

Comment on “Unconventional enhancement of ferromagnetic interactions in Cd-doped $\text{GdFe}_2\text{Zn}_{20}$ single crystals studied by ESR and ^{57}Fe Mössbauer spectroscopies”

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In the recent publication [Phys. Rev. B **102**, 144420 (2020)], Cabrera-Baez *et al.*, present a study of the effects of Cd substitution for Zn in the ferromagnetic compound $\text{GdFe}_2\text{Zn}_{20}$. As part of this paper they claim that for $\text{GdFe}_2\text{Zn}_{18.6}\text{Cd}_{1.4}$ the effective moment of Gd is reduced by 25%, and the saturated moment of Gd is reduced by over 40%. We regrew representative members of the $\text{GdFe}_2\text{Zn}_{20-x}\text{Cd}_x$ series and did not find any such reductions. In addition, we measured several crystals from the growth batch that was used by Cabrera-Baez *et al.* and did not see such reductions. Although there is a modest increase in T_C with Cd substitution, there is no significant change in the Gd effective moment or the saturated moment associated with the low-temperature ferromagnetic state.

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The $RT_2\text{Zn}_{20}$ (R = rare earth, T = transition metal) family of materials [1] is remarkable for its versatility and diversity of possible electronic and magnetic ground states. For $R = \text{Yb}$, a half dozen isostructural heavy fermions were discovered [2–4]; for $R = \text{Gd-Tm}$ diverse, well defined local moment behavior has been studied [5–9]; for $T = \text{Fe}$ and $R = \text{Y, Lu, and Gd-Tm}$, greatly enhanced ferromagnetic (or nearly ferromagnetic) behavior has been found [4–7,9,10]. $\text{YFe}_2\text{Zn}_{20}$ and $\text{LuFe}_2\text{Zn}_{20}$ are nearly ferromagnetic, being closer to the Stoner limit than elemental Pd [4,10]. As such, the $R\text{Fe}_2\text{Zn}_{20}$ ($R = \text{Gd-Tm}$) series manifests anomalously high Curie temperatures T_C , relative to the much lower Néel temperatures determined for the analogous $RT_2\text{Zn}_{20}$ ($T = \text{Co, Rh, Ir}$) compounds [5,6,8]. The Stoner enhancement seen for $\text{YFe}_2\text{Zn}_{20}$, $\text{LuFe}_2\text{Zn}_{20}$, and $\text{GdFe}_2\text{Zn}_{20}$ can be systematically and comprehensively tuned by Co substitution on the Fe site [4,10] as well as by Al substitution on the Zn site [9]. For all of these studies, the size of the Gd effective and saturated moment values has remained close to the expected Hund’s rules values: $7.9\mu_B$ and $7\mu_B$, respectively. This is not unusual given that Gd is often the go-to rare earth when studying rare-earth intermetallic series (e.g., RBiPt , RNi_2Ge_2 , RFe_2Ge_2 , RCo_2Ge_2 , and RAgSb_2) [11–15] to gain a basic understanding of the magnetic interactions without the potential complications of crystal electric-field (CEF) splitting (given that for Gd, $L = 0$) or hybridization (such as can occur for Ce, Yb, or sometimes Sm). For these reasons, Gd-based compounds are well known for reliably manifesting well-defined isotropic (in the paramagnetic state) local moment behavior with no hybridization or CEF effects.

The publication by M. Cabrera-Baez, *et al.* [16], caught our attention because, based on the authors’ study of the $\text{GdFe}_2\text{Zn}_{20-x}\text{Cd}_x$ system, there is a clear claim that there was, an unexpected increase in T_C for 86 to 96 K, together with

a reduction of the magnetic effective moment and saturated magnetic moment. Whereas the modest change in T_C is not unexpected, the dramatic reductions of the magnetic effective moment by 25% and saturated magnetic moment by over 40% were indeed incredible. These reductions were inferred, primarily, from temperature and field-dependent magnetization data $M(T)$ and $M(H)$ (see Fig. 1 which is based on Figs. 3 and 4 from Ref. [16]). Given our long-standing interest in the $RT_2\text{Zn}_{20}$ system [2–10,17] as well as our even longer-standing interest in the magnetism of rare-earth bearing intermetallic systems [11–15] we wanted to understand this potentially unique example of a Gd-based compound having such tunable effective and saturated moments.

We grew single crystals of $\text{GdFe}_2(\text{Zn}_{1-x}\text{Cd}_x)_{20}$ using the growth protocols we developed for the $RT_2\text{Zn}_{20}$ system described in Refs. [2,7,10]. So as to best reproduce the samples described in Ref. [16] we used similar stoichiometries of initial melts. Table I presents the elemental analysis from energy dispersive spectroscopy (EDS) for our four growth as well as the lattice parameter a , determined from powder x-ray diffraction. As can be seen, Cd substitutes for Zn in a monotonic manner with a systematic slight increase in the unit-cell dimension. So as to allow for more direct comparison of results, we will use the $\text{GdFe}_2\text{Zn}_{20-x}\text{Cd}_x$ notation adopted in Ref. [16]. The EDS analysis of our samples showed that we grew $x = 0, 0.71, 1.06$, and 1.52 . The data presented in Table I are in basic agreement with data presented in Ref. [16], strongly suggesting that the samples are similar. Although evaluation of the Curie temperatures was not the focus of our paper, we were able to infer an ~ 7 -K increase in T_C as Cd substitution was increased, again consistent with Ref. [16].

Figure 2 presents the $M(H)$ data for $T = 1.8$ K and the $H/M(T)$ data for $H = 10$ kOe for $x = 0, 0.71, 1.06$, and 1.52 Cd substitution. These two data sets are conspicuously different from the data presented in Ref. [16] and reproduced

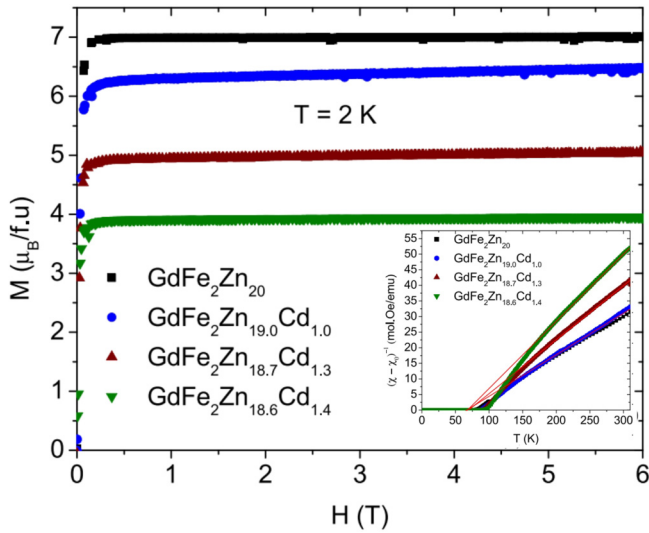


FIG. 1. Field-dependent magnetization $M(H)$ at 2 K for $\text{GdFe}_2\text{Zn}_{20-x}\text{Cd}_x$ for $0.0 \leq x \leq 1.4$. The inset: inverse magnetic susceptibility $(\chi - \chi_0)^{-1}$ as a function of temperature for the same samples. χ_0 is the temperature-independent susceptibility component. The figure is based on Figs. 3 and 4 from Ref. [16].

in Fig. 1. These data show that there is little or no systematic change in either the effective or the saturated moment of the $\text{GdFe}_2\text{Zn}_{20-x}\text{Cd}_x$ compounds as Cd is increased from $x = 0$ to 1.5. This result is consistent with the notion that Gd has a robust effective and saturated moment size and is not susceptible to CEF splitting or hybridization. This result is also qualitatively consistent with the specific-heat data presented in Fig. 2(a) of Ref. [16] which show no qualitative change in the specific-heat anomaly (or associated entropy change) as x increases. At a more quantitative level, this result is also consistent with the magnetic hyperfine field data measured with ^{57}Fe Mossbauer spectroscopy (Fig. 6 of Ref. [16]) where the $T = 3\text{-K}$ hyperfine field is identical for $x = 0$ and $x = 1.4$ samples. Whereas this is very unlikely to happen if the $x = 1.4$ compounds saturated moment is reduced by over 40%, it is expected if the $x = 0$ and $x = 1.4$ compounds have saturated moments that are virtually identical.

So as to further resolve the clear discrepancy between our data (Fig. 2) and the data presented in Ref. [16], we were able to measure samples from the same batch of crystals

TABLE I. Results of EDS analysis of four Ames samples and two samples identified as $\text{GdFe}_2\text{Zn}_{18.6}\text{Cd}_{1.4}$ in Ref. [16]. The columns are as follows: atomic percents of Gd, Fe, Zn, and Cd from EDS analysis, the value of x in the $\text{GdFe}_2\text{Zn}_{20-x}\text{Cd}_x$ notation, and the lattice parameter a for Ames samples.

Sample	Gd	Fe	Zn	Cd	x	a (Å)
Ames 1	4.49	8.71	86.7	0	0	14.125
Ames 2	4.42	8.83	83.66	3.08	0.71	14.159
Ames 3	4.32	8.79	81.88	4.58	1.06	14.179
Ames 4	4.43	8.78	79.90	6.55	1.52	14.200
Ref. [16] A	4.46	8.87	79.09	7.58	1.74	
Ref. [16] D	4.52	8.92	78.79	7.77	1.80	

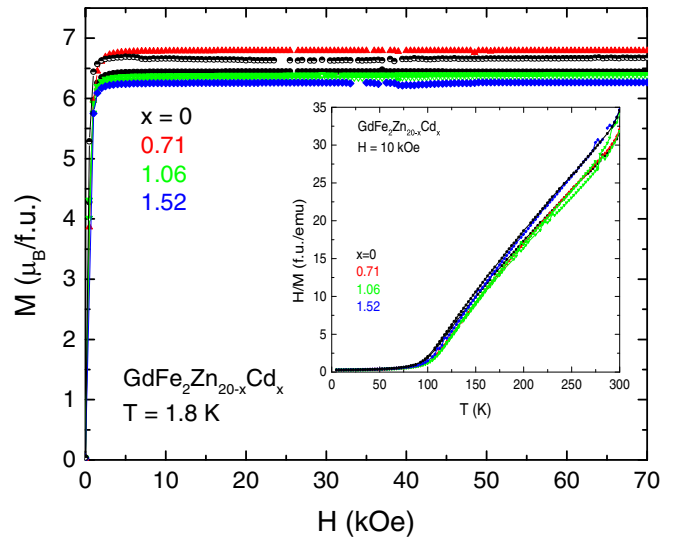


FIG. 2. Field-dependent magnetization $M(H)$ at 1.8 K for $\text{GdFe}_2\text{Zn}_{20-x}\text{Cd}_x$ for Ames samples. The inset: inverse magnetic susceptibility H/M , measured in $H = 10\text{ kOe}$ as a function of temperature for the same samples. Note: Molar masses were calculated using the Zn:Cd ratio from Table I and assuming full occupancy of all crystallographic sites resulting in the Gd:Fe:(Zn + Cd) = 1:2:20 ratio.

that the $\text{GdFe}_2\text{Zn}_{18.6}\text{Cd}_{1.4}$ samples used in Ref. [16] came from Ref. [18]. We measured $M(H)$ at 1.8 K on six different crystals (Fig. 3). As can be seen the $M(H)$ data have μ_{sat} values between 6 and $7\mu_{\text{B}}/\text{f.u.}$, consistent with the μ_{sat} values we found for our $\text{GdFe}_2\text{Zn}_{20-x}\text{Cd}_x$ series (Fig. 2) and inconsistent with the data presented in Ref. [16] (shown in

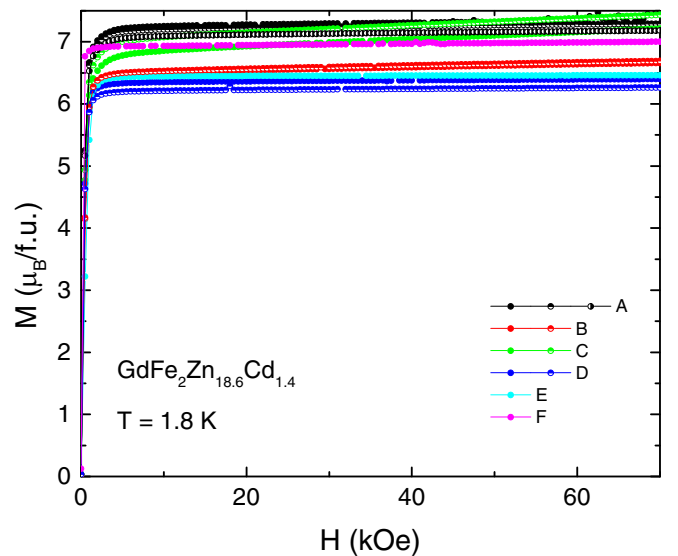


FIG. 3. Field-dependent magnetization $M(H)$ at 1.8 K for $\text{GdFe}_2\text{Zn}_{18.6}\text{Cd}_{1.4}$ samples from the same batch [18] as those used in Ref. [16]. Note, multiple samples were measured more than once as marked by different symbols in the legend. Note: Molar masses were calculated using the Zn:Cd ratio from Table I and assuming full occupancy of all crystallographic sites resulting in the Gd:Fe:(Zn + Cd) = 1:2:20 ratio.

Fig. 1 above). For completeness, we used EDS to determine the compositions of the two crystals with extreme values of μ_{sat} (labeled *A* and *D*) and include these data at the bottom of Table I. As can be seen the Cd substitution level of these samples is comparable to (albeit slightly larger than) our $x = 1.52$ sample.

Given that these samples are grown out of excess Zn, it is possible that the specific samples used for $M(T)$ and $M(H)$ measurements in Ref. [16] may have had some excess Zn on/in them. Since Zn is nonmagnetic, this would lead to an apparent decrease in the effective and saturated moments inferred for the samples. This would also be consistent with the need to subtract off nontrivial χ_0 terms when analyzing the effective moments (as was performed in Fig. 3 of Ref. [16]). It should also be noted that, based on the analysis of the data above, it seems likely that a similar error was made for the $x = 1.3$ data presented in Ref. [16] since the μ_{sat} value for this sample is also well below the values we found for our doping series (Fig. 2) or the measurements we made on the crystals associated with Ref. [16] (Fig. 3).

All in all we have to conclude that the data shown in Figs. 3 and 4 of Ref. [16] (reproduced in Fig. 1 above) are incorrect and that the conclusions drawn from these data are also incorrect. There is no dramatic reduction of the Gd effective or saturated moment as Cd is substituted for Zn in the $\text{GdFe}_2\text{Zn}_{20-x}\text{Cd}_x$ series. Given that the Gd moment is not changing in any significant manner with Cd substitution for Zn, the modest change in T_C is not unexpected either. For the $\text{GdFe}_2(\text{Zn}_{1-x}\text{Al}_x)_{20}$ series T_C changes from 86 K (for $x = 0$) to 10 K (for $x = 0.122$); for $\text{Gd}(\text{Fe}_{1-x}\text{Co}_x)_2\text{Zn}_{20}$ a T_C of 86 K (for $x = 0$) changes to a T_N of 5.7 K (for $x = 1.0$). These changes have been very clearly correlated with changes in how close the electronic system is to the Stoner limit with the addition of extra electrons to the conduction band (via Co or Al substitutions) moving the system away from this limit. Cd, on the other hand, is isoelectronic, so such dramatic changes in T_C are not anticipated. An increase in T_C with an increasing lattice parameter is anticipated, although, based on hydrostatic pressure studies of pure $\text{GdFe}_2\text{Zn}_{20}$ which showed

that T_C decreased by ~ 1.2 K under 7 kbar of pressure [5]. This result implies that negative chemical pressure (i.e., increases in the lattice parameter, such as are seen with Cd substitution) would be expected to lead to increases in T_C . Using calculated bulk modulus for $\text{YFe}_2\text{Zn}_{20}$, $K = 1.48$ Mbar [19], relative volume change $\Delta V/V_0 \approx 0.016$ between $x = 0$ and $x = 1.52$ from the lattice parameters in Table I, measured [5] pressure derivative $dT_C/dP = -0.17$ K/kbar, and assuming equivalence of physical and chemical pressures, we evaluate an expected increase in T_C of ~ 4 K. Despite the oversimplified assumptions, this estimate is within factor 2 of the observed $\Delta T_C \sim 7$ K.

To summarize, whereas Cd substitution for Zn in $\text{GdFe}_2\text{Zn}_{20-x}\text{Cd}_x$ does lead to a modest increase in the ferromagnetic Curie temperature T_C , the size of the Gd effective and saturated moments is unaffected as x varies from 0 to 1.5.

Note added in proof. The magnetization data shown above in Figs. 2 and 3, of the Ames Laboratory grown samples and the remeasured samples from Brazil respectively, are also cited in an Errata to [16] (Ref. [20]) as corrections to the initial data shown in [16].

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