

Reply to comment on 'Visualizing high-temperature spin dynamics in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ from a mapping of EPR linewidth and g factor'

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REPLY

Reply to comment on ‘Visualizing high-temperature spin dynamics in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ from a mapping of EPR linewidth and g factor’

Y Liu

Department of Modern Physics, University of Science and Technology of China,
Hefei 230026, People’s Republic of China

E-mail: yliu@ustc.edu.cn

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Abstract

In the comment by Shames and Rozenberg, they indicated that using equation (1) from our earlier paper (Liu *et al* 2007 *J. Phys.: Condens. Matter* **19** 196213) to extract g factors leads to a systematic error because the linewidth ΔH of the electron paramagnetic resonance (EPR) spectrum is comparable with the magnetic field scan ~ 0.8 T. According to their suggestions, the values of the g factor were extracted at a local minimum of the second-derivative curves d^2P/dH^2 , and then the data were compared with those obtained by numerical fittings with the above cited equation (1). It is shown that the previous results are still applicable on the basis of these new data. The different g factors reported by several groups suggest that the shifts of line position might be related to sample dependent effects.

(Some figures in this article are in colour only in the electronic version)

In [1], the temperature dependence of the electron paramagnetic resonance (EPR) spectrum for polycrystalline samples of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (LCMO) at the commensurate carrier concentrations of $x = N/8$ ($N = 1, 2, 3, 4, 5, 6,$ and 7) was measured using a Bruker ER200D spectrometer at 9.61 GHz (X band) upon warming within the temperature range $100 \text{ K} \leq T \leq 450 \text{ K}$. The EPR parameters, i.e. the resonance field (g factor) and linewidth ΔH , were then determined by numerical fittings using the following equation [2]:

$$\frac{dP}{dH} \propto \frac{d}{dH} \left(\frac{\Delta H}{(H - H_r)^2 + \Delta H^2} + \frac{\Delta H}{(H + H_r)^2 + \Delta H^2} \right), \quad (1)$$

where H_r is the resonance field and ΔH is the linewidth. As commented by Shames and Rozenberg [3], this equation cannot be adapted to the case of the high-temperature region, where the linewidth ΔH is comparable with the magnetic field scan ~ 0.8 T. Now, let us turn to figure 2 of [1]. It is

clearly seen that the magnetic field scan ~ 0.8 T is high enough to accommodate the whole EPR spectrum for the samples except those with $x = 6/8$ and $7/8$, even considering the high-temperature limitation ~ 450 K. (Hence figure 2 of [1] is essential for the readers’ convenience in a sense.)

According to the suggestions of Shames and Rozenberg [3], the values of the g factor should preferably be extracted at a local minimum of the second-derivative curves d^2P/dH^2 . Figure 1(a) illustrates the second-derivative d^2P/dH^2 curves of the EPR spectrum for the samples around 400 K. A minimum is located at around 3500 G. After extracting the minimum values of d^2P/dH^2 curves, we have compared them with the data obtained by numerical fittings with equation (1) in figure 1(b). It can be seen that the g factors extracted from the minima of the d^2P/dH^2 curves show a slight increase, but they are still below 1.98, as is observed by Shames and Rozenberg [3]. Furthermore, the values of the g factor do not concentrate around a constant as claimed by

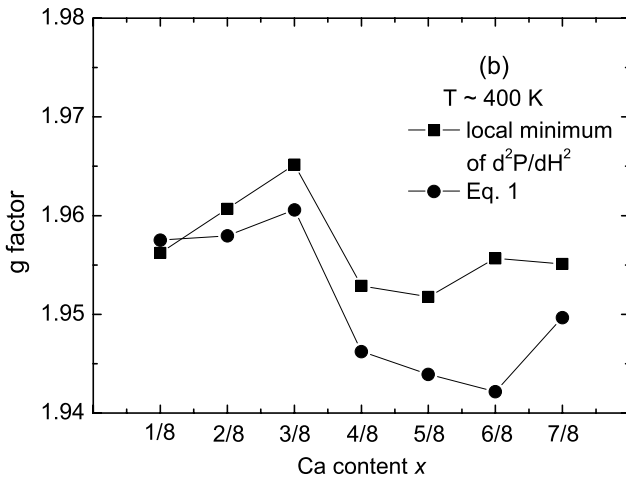
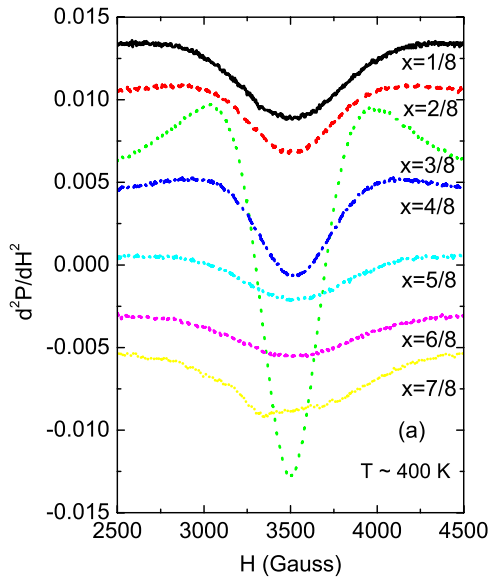


Figure 1. (a) The illustrations of the second-derivative d^2P/dH^2 curves for the EPR spectra of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = N/8$, $N = 1, 2, 3, 4, 5, 6, \text{ and } 7$) powder samples at $T \sim 400$ K. A minimum is located at around 3500 G for the samples. The curves are shifted for clarity. (b) The doping dependence of the resonance field (H_r) of the EPR signals represented by the g factors for the samples. The solid squares and circles correspond to the g factor obtained from the minimum of the second-derivative d^2P/dH^2 curves and numerical fittings with equation (1), respectively.

Shames and Rozenberg [3]. A feature of electron-hole asymmetry about the g factor can still be found. Interestingly, the g value reaches a maximum at $x = 3/8$, where the linewidth ΔH becomes narrowest at the same temperature with varying doping levels. The charge carriers behave more like free electrons at $x = 3/8$, where double-exchange (DE) interactions become strongest. So the main features in the mappings of the g factor and linewidth ΔH for the LCMO system can be uniquely explained within the framework of DE interactions.

It is noted that the g values for the LCMO system were reported as ~ 2 in the early literature [4–7], close to the free electron value $g_e \sim 2.0023$. It is suggested that the shift of the g factor might be related to some sample dependent effects. As far as our results are concerned, we would like to refer

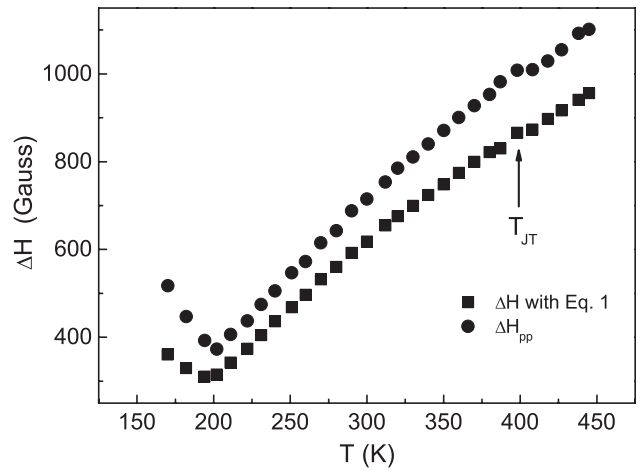


Figure 2. Temperature dependences of the linewidth ΔH and ΔH_{pp} for the sample with $x = 1/8$. The arrow indicates the Jahn–Teller transition temperature T_{JT} .

the reader to the results of Ivanshin *et al* [2]. For the lightly doped $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) system $0 \leq x \leq 0.2$, the g value was found to be nearly isotropic, $g \sim 1.98$, for both the orthorhombic (O) and the rhombohedral (R) phase, but there was a weak anisotropy $1.94 \leq g \leq 1.98$ within the Jahn–Teller distorted O' phase [2]. Next we will discuss how the Jahn–Teller transition is also evidenced in the evolution of the linewidth ΔH with decreasing temperature for our lightly Ca doped sample with $x = 1/8$.

Figure 2 shows the temperature dependences of the linewidth ΔH and ΔH_{pp} for the sample with $x = 1/8$, where ΔH_{pp} corresponds to the peak to peak value for the EPR spectrum. It is found that a jump is located at around 400 K, which is similar to what is observed for LSMO [2] and excess oxygen doped $\text{LaMnO}_{3+\delta}$ samples [8]. It should be pointed out that this Jahn–Teller transition temperature (~ 400 K) agrees well with the phase diagram presented by Biotteau *et al* [9], which was determined from neutron scattering measurements on single crystals. This result strongly suggests that the $x = 1/8$ sample is relevant for the study. However, the Ivanshin *et al* results imply that our remaining six samples could show g values around 1.98 because the Jahn–Teller distortions tend to weaken with increasing Ca content. Anyway, structural distortions can affect the line position of the EPR spectrum. Therefore, the variation of the g values reported by several groups might be related to some sample dependent effects associated with the sintering process, where certain structural distortions seem to remain in the metastable samples without relaxation. On the other hand, Shames and Rozenberg [3] suggested that the self-doping due to vacancies at La or Mn sites can lead to a broad EPR signal around $g \sim 1.91$. Thus the inhomogeneous composition of LCMO compounds is also a possible reason for the various g values observed by different groups. But it is hard to believe that the sample dependent effects will give rise to an electron-hole asymmetry of the g factor.

As far as the linewidth is concerned, the fittings with equation (1) deteriorate at temperatures approaching

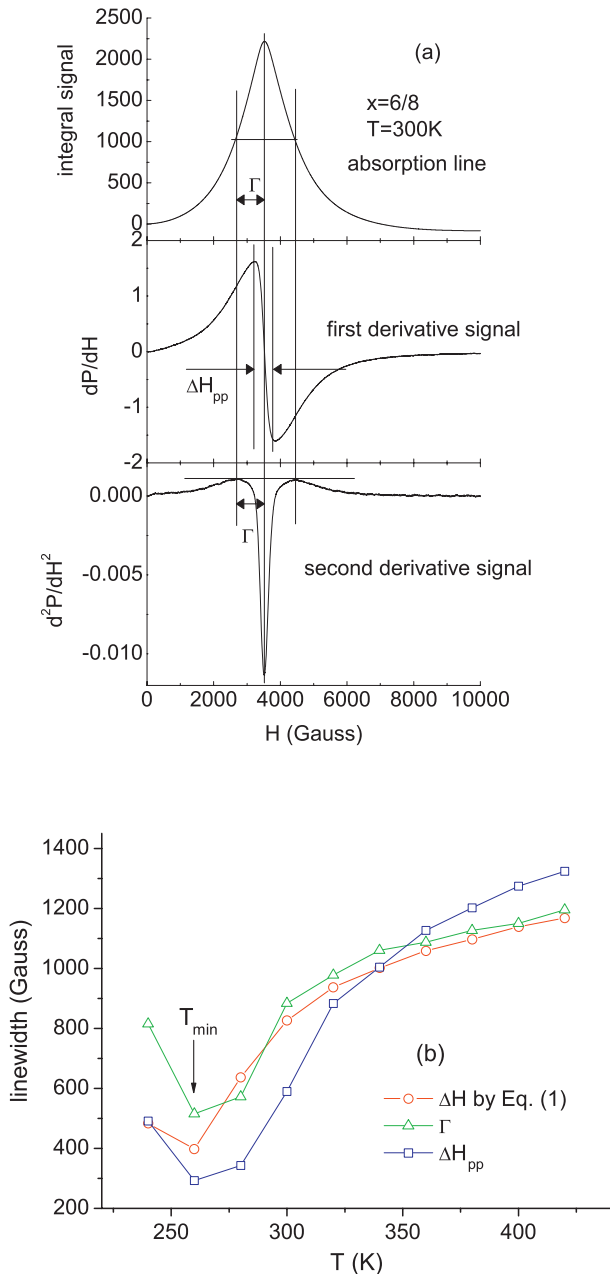


Figure 3. (a) Illustrations of the methods used to determine the linewidth: halfwidth Γ at half-maximum for the absorption line and peak to peak value ΔH_{pp} . (b) The temperature dependence of the linewidth ΔH determined with equation (1), Γ , and ΔH_{pp} for the sample with $x = 6/8$.

to ordering temperatures, where the line shape of the EPR spectrum becomes distorted. But for the sample with $x = 6/8$, the discrepancy between the experimental data and the calculated ones occurs up to as high as 340 K even though the line shape of the EPR signal remains symmetric. The discrepancy further enlarges with decreasing temperature. What causes the discrepancy is unclear. We note that the linewidth of the sample with $x = 7/8$ is strikingly broad.

It is suggested that there is a crossover behavior at $x = 6/8$. Beyond this point, the double-exchange interaction is very weak, while a superexchange interaction dominates, which might give rise to anomalous temperature dependence of the line shape at $x = 6/8$.

In general, the linewidth of the EPR spectrum is defined in two ways: (I) as the halfwidth Γ at half-maximum of the absorption line; (II) as the peak to peak value ΔH_{pp} . Figure 3(a) illustrates Γ and ΔH_{pp} for the sample with $x = 6/8$ at 300 K. In practice, one can obtain Γ by calculating the halfwidth between two peaks in the second-derivative d^2P/dH^2 curve. Figure 3(b) shows a comparison of linewidth ΔH determined with equations (1), Γ , and ΔH_{pp} for the sample with $x = 6/8$. Three curves show similar temperature dependent behaviors. Obviously, ΔH_{pp} decreases more rapidly than ΔH and Γ below 340 K. The linewidths ΔH determined with equation (1) in the temperature range $360\text{ K} < T < 420\text{ K}$ are close to Γ . Thus we can replace the linewidth ΔH with Γ , while avoiding any disturbance resulting from using two different methods over the whole doping range.

We have demonstrated that the product $\Delta H \times I$ is proportional to the inverse temperature far above the ordering temperatures. A linear behavior is clearly observed in the high-temperature regime. The result is in good agreement with a spin-only relaxation mechanism.

In summary, we have compared the g values obtained at a local minimum of the second-derivative curves d^2P/dH^2 with those from numerical fittings with equation (1). The results suggest that the variations in g values reported by the different groups seem to be related to sample dependent effects.

References

- [1] Liu Y, Wan S L and Li X G 2007 *J. Phys.: Condens. Matter* **19** 196213
- [2] Ivanshin V A, Deisenhofer J, Krug von Nidda H A, Loidl A, Mukhin A A, Balbashov A M and Eremin M V 2000 *Phys. Rev. B* **61** 6213
- [3] Shames A I and Rozenberg E 2007 Comment on ‘Visualizing high-temperature spin dynamics in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ from a mapping of EPR linewidth and g -factor’ *J. Phys.: Condens. Matter* **20** 058001
- [4] Oseroff S B, Torikachvili M, Singley J, Ali S, Cheong S W and Schultz S 1996 *Phys. Rev. B* **53** 6521
- [5] Rettori C, Rao D, Singley J, Kidwell D, Oseroff S B, Causa M T, Neumeier J J, McClellan K J, Cheong S W and Schultz S 1997 *Phys. Rev. B* **55** 3083
- [6] Causa M T, Tovar M, Caneiro A, Prado F, Ibañez G, Ramos C A, Butera A, Alascio B, Obradors X, Piñol S, Rivadulla F, Vázquez-Vázquez C, López-Quintela M A, Rivas J, Tokura Y and Oseroff S B 1998 *Phys. Rev. B* **58** 3233
- [7] Rivadulla F, Freita-Alvite M, López-Quintela M A, Hueso L E, Miguéns D R, Sande P and Rivas J 2002 *J. Appl. Phys.* **91** 785
- [8] Tovar M, Alejandro G, Butera A, Caneiro A, Causa M T, Prado F and Sánchez R D 1999 *Phys. Rev. B* **60** 10199
- [9] Biotteau G, Hennion M, Moussa F, Rodríguez-Carvajal J, Pinsard L, Revcolevschi A, Mukovskii Y M and Shulyatev D 2001 *Phys. Rev. B* **64** 104421