Comment on "Magnetism and structure of Li_xCoO_2 and comparison to Na_xCoO_2"

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In the article [Phys. Rev. B **77**, 075119 (2008)], effective magnetic moments p_{eff} per Co site have been determined from magnetic susceptibility measurements for a series of Li_xCoO_2 samples. The nominal Li content x (ranging theoretically from 1 to 0) determines the concentration of Co^{3+} (x) and Co^{4+} $(1-x)$ that occupy the Co sites. Assuming that the Co^{3+} species is diamagnetic, the effective magnetic moment p_{eff} per Co^{4+} ion has been calculated from the experimentally determined effective magnetic moment p_{eff} per Co site and the nominal Co^{4+} concentration in the cited publication [Phys. Rev. B **77**, 075119 (2008)] by assuming a purely linear relation between the effective magnetic moments and the concentrations. From the viewpoint of this comment's author, this linear approach is not valid and the linear effective magnetic moments p_{eff} utilized in the formulas in the cited article should be replaced by their squared values p_{eff}^2. This comment provides the correct formulas for the calculations aimed to be performed in [Phys. Rev. B **77**, 075119 (2008)] and recalculates the published values. Since for low Co^{4+} concentrations a high-spin species is discussed to exist in Li_xCoO_2 in numerous publications, correct handling of effective magnetic moments is of general interest in this discipline of research.

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Firstly, the part from Ref. [1] that gave rise to write this comment will shortly be recapitulated: For a series of Li_xCoO_2 samples the effective magnetic moment p_{eff} per Co site has been obtained from Curie-Weiss fits to inverse magnetic susceptibility data. These effective moments per Co site have been used (i) for two samples with very small $1-x$ (means small nominal Co^{4+} concentration) to determine the concentration of Co^{4+} that has been assumed to be present as a high-spin species with an effective magnetic moment of $5.9\mu_B$ and (ii) in general to determine the effective magnetic moment for the Co^{4+} species that was assumed to be present at a concentration according to the nominal delithiation $1-x$ for all samples. The results have been presented in Table I in Ref. [1] and the most important values are summarized in Table I of this comment. For the fully lithiated sample ($x = 1.00$), the nominal oxidation state of Co was assumed to be $+3$ (assuming that oxygen is present as O^{2-} and Li as Li^+). For each Li^+ that was extracted from the structure, it was assumed that one Co^{3+} is oxidized to Co^{4+}. Therefore, the Li content x equals the nominal concentration of Co^{3+} and correspondingly $1-x$ equals the nominal concentration of Co^{4+}. Co^{3+} was assumed to be present in a diamagnetic state (zero effective magnetic moment) while Co^{4+} was supposed to possess a magnetic moment that is either suggested to be in a high-spin state for very small amounts of delithiation (effective magnetic moment close to $5.9\mu_B$), but changes to a low-spin configuration for higher degrees of delithiation.

The authors of Ref. [1] then falsely used the following linear equation to determine the Co^{4+} concentration $(1-x')$ from the measured effective moment $p_{\text{eff[Co]}}$ per Co assuming that each Co^{4+} would be present in its high-spin state with $p_{\text{eff[Co4+]}} = 5.9\mu_B$ for the first two samples:

$$x' p_{\text{eff[Co3+]}} + (1-x')p_{\text{eff[Co4+]}} = p_{\text{eff[Co]}}, \tag{1}$$

$$(1-x') = \frac{p_{\text{eff[Co]}}}{5.9\mu_B}, \tag{2}$$

where x' represents the Lithium content calculated by this method in contrast to the nominal Li content x. The values of the so calculated Li contents x' for the first two samples are listed in round brackets in the first column of Table I in Ref. [1] and are repeated for convenience again in the first column of Table I of this comment.

Further, for all samples except for the first one with $x = 1.00$, the effective magnetic moments $p_{\text{eff[Co4+]}}$ per Co^{4+} have been calculated according to the following inappropriate linear equation:

$$x p_{\text{eff[Co3+]}} + (1-x)p_{\text{eff[Co4+]}} = p_{\text{eff[Co]}}, \tag{3}$$

$$p_{\text{eff[Co4+]}} = \frac{p_{\text{eff[Co]}}}{(1-x)}, \tag{4}$$

where the nominal Co^{4+} concentration has been calculated as $1-x$ from the Li content x. The values of the so calculated values of $p_{\text{eff[Co4+]}}$ per Co^{4+} are listed in the sixth column of Table I in Ref. [1] and are repeated for convenience again in the third column of Table I of this comment.

This comment questions the mathematical procedure how (i) the concentration of a Co^{4+} species with assigned effective magnetic moment of $5.9\mu_B$ was calculated from the

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TABLE I. Nominal Li content x, effective magnetic moment p_{eff} per Co site, effective magnetic moment p_{eff} per Co^{4+}, and calculated Li content x' given in round brackets as published in Ref. [1] (first three columns). All values that have been recalculated within this comment are marked with an asterisk sign "$*$": the two recalculated Li contents x' in squared brackets and the recalculated effective magnetic moments p^*_{eff} per Co^{4+}. See text for details.

Li content x	p_{eff} $(\mu_{\mathrm{B}}/\mathrm{Co})$	p_{eff} $(\mu_{\mathrm{B}}/\mathrm{Co}^{4+})$	p^*_{eff} $(\mu_{\mathrm{B}}/\mathrm{Co}^{4+})$
1.00 (0.985)[0.9998*]	0.09	(5.9)	[5.9]
0.97 (0.961) [0.9985*]	0.23	7.67(5.9)	1.33*[5.9]
0.78	0.38	1.72	0.81*
0.72	0.43	1.54	0.81*
0.70	0.49	1.63	0.89*
0.62	0.48	1.26	0.78*
0.59	0.37	0.90	0.58*
0.58	0.36	0.86	0.56*
0.51	0.37	0.76	0.53*

determined effective magnetic moment per Co in a linear approach [Eq. (2)] and (ii) how the effective magnetic moment of the Co^{4+} species has been calculated from the effective magnetic moment per Co and the Co^{4+} concentration $(1-x)$ also in a purely linear approach [Eq. (4)]. From the viewpoint of this comment's author, a "quadratic" approach is necessary to treat the effective magnetic moments correctly. Especially for $\mathrm{Li}_x\mathrm{CoO}_2$ with the hypothesis of a high-spin Co^{4+} species for the very low delithiation states, a correct effective moment assignment is mandatory. For the calculations in this comment the Gaussian and cgs emu unit system [2] has been used and the following definition of the Curie constant can be found in standard text books or journal publications about solid state physics and magnetism [3–6].

When a number of N_{A} (Avogadro's number) Co lattice points i are all occupied by identical Co ions that are at a certain oxidation state with a corresponding total spin S, the molar Curie constant $C_{\mathrm{mol[Co]}}$ is calculated as

$$C_{\mathrm{mol[Co]}} = \frac{\mu_{\mathrm{B}}^2 g_{\mathrm{e}}^2 S(S+1) N_{\mathrm{A}}}{3k_{\mathrm{B}}} \tag{5}$$

$$= \frac{p^2_{\mathrm{eff[Co]}}\mu_{\mathrm{B}}^2 N_{\mathrm{A}}}{3k_{\mathrm{B}}}, \tag{6}$$

with the effective magnetic moment $p_{\mathrm{eff[Co]}} = g_{\mathrm{e}}\sqrt{S(S+1)}\mu_{\mathrm{B}}$ for the single Co site with spin S, the g-factor $g_{\mathrm{e}} \approx 2$ for a free electron, the Boltzmann constant k_{B}, and the Bohr magneton μ_{B}. In the case that the Co lattice points i are not all occupied by identical but by individual effective magnetic moments $p_{\mathrm{eff[Coi]}}$, the expression for $p^2_{\mathrm{eff[Co]}}$ from Eq. (6) becomes

$$p^2_{\mathrm{eff[Co]}} = \frac{1}{N_{\mathrm{A}}}\sum_{i=1}^{N_{\mathrm{A}}} p^2_{\mathrm{eff[Coi]}}. \tag{7}$$

The special case that only two different species Co(1) and Co(2) would occupy the Co sites with the concentrations c_1 and c_2 (with $c_1 + c_2 = 1$) can then be written as

$$p^2_{\mathrm{eff[Co]}} = \frac{1}{N_{\mathrm{A}}}\left(c_1 N_{\mathrm{A}} p^2_{\mathrm{eff[Co(1)]}} + c_2 N_{\mathrm{A}} p^2_{\mathrm{eff[Co(2)]}}\right) \tag{8}$$

$$= c_1 p^2_{\mathrm{eff[Co(1)]}} + c_2 p^2_{\mathrm{eff[Co(2)]}}, \tag{9}$$

To further adopt the equation to the scenario considered in Ref. [1], Co^{3+} represents the first Co species that is diamagnetic with spin $S = 0$ and $p_{\mathrm{eff[Co3+]}} = 0$, and Co^{4+} represents the second Co species that has an effective magnetic moment $p_{\mathrm{eff[Co4+]}} > 0$. As outlined above, the Co^{3+} species is present at a concentration equal to the Li content x and the Co^{4+} species correspondingly at a concentration $1-x$ with the sum always equal to one.

$$p^2_{\mathrm{eff[Co]}} = x p^2_{\mathrm{eff[Co+3]}} + (1-x) p^2_{\mathrm{eff[Co+4]}}. \tag{10}$$

Since $p_{\mathrm{eff[Co3+]}} = 0$ the expression can further be simplified to

$$p^2_{\mathrm{eff[Co]}} = (1-x) p^2_{\mathrm{eff[Co+4]}}. \tag{11}$$

Equation (11) is the fundamental relation that can be used to recalculate the values from Ref. [1] in the following.

In analogy to what has been calculated in Ref. [1] by applying Eq. (2) (see above), this comment suggest instead to calculate the Co^{4+} concentration $(1-x')$ by the measured effective magnetic moment per Co by the following equation derived from Eq. (11) by setting the effective paramagnetic moment of the Co^{4+} in high-spin again to $p_{\mathrm{eff[Co4+]}} = 5.9\mu_{\mathrm{B}}$:

$$(1-x') = \frac{p^2_{\mathrm{eff[Co]}}}{p^2_{\mathrm{eff[Co+4]}}} \tag{12}$$

$$= \frac{p^2_{\mathrm{eff[Co]}}}{(5.9\mu_{\mathrm{B}})^2}. \tag{13}$$

The correct values obtained for the calculated Co^{4+} concentrations $(1-x')$ by applying Eq. (13) are added in square brackets to the first column of Table I of this comment.

For the recalculation of the effective magnetic moments per Co^{4+} according to this comment, Eq. (11) is rearranged appropriately:

$$p^2_{\mathrm{eff[Co]}} = (1-x) p^2_{\mathrm{eff[Co+4]}}, \tag{14}$$

$$p_{\mathrm{eff[Co+4]}} = p_{\mathrm{eff[Co]}}/\sqrt{1-x}. \tag{15}$$

The correct values for the effective magnetic moment $p_{\mathrm{eff[Co4+]}}$ per Co^{4+} were calculated from the experimentally determined values of the effective magnetic moment $p_{\mathrm{eff[Co]}}$ per Co and the nominal Co^{4+} concentration $(1-x)$ according to Eq. (15) and the corrected values are listed in the fourth column of Table I of this comment. For the slightly delithated sample with nominal Li content $x = 0.97$, the correct magnetic moment per Co^{4+} is recalculated to $p_{\mathrm{eff[Co4+]}} = 1.33\mu_{\mathrm{B}}$, i.e., a value even slightly below the low-spin value for Co^{4+} of $1.73\mu_{\mathrm{B}}$. In contrast, by applying inappropriate formulas, a very high effective magnetic moment per Co^{4+} of $p_{\mathrm{eff[Co4+]}} = 7.67\mu_{\mathrm{B}}$ was published in Ref. [1] for this sample, a value that is even well above the theoretical spin-only magnetic moment for a Co^{4+} high-spin of $5.9\mu_{\mathrm{B}}$.

DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the author.

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