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## COMMENT

# 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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## Abstract

In a recent paper (Liu *et al* 2007 *J. Phys.: Condens. Matter* **19** 196213), Liu *et al* reported measurements of the electron paramagnetic resonance (EPR) of polycrystalline  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  (LCMO) manganites, and a study of the temperature and concentration ( $x$ ) dependences of the EPR signal parameters. In particular, the authors claimed notable asymmetry of the paramagnetic (PM) linewidth  $\Delta H_{\text{pp}}$  and  $g$  factor versus  $x$ . It is suggested in this comment that such a claim seems to be wrong as regards the PM  $g$  factor for the LCMO system. The reason for the above noted invalid conclusion of Liu *et al* may be the use of an inadequate method for extracting PM  $g$  factor values. It is noted that real electron–hole doping asymmetry manifests itself in, e.g., low-temperature behavior of the resonance signal intensity in accordance with the LCMO phase diagram. Numerous uncertainties and obscurities are also characteristic of the paper commented on.

Liu *et al* reported in their recent paper [1] data on electron paramagnetic resonance (EPR) measured for polycrystalline  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  (LCMO) manganites at the commensurate carrier concentrations of  $x = N/8$  ( $N = 1, 2, 3, 4, 5, 6,$  and  $7$ ). Using numerical fittings of the EPR spectra ( $dP/dH$ ), where  $P$  is a microwave energy absorbed by the sample and  $H$  is an external magnetic field, they extracted the temperature ( $T$ ) and concentration dependences of the EPR signal linewidth  $\Delta H_{\text{pp}}$  and  $g$  factor within the interval  $100 \text{ K} \leq T \leq 450 \text{ K}$ . The temperature dependences of  $\Delta H_{\text{pp}}$  and the EPR signal intensity ( $I$ ) were further discussed by the authors in the framework of known models [2–6] and they claimed, as a result of this analysis, that ‘An electron–hole asymmetry can be clearly observed in the mapping of the  $g$  factor and linewidth  $\Delta H$ ’. Let us state that this strong claim by Liu *et al* seems to be definitely wrong as regards the paramagnetic (PM)  $g$  factor of the LCMO system. A possible reason for

this invalid conclusion may be an inadequate method of PM  $g$  factor extraction used by the authors. Thus, it seems useful to comment on this and some other points of [1].

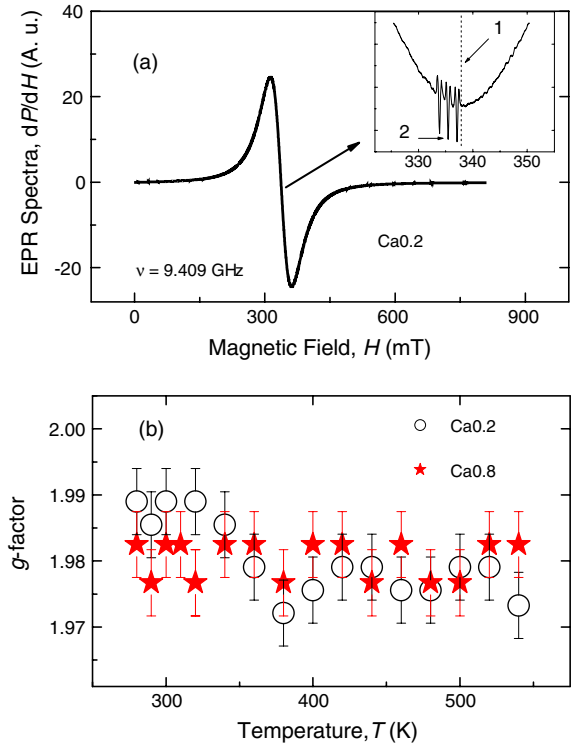
Liu *et al* followed the previous approach of Joshi *et al* [7] in their numerical fittings of EPR spectra; see equation (1) in [1]. It must be especially emphasized that the fitting of the experimental  $dP/dH$  with equation (1) like formulas leads to unavoidable errors in the values obtained for the PM  $g$  factor, which notably exceed  $\pm 0.002$ , in spite of the claim of Joshi *et al*—see page 2872 of [7] and further discussion. Note also that no information on the precision of the  $g$  factor determination is available in [1].

It seems useful to make some general remarks on the  $g$  factor of doped manganites. First of all, only the concept of a PM  $g$  factor measured at temperatures far above any magnetic and/or charge ordering transition points is meaningful. Thus, the 2D ( $x, T$ ) mapping of the  $g$  factor has very limited

sense, just demonstrating deviations from its PM value on approaching the magnetic transition  $T$ , which vary with  $x$  for the LCMO system. In contrast, comparison of  $g$  values at their high-temperature PM limit for different LCMO compounds has some real meaning. In this connection, Liu *et al* presented very strange values of  $g$  factors; see figure 4(a) in [1]. For example, PM  $g$  factors for hole doped LCMO ( $x < 0.5$ ) were found to be below 1.97, while those for the electron doped compounds ( $x > 0.5$ ) are reported to be  $\sim 1.95$  (and below) at  $T > 350$  K. Let us emphasize again that no information on the precision of the  $g$  factor determination is present in [1] (e.g., no error bars are shown in figure 4(a)). These values definitely contradict the EPR data on hole and electron doped LCMO published earlier in, for instance, [8, 12]. It seems to us that the method of  $g$  factor extraction used by Liu *et al* results in a systematic error. Indeed, the applicability of the simplified equation (1) for fitting of weak broad EPR lines at high temperatures is very questionable due to: (a) the limited magnetic field scan (0.8 T in the measurements by Liu *et al*; see figure 2 in [1]), which becomes comparable with the linewidth; and (b) the strong dependence of the true resonance field value on the broad background signals (from the cavity, Dewar insert etc), which may be comparable in intensity with the true EPR signals. Both of these factors may affect the determination of the  $g$  factor. The preferred way to obtain the true PM  $g$  factor value is to find a minimum of a second derivative of EPR absorption ( $d^2P/dH^2$ ). This method shows reliable results, which are practically independent of broad background signals.

We employed this very method combined with the use of a spin label marker (see [8]) for studying the real electron–hole asymmetry of EPR parameters for LCMO manganites ( $x = 0.2$  and  $0.8$ ). Detailed data regarding the PM  $g$  factors of both single-crystalline  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$  and polycrystalline  $\text{La}_{0.2}\text{Ca}_{0.8}\text{MnO}_3$  manganites (labeled further as  $\text{Ca}_{0.2}$  and  $\text{Ca}_{0.8}$  samples) are presented in figure 1. In particular, figure 1(a) shows the EPR spectrum of the  $\text{Ca}_{0.2}$  sample at  $T = 290$  K and the inset demonstrates its  $d^2P/dH^2$  profile in the vicinity of the resonance field. Note that the relatively broad minimum of  $d^2P/dH^2$  (marked as 1) reveals  $g = 1.985$  for  $\text{Ca}_{0.2}$ . To control this value, three narrow minima of the spin marker (see the inset in figure 1(a)) were used; e.g., the central one labeled as 2 conforms to the tabulated  $g = 2.0059 \pm 0.0001$ . To extract  $g$  factor values for both  $\text{Ca}_{0.2}$  and  $\text{Ca}_{0.8}$  compounds, the same procedure was employed for the temperature interval  $280 \text{ K} \leq T \leq 550 \text{ K}$ ; see figure 1(b). The definite conclusion is that the two series of  $g$  factors merge into a unique value  $1.98 \pm 0.01$  within the above interval of  $T$ , i.e., no signatures of PM  $g$  factor asymmetry are observed, in strong contrast to the case for the data of Liu *et al*—figure 4(a) in [1]. Moreover, the above  $g = 1.98 \pm 0.01$  value is very close to those for  $\text{Mn}^{4+}$  ions.

To discuss these results, let us examine the data of [9, 10] on the EPR probing of the  $\text{LaMnO}_3$  (LMO) compound, which is the end member of the LCMO system and self-doped due to vacancies at La or Mn sites. Note that a broad EPR signal with  $g = 1.91 \pm 0.01$  is recorded for pure LMO in the PM state; this is characteristic for the system of exchange coupled  $\text{Mn}^{3+}$  spins (see also [11]). However, increase of the



**Figure 1.** The data of [8] on the EPR of a single crystal of  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$  ( $\text{Ca}_{0.2}$ ) and polycrystalline  $\text{La}_{0.2}\text{Ca}_{0.8}\text{MnO}_3$  ( $\text{Ca}_{0.8}$ ) manganites. (a) The EPR spectrum of  $\text{Ca}_{0.2}$  at  $T = 290$  K. Inset—the derivative of this spectrum ( $d^2P/dH^2$ ) in the vicinity of the resonance field. The marks 1 and 2 conform to  $g$  factor values of 1.985 and 2.0059, respectively. (b) The temperature dependences of PM  $g$  factors for  $\text{Ca}_{0.2}$  (circles) and  $\text{Ca}_{0.8}$  (stars) samples; the error bars are equal to  $\pm 0.005$ .

(This figure is in colour only in the electronic version)

self-doping level (increase of the  $\text{Mn}^{4+}$  ion content) leads to the appearance of relatively narrow and intense EPR signals with  $g = 1.98 \pm 0.01$ ; see figure 10 in [9], as well as figures 1 and 2 in [10]. The latter PM signal with  $g = 1.98(1)$  becomes dominant for, e.g., just 6% of vacancies at Mn sites of LMO and no additional EPR lines with  $g \neq 1.98(1)$  are observed [10]. It is natural to associate this signal with those of double-exchange coupled  $\text{Mn}^{3+}\text{--Mn}^{4+}$  ion clusters ('FM polarons' according to Liu *et al*; see page 7 in [1]). Note that this scheme may be easily extended to the LCMO system; i.e., the appearance of  $\text{Mn}^{4+}$  ions due to the doping at La sites of LMO with Ca (or, symmetrically, the appearance of  $\text{Mn}^{3+}$  ions due to the doping at Ca sites of  $\text{CaMnO}_3$  with La) must result in the same EPR signal of exchange coupled  $\text{Mn}^{3+}\text{--Mn}^{4+}$  clusters independently of the Ca concentration  $x$ . Our data on the EPR for  $x = 0.1$  and  $0.9$  LCMO samples [12] also support this claim. To explain the closeness of the observed  $g = 1.98 \pm 0.01$  value to those for pure  $\text{Mn}^{4+}$  ions, we suggested [13] the model of EPR  $\text{Mn}^{3+}\text{--Mn}^{4+}$  resonance centers in doped manganites, according to which the Jahn–Teller  $\text{Mn}^{3+}$  ions are stable/exist only virtually, while the valence of the Mn ions fluctuates between  $4+$  and  $3+$  with the electron hopping frequency. Note that such an approach agrees with those of Shengelaya *et al* [14].

The following remarks regarding the form of presentation and the data of [1] may also be made.

- (i) It was brought out clearly in the seminal work from this field [15] that lightly Ca doped ( $x \leq 0.20$ ) polycrystalline LCMO samples sintered in an air are non-stoichiometric and demonstrate much higher effective doping level than the nominal one (see also [16]). This means that the data obtained by Liu *et al* for their  $x = 1/8$  LCMO sample are irrelevant.
- (ii) The fit of the product  $\Delta H_{pp} \times I$  versus the inverse of  $T$  in figure 7 of [1], combining Huber [2] and Oseroff [5] like approaches, is very rough, especially for the  $x = 2/8$  sample. This evidences that additional strong mechanisms are involved in PM spin relaxation of LCMO. Namely, it has been shown recently [17] that increasing the Ca concentration in LCMO from 0 to 0.30 results in successive suppressions of the ion–ion spin relaxation [2] and in enhancement of the ion spin–carrier orbit relaxation mechanism. So, the very general conclusion of Liu *et al*: ‘... EPR signal is dominated by spin–spin exchange interaction’ is inappropriate.
- (iii) [1] contains a lot of superfluous information, e.g., the huge figure 2 on pp 4, 5, which is not useful to a reader. In addition to this, numerous trivialities such as ‘It is found that the drop of linewidth with decreasing temperature in the mapping resembles the contour of the ferromagnetic transition curve in the LCMO phase diagram’ on p 6 or ‘Our observation naturally suggests that the exchange correlation provides the ‘glue’ for the formation of FM coupled polarons’ on p 7 appear in the text of [1].
- (iv) Note especially an erroneous claim on p 3: ‘...  $\Delta H$  can be defined as the halfwidth at half-maximum of the absorption line. In practice, one can obtain an equivalent value by calculating the halfwidth between two peaks in the second-derivative  $d^2P/dH^2$  curve’. In reality it is commonly accepted that the value which is equivalent (with a coefficient depending on the type of the line shape) to the halfwidth at half-maximum of the absorption line is the halfwidth between two peaks in the first-derivative ( $dP/dH$ ) curve, i.e. in the conventional EPR spectrum.

To conclude, it appears that an inadequate method of experimental data fitting results in inappropriate conclusions by Liu *et al* [1] on the notable electron–hole asymmetry observed for the PM  $g$  factor of LCMO. It is emphasized in this comment that careful analysis of the temperature dependences of the PM  $g$  factor of LCMO [8, 12] demonstrates no signatures

of such asymmetry with  $\pm 0.01$  error, as they are much smaller than the effect proclaimed by Liu *et al*; see figure 4(a) in [1]. At the same time, the real electron–hole asymmetry of resonance parameters of LCMO manifests itself in, e.g., low-temperature behavior of the resonance signal intensity (in accordance with the LCMO phase diagram) [8]. Numerous uncertainties and obscurities are also characteristic of the paper [1] being commented upon.

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