Comment on "Spin crossover in (Mg,Fe)O: A Mössbauer effect study with an alternative interpretation of x-ray emission spectroscopy data"

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Electronic spin-pairing transition of iron in ferropericlase-(Mg,Fe)O has been recently studied with x-ray emission and Mössbauer spectroscopies under high pressures. While these studies reported a high-spin to low-spin transition of iron to occur at pressures above approximately 50 GPa, the width of the observed transition varies significantly. In particular, Kantor *et al.* [Phys. Rev. B **73**, 100101(R) (2006)] reported that the transition in $(Mg_{0.8}, Fe_{0.2})O$ occurs over a pressure range of approximately 50 GPa in high-pressure Mössbauer measurements. To account for the discrepancy in the transition pressure, Kantor *et al.* reanalyzed the x-ray emission spectra by Lin *et al.* [Nature (London) **436**, 377 (2005)] using a simple spectral decomposition method and claimed that x-ray emission measurements are also consistent with a spin crossover of iron at high pressures. Here, we show that the proposed fitting method is inadequate to describe the x-ray emission spectrum of the low-spin FeS_2 and would result in an erroneous satellite peak ($K\beta'$) intensity, leading to an artificial high-spin component and, consequently, to invalid conclusions regarding the width of the pressure-induced transition in ferropericlase. Furthermore, we show that an energy decrease of ~ 1.6 eV in the $K\beta_{1,3}$ main peak was observed across the spin transition in ferropericlase, which can be used as an additional line of evidence for the electronic spin-pairing transition of iron in (Mg,Fe)O.

Pressure-induced electronic spin-pairing transitions of iron in ferropericlase-(Mg,Fe)O have been reported by x-ray emission spectroscopy (XES),[1–3] Mössbauer spectroscopy,[3–5] x-ray diffraction,[2,4] and theoretical calculations.[6–8] While these experimental studies all support that a high-spin to low-spin transition of iron in ferropericlase occurs at approximately 50 GPa,[1–5] the reported width of the transition varies significantly from 18 GPa (Refs. [2–4]) to approximately 55 GPa.[5] On the other hand, recent theoretical predictions indicate that the electronic spin-pairing transition of iron in ferropericlase occurs over a very narrow range of pressure at room temperature but turns to an electronic spin crossover with an extended transition pressure of approximately 30 to 50 GPa at the lower mantle temperatures.[7,8] Since ferropericlase is considered to constitute a considerable volume fraction of the Earth's lower mantle ($\sim 20\%$ by volume), an understanding of the width of the transition is crucial in interpreting the consequent effects of the transition on the physical properties of ferropericlase in the Earth's lower mantle.[9] Here, we comment on the recent high-pressure Mössbauer study of $(Mg_{0.8}, Fe_{0.2})O$ and the proposed alternative interpretation of the high-pressure XES spectra of $(Mg_{0.75}, Fe_{0.25})O$.[5] We show that the proposed spectral decomposition method by Kantor *et al.* is inadequate, leading to an erroneous interpretation of the transition pressure, and that the wide range of the transition pressures in the Mössbauer measurements[5] of Kantor *et al.* may be simply explained by the very large, thick sample under nonhydrostatic experimental conditions.

An electronic spin crossover of iron in $(Mg_{0.8}, Fe_{0.2})O$ has been reported to occur from approximately 55 to 105 GPa by high-pressure Mössbauer studies.[5] To account for the

wide transition pressure and the discrepancy between high-pressure Mössbauer and XES studies,[2] a simple spectral decomposition method using a Pearson-IV peak shape and a Gaussian peak shape is used to reanalyze the XES spectra reported by Lin *et al.*[2,5] To test the validity of the proposed method, here we use the proposed method to analyze the x-ray emission spectrum of the low-spin FeS_2,[10] a commonly used standard in the XES, and show that it cannot be fitted with a simple Pearson-IV peak shape [Fig. 1(b)]; a significant misfit occurs in the satellite peak region. Although the spectrum can be well fitted with two peaks, a Pearson-IV peak for the $K\beta_{1,3}$ main peak and a Gaussian peak for the $K\beta'$ satellite peak as proposed by Kantor *et al.*,[5] the use of the Gaussian peak produces an artificial high-spin component even though the sample is completely in the low-spin state [Fig. 1(a)]. Consequently, the two-peak fitting method used for decomposing the XES spectra of the low-spin $(Mg_{0.75}, Fe_{0.25})O$ would give rise to an artificial, invalid satellite peak for the high-spin component, which was used to incorrectly derive an average spin number of approximately one for the low-spin $(Mg_{0.75}, Fe_{0.25})O$ at ~ 79 GPa by Kantor *et al.* (see Fig. 2 in the paper of Kantor *et al.*[5]); we note that the intensity of the satellite peak is not a simple function with the average spin number and should be used with caution.[11] That is, the fitting procedure with the Gaussian peak would always give a high-spin component and would not produce a single, complete low-spin state. As a matter of fact, independent analyses of the XES spectra of $(Mg_{0.75}, Fe_{0.25})O$ by Vankó and de Groot[12] (using the line-shape analyses described previously),[13] and Rueff[14] give results that are in agreement with what Lin *et al.* had reported[2] and are consistent with recent synchrotron Mössbauer studies
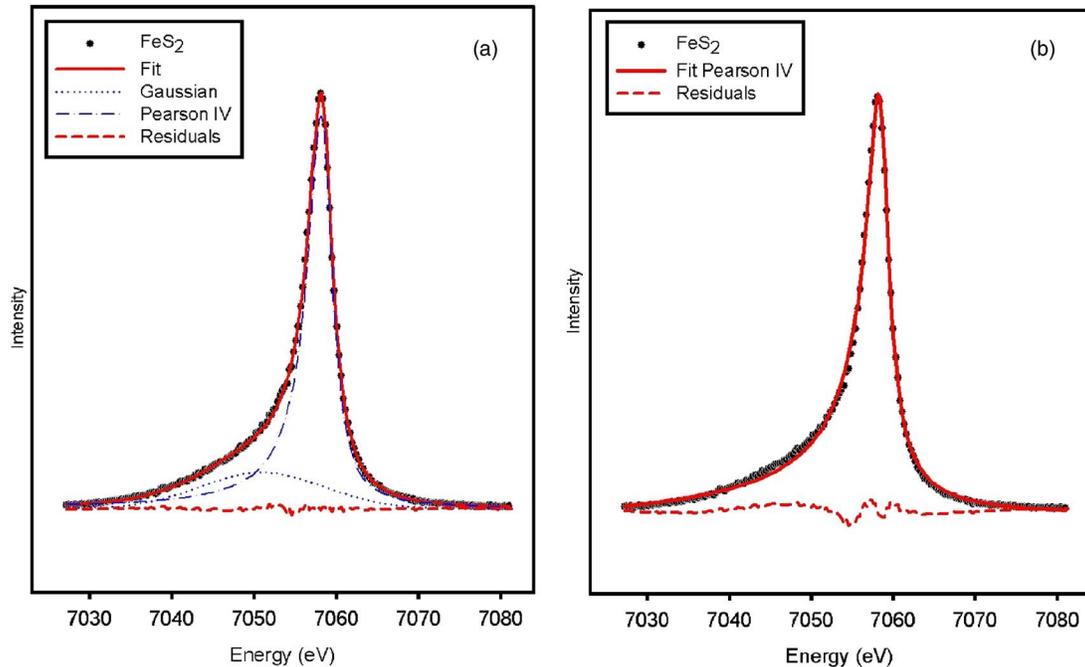
FIG. 1. (Color online) X-ray emission spectrum of the low-spin FeS_2 at ambient conditions (gray dots). (a) Red solid line, fitting with decomposition model of Kantor *et al.* (Ref. [5]): dashed-dotted line, fitting with a Pearson-IV peak; dotted line, fitting with a Gaussian peak; dashed line, residuals. (b) Red solid line, fitting with a Pearson-IV peak; dashed line, residuals. We note that FeS_2 is known to be in low-spin state under ambient conditions. (Ref. [10]). The fitting method based on the spectral decomposition model of Kantor *et al.* gives an erroneous satellite peak [Fig. 1(a), blue dotted line], whereas a misfit occurs in the satellite peak region when fitting with a single Pearson-IV peak [Fig. 1(b)].

of the same composition,[3] as opposed to what is claimed by Kantor *et al.*[5]

To better understand the electronic spin-pairing transition in the (Mg,Fe)O system, here we also reanalyzed the high-pressure XES spectra of $(Mg_{0.95},Fe_{0.05})O$ and $(Mg_{0.75},Fe_{0.25})O$ (Fig. 2).[2,3] The very dilute concentration of Fe^{2+} in the $(Mg_{0.95},Fe_{0.05})O$ allows observation of the transition at relatively low pressures and reduces possible iron-iron exchange interaction in the system.[3] All XES spectra of the $(Mg_{0.95},Fe_{0.05})O$ sample were collected with the same system setup from the same sample, ensuring that the energy calibration remained intact throughout the collection of the spectra. The integrated and normalized intensity of the $K\beta'$ satellite peak in the $(Mg_{0.95},Fe_{0.05})O$ sample as a function of pressure showed the presence of the satellite peak below 46 GPa and the absence of the satellite peak above 55 GPa, indicating a high-spin to low-spin transition of iron between 46 and 55 GPa [Fig. 2(a)]. Our analyses of the XES spectra are also consistent with the analyses using the line-shape analyses by integrating the absolute difference of the spectra, and comparing these integrals to that obtained in references (IAD analyses) [Fig. 2(a)].[12] An energy decrease of $\sim$1.6 eV in the $K\beta_{1,3}$ main peak was also observed in $(Mg_{0.95},Fe_{0.05})O$ between 46 and 55 GPa [Fig. 2(b)], while no energy shift was observable between 55 and 70 GPa. Analyzing the reported XES data of Lin *et al.*[2] also showed a similar energy decrease of $\sim$1.6 eV in $(Mg_{0.75},Fe_{0.25})O$ between 47 and 67 GPa [Fig. 2(b)]. The energy shift of the main $K\beta_{1,3}$ peak across the spin transition has been predicted by theory and explained by the preservation of the center of

gravity of the spectra: when the high-spin satellite intensity disappears, main peak shifts toward the center of gravity of the emission spectrum in order to keep the center of the mass of the emission line fixed.[15–17] The observation of the energy shift is consistent with the change of the satellite intensity and can be used as an additional line of evidence for the electronic spin-pairing transition of iron in (Mg,Fe)O. Consequently, our analyses here show that the energy difference between the main peak and the satellite peak derived by Kantor *et al.* using their decomposition method is also inadequate (see Fig. 4 in the paper of Kantor *et al.*[5]).

Comparing the abundance of the high-spin and low-spin states of iron in ferropericlase as determined by recent high-pressure measurements,[3–5] the range of the reported transition pressures varies significantly from 18 GPa at 300 K for $(Mg_{0.75},Fe_{0.25})O$,[3] to 20 GPa at 6 K for $(Mg_{0.8},Fe_{0.2})O$,[4] to approximately 50 GPa at 300 K for $(Mg_{0.8},Fe_{0.2})O$.[5] Such discrepancy may arise from different experimental conditions used, such as the sample size and thickness,[18] hydrostaticity in the sample chamber, and the beam size of the x-ray source. The natural width of the spin transition remains to be further understood by conducting future high-pressure experiments under hydrostatic conditions.

In conclusion, we show that the x-ray emission analysis method proposed by Kantor *et al.*[5] was ill-founded, leading to an invalid conclusion regarding the width of the pressure-induced transition in ferropericlase. We also show that an energy decrease of $\sim$1.6 eV in the $K\beta_{1,3}$ main peak can be used as an additional line of evidence for the electronic spin-pairing transition of iron in ferropericlase.
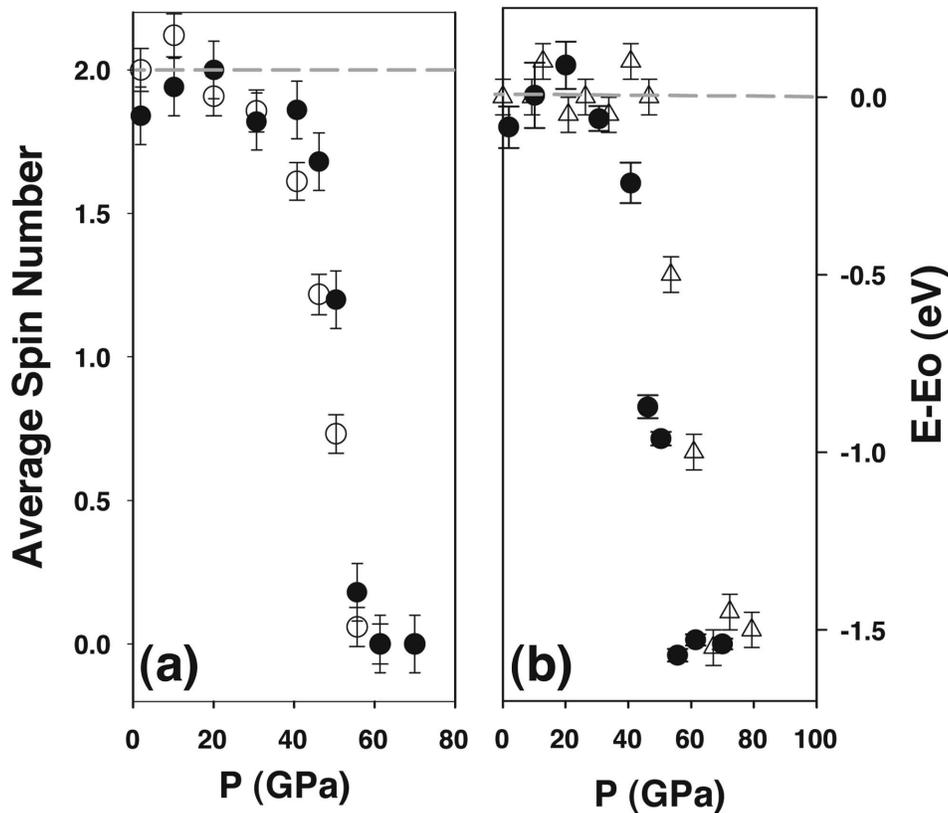
FIG. 2. (a) Average quantum spin number of Fe^{2+} in $(Mg_{0.95},Fe_{0.05})O$ based on the integrated and normalized intensity of the satellite peak of the x-ray emission spectra (solid circles) and the integration of the absolute difference of the spectra and comparison of these integrals to that obtained on references (IAD analyses) (open circles) (Ref. 12) as a function of pressure. The intensity of the satellite peak in the solid circles was obtained by subtracting each spectrum from the one at the highest pressure of 70 GPa (low-spin state) (Ref. 2). The errors in the integrated intensity were propagated from statistical errors in the original spectra. (b) Energy shift of the main emission peak ($K\beta$) as a function of pressure for $(Mg_{0.95},Fe_{0.05})O$ (solid circles) and $(Mg_{0.75},Fe_{0.25})O$ (open triangles) (Ref. 2). An energy decrease of $\sim$1.6 eV in the $K\beta$ main peak was observed in both $(Mg_{0.95},Fe_{0.05})O$ and $(Mg_{0.75},Fe_{0.25})O$ across the spin-pairing transition (Ref. 2). The energy of the $K\beta$ peak in $(Mg_{0.95},Fe_{0.05})O$ was located at $\sim$7058 eV in the high-spin state, and an energy decrease of $\sim$1.6 eV was observed between 46 and 55 GPa. No energy shift was observable away from the spin transition region, indicating that pressure alone has negligible effect on the absolute energy of the $K\beta$ peak in the pressure range studied.

[1] J. Badro, G. Fiquet, F. Guyot, J. P. Rueff, V. V. Struzhkin, G. Vankó, and G. Monaco, Science **300**, 789 (2003).

[2] J. F. Lin, V. V. Struzhkin, S. D. Jacobsen, M. Hu, P. Chow, J. Kung, H. Liu, H. K. Mao, and R. J. Hemley, Nature (London) **436**, 377 (2005).

[3] J. F. Lin, A. G. Gavriliuk, V. V. Struzhkin, S. D. Jacobsen, W. Sturhahn, M. Y. Hu, P. Chow, and C. S. Yoo, Phys. Rev. B **73**, 113107 (2006).

[4] S. Speziale, A. Milner, V. E. Lee, S. M. Clark, M. Pasternak, and R. Jeanloz, Proc. Natl. Acad. Sci. U.S.A. **102**, 17918 (2005).

[5] I. Yu. Kantor, L. S. Dubrovinsky, and C. A. McCammon, Phys. Rev. B **73**, 100101(R) (2006).

[6] D. M. Sherman, J. Geophys. Res. **96**, 14299 (1991).

[7] W. Sturhahn, J. M. Jackson, and J. F. Lin, Geophys. Res. Lett. **32**, L12307 (2005).

[8] T. Tsuchiya, R. M. Wentzcovitch, C. R. S. da Silva, and S. de

Gironcoli, Phys. Rev. Lett. **96**, 198501 (2006).

[9] J. F. Lin, S. D. Jacobsen, W. Sturhahn, J. M. Jackson, J. Zhao, and C. S. Yoo, Geophys. Res. Lett. **33**, L22304 (2006).

[10] K. Persson, G. Ceder, and D. Morgan, Phys. Rev. B **73**, 115201 (2006).

[11] K. Tsutsumi, H. Nakamori, and K. Ichikawa, Phys. Rev. B **13**, 929 (1976).

[12] G. Vankó and F. de Groot, this issue, Phys. Rev. B **75**, 177101 (2007); (private communication).

[13] G. Vankó, T. Neisius, G. Molnar, F. Renz, S. Karpati, A. Shukla, and F. M. F. de Groot, J. Phys. Chem. B **110**, 11647 (2006).

[14] J. P. Rueff (private communication).

[15] F. de Groot, Chem. Rev. (Washington, D.C.) **101**, 1779 (2001).

[16] P. Glatzel and U. Bergmann, J. Am. Chem. Soc. **126**, 9946 (2004).

[17] P. Glatzel and U. Bergmann, Coord. Chem. Rev. **249**, 65 (2005).

[18] A. G. Gavriliuk, J. F. Lin, I. S. Lyubutin, and V. V. Struzhkin, JETP Lett. **84**, 161 (2006).