agent which improves the magnetic properties and limits grain growth, preventing the deterioration of the coercivity at elevated sintering temperatures [22]. The solubility of Al3+ in the hexaferrite is high, allowing for a wide range of tunable coercivity. Specifically, it was found that it is possible to substitute up to 50% of the Fe3+ ions in BaM, and 100% in SrM, by Al3+ ions to produce nanoparticles promising for imaging applications [23]. Further studies confirmed the effectiveness of Al3+ substitution for Fe3+ for enhancing the coercivity. Specifically, 6.7% substitution resulted in a 43% enhancement of the coercivity (from 4.2 kOe to 6.0 kOe), and a 45% increase of the magnetocrystalline anisotropy field, but a reduction of the saturation magnetization from 72 emu g−1 to 50 emu g−1 [24]. Higher levels of Al3+ substitution resulted in a significant increase of the coercivity and a larger decrease in saturation magnetization [25–27].

Partial substitution of RE elements for Ba or Sr was carried out by several investigators in attempts to improve the magnetic properties of M-type hexaferrites [28–32]. Substituting La3+ for Sr in Sr1–xLa1xFe12O19 hexaferrites improved the saturation magnetization and coercivity up to x = 0.3, whereas higher substitution levels resulted in deterioration of the magnetic properties [31]. On the other hand, the substitution of Sr by Pr resulted in an improvement of the coercivity with practically constant saturation magnetization and remanence up to x ∼ 0.11, but a decline of both parameters at x = 0.2 [33]. Also, the substitution of different RE elements for Sr in Sr0.9RE1.1Fe10Al2O19 hexaferrites prepared by auto-combustion resulted in a significant increase of the coercivity, accompanied with a decrease in saturation magnetization [27]. However, the previous studies did not address the effect of substitution of the high Z end of the RE series. Due to the effectiveness of high-level Al substitution in significantly increasing the coercivity of SrM ferrite, the present study was designed to prepare Sr1–xRExAl12Fe10O19 (RE = La, Ce, Tb, and Dy; x = 0.0 and 0.1) hexaferrites by high energy ball milling, and investigate their structural and magnetic properties, with the objective of examining the effect of preparation method, and extending the study to include Tb and Dy at the far end of the RE series.

2. Experimental procedure

Ferrite samples of Sr1–xRExAl12Fe10O19 (RE = La, Ce, Tb and Dy; x = 0, 0.1) were prepared from specpure SrCO3, Fe2O3, Al2O3 and RE2O3 powders (Sigma Aldrich-make). Wet milling in an acetone bath was performed in two zirconia cups, using zirconia balls, with ball-to-powder mass ratio of (12:1). The milling was carried out at a rotational speed of (250 rpm) for 16 h, and the resulting powder was left to dry in air at room temperature. The dry powder was collected, and disk-shaped pellets (approximately 1.25 cm diameter and ~1 mm thickness) were compacted under a force of 5 tons. The disks were then sintered in air at 1200 °C for 6 h in a zirconium oxide crucible.

XRD measurements were made in the angular range 20° ≤ 2θ ≤ 70° using Cu-Kα radiation (λ = 1.5405 Å) in an XRD 7000-Shimadzu diffractometer. Data analysis included phase identification using X’Pert PRO HighScore and structural refinement using FULLPROF software [34]. The size and morphology of the particles in the samples were examined by SEM using FEI-Inspect F50/FEG electron microscope. The magnetic measurements in applied magnetic field strength up to 70 kOe were obtained at room temperature (305 K) and at 5 K using an MPMS 3 SQUID Quantum Design magnetometer. Thermomagnetic measurements, at a constant applied field of 100 Oe, were performed in the temperature range from room temperature to well above the Curie temperature, using a VSM Micromag 3900, Princeton Measurements Corporation vibrating sample magnetometer.

3. Results and discussion

3.1. Rietveld analysis

Rietveld refinement of the XRD patterns of the Sr1–xRExAl12Fe10O19 (RE = La, Ce, Tb and Dy; x = 0, 0.1) hexaferrites was carried out to explore the crystallographic phases in the samples, and determine the refined structural parameters. Figure 1 shows the refined patterns of the samples with x = 0 (SAF), and with La–Al substitution (SLAF), where the black solid spheres represent the experimental data, the red continuous line represents the refined theoretical pattern, and the blue line below the pattern represents the difference curve. The horizontal difference curve with small ripples only at the positions of the Bragg peaks, together with the relatively low values of the Rp and Rp reliability factors and goodness of fit χ², are indications of a reliable fit of the experimental data with the theoretical pattern for SrM hexagonal phase with the standard pattern (ICPDS: 00-033-1340). The Bragg peak positions of the standard phase are indicated by the set of small vertical (green)
ticks below the patterns. The absence of any signature of other impurity phases indicated that the substituted 
Al$^{3+}$ ions in these two samples were completely incorporated in replacing Fe$^{3+}$ ions in the hexaferrite lattice. The 
refined lattice parameters and reliability factors are listed in table 1.

Rietveld refinement of the XRD patterns of the remaining samples (figure 2), however, revealed 
crystallization of a major SrM hexaferrite phase, in addition to traces of α-Fe$_2$O$_3$ (whose Bragg peak positions are 
indicated by the second set of vertical green ticks) and other minor phases (with Bragg peak positions indicated 
by the third set of vertical green ticks). Specifically, the third phase is CeO$_2$ (JCPDS: 00-034-0394) for Ce–Al substitution (SCAF), Tb$_5$Fe$_{12}$O$_{31}$ (JCPDS: 01-071-0697) for Tb–Al substitution (STAF), and Dy$_2$O$_3$ (JCPDS: 00-018-0475) for Dy–Al substitution (SDAF). The presence of secondary RE oxide phases was also confirmed in Nd- and Pr-substituted SrM hexaferrites, and was attributed to limited solubility of these rare earths in the 
hexaferrite [35]. The refined lattice parameters ($a$ and $c$), cell volume ($V$), reliability factors ($R_b$ and $R_p$), and the 
measure of the goodness of fit ($\chi^2$) of SrM phase in the samples are also listed in table 1. The results indicated

![Rietveld refined XRD patterns of SrAl$_2$Fe$_{10}$O$_{19}$ and Sr$_{0.9}$La$_{0.1}$Al$_2$Fe$_{10}$O$_{19}$ samples. The standard pattern for SrM is shown for comparison.](image)
Table 1. Structural refinement results for $\text{Sr}_{1-x}\text{RE}_x\text{Al}_2\text{Fe}_{10}\text{O}_{19}$ (RE = La, Ce, Tb and Dy; $x$ = 0 and 0.1).

| Sample                  | $a$ (Å) | $c$ (Å) | $V$ (Å³) | $R_B$ | $R_F$ | $\chi^2$ |
|-------------------------|---------|---------|----------|-------|-------|----------|
| SAF ($\text{SrAl}_2\text{Fe}_{10}\text{O}_{19}$) | 5.84    | 22.96   | 678.1    | 0.80  | 0.72  | 1.61     |
| SLAF ($\text{Sr}_{1-x}\text{La}_x\text{Al}_2\text{Fe}_{10}\text{O}_{19}$) | 5.83    | 22.91   | 674.4    | 0.81  | 1.22  | 1.70     |
| SCAF ($\text{Sr}_{1-x}\text{Ce}_x\text{Al}_2\text{Fe}_{10}\text{O}_{19}$) | 5.83    | 22.94   | 675.2    | 2.9   | 3.05  | 1.06     |
| STAF ($\text{Sr}_{1-x}\text{Tb}_x\text{Al}_2\text{Fe}_{10}\text{O}_{19}$) | 5.84    | 22.95   | 677.9    | 1.11  | 1.65  | 1.53     |
| SDAF ($\text{Sr}_{1-x}\text{Dy}_x\text{Al}_2\text{Fe}_{10}\text{O}_{19}$) | 5.84    | 22.95   | 677.9    | 1.04  | 1.68  | 1.60     |

Figure 2. Rietveld refined XRD patterns of $\text{Sr}_{0.9}\text{RE}_{0.1}\text{Al}_2\text{Fe}_{10}\text{O}_{19}$ (RE = Ce, Tb, and Dy) samples.
The low porosity of all samples exhibited a decreasing tendency with substitution La except for Tb substitution, which could be associated with the smaller ionic radii for the RE elements compared with Sr [37]. However, these structural parameters revealed a slight increasing tendency from La→Al→Dy→Al substitution, which is contrary to expectations based on the decrease of ionic radius in the sequence La→Ce→Tb→Dy [37]. This result could therefore be associated with lattice distortions, which increase with the increasing difference between the radius of the RE element and the Sr element. Such distortions were reported to occur when Ba$^{2+}$ ions were replaced by the smaller Sr$^{2+}$ ions in M-type hexaferrites [36].

The x-ray densities ($\rho_x$) for the samples were calculated using the relation:

$$\rho_x = \frac{2M_W}{N_A V}$$

(1)

Here $M_W$ is the molecular mass, $N_A$ is Avogadro’s number and $V$ is the unit cell volume. The results listed in table 2 indicated that the x-ray density for all RE–Al substituted samples was 0.6%–1.0% higher than the density of the RE-free sample. The small increase is partially attributed to the increase of the molecular mass with RE substitution (RE elements La→Dy have molecular masses of 138.91 g mol$^{-1}$→162.5 g mol$^{-1}$, which are higher than 87.62 g mol$^{-1}$ for Sr), and partially to the decrease of the cell volume. However, the x-ray density exhibited a decreasing tendency with substitution La→Dy, despite the increase of molecular mass (1099.09 g mol$^{-1}$→1011.45 g mol$^{-1}$). Here, the % increase of the cell volume (674.4 Å$^3$→677.9 Å$^3$) is greater than the % increase of the molecular mass in this direction, resulting in an expected net decrease of the density as suggested by equation (1).

The bulk density ($\rho_b$) of all samples was measured by Archimedes method, and the results are listed in table 2. The bulk density is usually lower than the theoretical x-ray density due to the porous ceramic structure of the ferrites. The porosity ($p$) of the sample is defined by the relation:

$$p = 1 - \frac{\rho_b}{\rho_x}$$

(2)

The results in table 2 indicated that the measured bulk density was high, approaching the theoretical density. The low porosity of all samples (<5%) makes it possible to prepare highly dense magnets (with density up to >90% of the theoretical density) from the prepared hexaferrite powders. Further, a tendency of decreasing porosity with RE substitution (except for Tb) was observed, where the lowest porosity of 2.4% was recorded in the case of Dy substitution.

The crystallite size ($D$) along a given crystallographic direction perpendicular to a reflecting plane ($hkl$) was calculated using the Stokes-Wilson formula [38]:

$$D = \frac{\lambda}{\beta \cos \theta}$$

(3)

Here $\lambda$ is the wavelength of x-ray radiation (1.5406 Å), $\theta$ is the position of the peak corresponding to the ($hkl$) reflection, and $\beta$ is the integral breadth of the diffraction peak (ratio of the peak area to peak maximum). The integral breadth of the peak was determined by fitting the peak, and then corrected for instrumental broadening using a Si standard sample. The (110) peak at 2$\theta \approx 30.3^\circ$ and the (107) peak at 2$\theta \approx 32.2^\circ$ were used to probe the crystallite sizes in the direction perpendicular to the corresponding crystallographic planes, and the results are listed in table 3. The results indicated that all samples were nanocrystalline. Also, within experimental uncertainty (±10 nm), the crystallite size in the two directions were similar for all samples except for the STAF sample, where the crystallite size along the basal plane (110) was obviously larger. This suggests that the crystallites in this latter sample grew in platelet-like shapes, whereas in the rest of the samples the crystallites grew almost uniformly in all crystallographic directions.

### Table 2. Bulk density $\rho_b$, x-ray density $\rho_x$, and the porosity of the (Sr$_{1-x}$RE$_x$Fe$_{12}$O$_{19}$, RE = La, Ce, Tb and Dy; $x = 0$ and 0.1).

| Sample | $\rho_b$ (g cm$^{-3}$) | $\rho_x$ (g cm$^{-3}$) | $p$ (%) |
|--------|------------------------|------------------------|--------|
| SAF    | 4.92                   | 4.71                   | 4.3    |
| SLAF   | 4.97                   | 4.76                   | 4.2    |
| SCAF   | 4.96                   | 4.78                   | 3.6    |
| STAF   | 4.95                   | 4.72                   | 4.6    |
| SDAF   | 4.95                   | 4.83                   | 2.4    |
3.2. SEM results
SEM images in figure 3 were used to investigate the particle size and morphology in the Sr$_{1-x}$RE$_x$Al$_2$Fe$_{10}$O$_{19}$ (RE = La, Ce, Tb and Dy, $x = 0$ and 0.1) samples. The images indicated that all samples consisted of agglomerations of particles with small size, and the morphology did not change noticeably with different RE substitutions. However, evidence of growth of platelet-like particles was observed in the STAF sample, as demonstrated by the encircled particles in the image of this sample. This result is consistent with the platelet-like crystallite growth in this sample as concluded from the analysis of the XRD patterns. The majority of the particles in all samples demonstrated a size distribution in the range 300 nm–400 nm, which is within the critical single domain size [39].

3.3. Magnetic measurements
The hysteresis loops of the Sr$_{1-x}$RE$_x$Al$_2$Fe$_{10}$O$_{19}$ (RE = La, Ce, Tb and Dy; $x = 0$ and 0.1) samples were measured at room temperature (305 K) and at 5 K, in an applied field strength up to 70 kOe. The room temperature hysteresis loops (figure 4) indicated that all samples are magnetically hard, and full magnetic saturation was not reached even at an applied field of 70 kOe. Therefore, the law of approach to saturation was used to determine the saturation specific magnetization ($\sigma_s$) for each sample. However, the remnant specific magnetization ($\sigma_r$), and the intrinsic coercivity ($H_{M}$) were obtained directly from the hysteresis loops, and the results are listed in table 4. Also, the $B$-$H$ curves were constructed from the hysteresis loops, where the magnetic induction is $B = H + 4\pi M$ ($M$ is the magnetization in emu/cm$^3$). A representative $B$-$H$ curve for the sample SAF is shown in figure 5 in the field range from $-15$ kOe to $+15$ kOe. Such curves were used to determine the

| Sample | Crystallite size $D$ (nm) |
|--------|--------------------------|
| SAF    | 53 56                    |
| SLAF   | 55 67                    |
| SCAF   | 65 79                    |
| STAF   | 103 74                   |
| SDAF   | 74 80                    |

Table 3. The crystallite size of the SrM phase in Sr$_{1-x}$RE$_x$Al$_2$Fe$_{10}$O$_{19}$ samples.
physical coercivity ($H_{cB}$) listed in Table 4, and to investigate the linearity of the $B$–$H$ relation in the second quadrant, which is a critical parameter for the stability of the magnet performance. Figure 6 shows that the $B$–$H$ relations in the second quadrant are linear, indicating stable permanent magnet performance up to $H_{cB}$. It is
worth mentioning that the sudden drop in the magnetization of the sample STAF when a small reverse field is applied could be associated with the presence of the soft garnet phase in this sample, as confirmed by the XRD analysis.

The room temperature magnetic data listed in table 4 revealed superior magnetic properties of the SAF, SLAF, and SCAF samples compared with samples prepared by the sol—gel method and sintered at 1100 °C [27]. Further, the magnetic parameters for the STAF and SDAF samples were similar to the highest parameters reported for other RE substituted SrAl₂Fe₁₀O₁₉ samples [27]. However, in a recent study [40], it was shown that the Ca–Al substitution in SrM hexaferrites was more effective, were a coercivity of 21.3 kOe, close to the higher end of the coercivity of the Sm–Co magnets, was reported for Sr₀.₆₇Ca₀.₃₃Fe₈Al₄O₁₉ compound. The Ca–Al substituted ferrites, in spite of the rather low saturation magnetization they exhibited, demonstrated potential for the production of low cost materials with very high coercivity and sub-terahertz natural ferromagnetic resonance [40]. The saturation magnetization of the present samples, as well as that reported for other Al-substituted M-type hexaferrites, was lower than the value of \( \sim 70 \) emu g\(^{-1}\) reported for the unsubstituted SrM hexaferrite. The observed decrease could be associated mainly with two factors, namely, the preferential substitution of Al\(^{3+}\) ions at spin-up Fe\(^{3+}\) sites, and spin canting due to the reduction of the superexchange interactions between spin-up and spin-down sublattices [41]. The reduction of the saturation magnetization due to partial RE substitution for Sr in M-type hexaferrites was also reported by others [30, 42, 43].

Further, the hysteresis loops for all samples were measured at 5 K and compared with the hysteresis loops at 305 K. Representative curves for the SAF and STAF samples are shown in figure 7. These loops exhibited the usual higher magnetization at 5 K, and the decrease in the coercivity, which is a characteristic feature of the M-type hexagonal ferrite. The afore mentioned sharp drop in the magnetization of the STAF sample under a small applied reverse field is shown in figure 7(b). No other sample exhibited such behavior, thus confirming the structural results which revealed the presence of a secondary garnet phase (which is magnetically soft), only in the STAF sample. At 5 K, the squareness ratio \( (\sigma_r = \sigma_r / \sigma_s) \) for all samples was very close to 0.5, which is characteristic of single magnetic domain uniaxial particles with random orientations of the domain magnetic moments. This result is consistent with the measured crystallite size of \( \leq 103 \) nm, and the SEM images which indicated that the particle size distribution in all samples is dominated by sizes below the critical single domain size of \( \sim 0.5 \) µm for hexaferrites. Also, the low-temperature squareness ratios indicated that all samples exhibited a collinear spin structure at 5 K, where the remnant magnetization is practically half the saturation magnetization. The squareness ratio at 305 K, however, exhibited a lower value for all samples as the results in table 5 demonstrated. This discrepancy can be associated with a canted spin structure at room temperature. We attribute the reduction of the squareness ratio at 305 K to the reduction of the remnant magnetization due to spin canting in the absence on an applied magnetic field. In contrast, the magnetic state at the maximum applied field of 70 kOe is almost collinear.
3.4. Thermomagnetic measurements

Measurements of the temperature dependence of the magnetization at a fixed applied field can be used to determine the critical transition temperature (Curie temperature) of a magnetic material. The thermomagnetic curves for the Sr$_{1-x}$RE$_x$Al$_2$Fe$_{10}$O$_{19}$ samples are shown in figure 8. The curves exhibited a monotonic decrease of the magnetization with the increase of temperature, and then peaked just before the Curie temperature. The peak preceding the magnetic phase transition (Hopkinson peak) indicates the existence of small hexaferrite particles with superparamagnetic behavior just below the Curie temperature [44]. The Curie temperature was evaluated by extrapolating the thermomagnetic curve to zero magnetic moment, and the results are listed in table 6. Although the Curie temperature of all samples decreased significantly in comparison with the un-doped SrFe$_{12}$O$_{19}$, the values recorded for these compounds are still higher than the best NdFeB commercial magnets. The observed decrease in $T_c$ is attributed to the decrease of the superexchange interaction between iron magnetic sublattices as a consequence of magnetic dilution caused by Al$^{3+}$ ions replacing Fe$^{3+}$ ions.

Figure 7. Hysteresis loops of (a) SAF, and (b) STAF samples at measuring temperatures of 305 K and 5 K.

| Table 5. Squareness ratio ($\sigma_{rs}$) at 5 K and 305 K for all samples. |
|-----------------|-----|-----|-----|-----|-----|
| Sample          | SAF | SLAF | SCAF | STAF | SDAF |
| $\sigma_{rs}$ (5 K) | 0.499 | 0.502 | 0.502 | 0.495 | 0.487 |
| $\sigma_{rs}$ (305 K) | 0.474 | 0.478 | 0.488 | 0.474 | 0.472 |
4. Conclusions

High purity SrM hexaferrites with partial substitution of Fe by Al, and Sr by RE were successfully prepared by ball milling and sintering at 1200 °C. The values of the saturation magnetization and remnant magnetization of all samples, and the significant increase of more than 200% of the coercivity \( H_{cM} \) compared with the unsubstituted hexaferrite, render the present ferrites potentially important for permanent magnet applications. The low temperature and room temperature magnetic data revealed a collinear magnetic structure at 5 K, and a canted spin structure at room temperature. The preferred site selectivity of \( \text{Al}^{3+} \) ions for spin-up \( \text{Fe}^{3+} \) sites resulted in a reduction of the saturation magnetization, while the partial RE substitution generally resulted in an enhancement of the coercivity \( H_{cM} \), but a small reduction (<10%) of the Curie temperature. The present hexaferrites are therefore suitable for cheap ceramic-based magnets with enhanced coercivity, and relatively high operating temperatures. The performance of these ferrites as permanent magnets might be further improved by enhancing the remnant and saturation magnetization, without significantly reducing the coercivity. This possibility could be tested by adopting modified cationic substitutions, or by incorporating these hexaferrites in special composites with desired properties, which will be the focus of a future research work.

Acknowledgments

One of the authors (S H Mahmood) would like to acknowledge the financial support provided by the University of Jordan during his sabbatical leave at Michigan State University, where the high-field magnetic measurements were made, and this work was completed. Also, the support provided by Prof Jack Bass and Prof Norman Birge (Michigan State University), and the critical reading of the manuscript and suggestions made by them to improve it are highly appreciated. The technical assistance of Y Abu Salha and W Fares (The University of Jordan) is also acknowledged.

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