Comment on "Magnetoelastic model for the relaxation of lanthanide ions in YBa$_2$Cu$_3$O$_{7-δ}$ observed by neutron scattering"

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Lovesey and Staub have argued [S.W. Lovesey and U. Staub, Phys. Rev. B 61, 9130 (2000)] that experimental data on the temperature dependence of the paramagnetic relaxation of lanthanide ions doped into YBa$_2$Cu$_3$O$_{6+x}$ are in agreement with the predictions of a model that describes the relaxation as due to the scattering of phonons via a magnetoelastic interaction. By generalising their model I show that the level of agreement is strongly dependent on the number of intermediate lanthanide energy levels included in the calculation, and that inclusion of a more complete set of levels leads to very different results that do not necessarily support the phonon damping picture.

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In a recent paper, Lovesey and Staub considered how lattice vibrations could contribute to the relaxation of a transition between the crystal field split energy levels of a paramagnetic ion. Their work was prompted by a number of recent publications reporting neutron spectroscopic measurements of the temperature dependence of crystal field transition linewidths for various lanthanide ions doped into cuprate superconductors. Lovesey and Staub’s contention is that the relaxation observed for these materials is dominated by decay of the crystal field excitation into lattice vibrations, rather than into spin excitations on the CuO$_2$ planes as has been assumed by other authors. Lovesey and Staub arrive at this viewpoint by comparing experimental data with the results of a model that assumes a magnetoelastic interaction between the paramagnetic ion and the lattice.

The main purpose of this Comment is to raise awareness of an approximation made by Lovesey and Staub in calculating the relaxation from the magnetoelastic coupling model. The approximation involves the neglect of all but 3 of the crystal field split 4f levels in the relaxation calculation. For the case of Ho$^{3+}$ impurities in superconducting YBa$_2$Cu$_3$O$_{6+x}$ I will show that the use of this 3-level model has led the authors to obtain unreasonably good agreement between the calculated relaxation and the experimental data, and that inclusion of other thermally populated lanthanide energy levels gives results that do not differ significantly from those calculated with the exchange coupling model used previously. I will also show that the value of the coupling constant in the magnetoelastic model derived from the data depends strongly on the number levels included in the calculation.

I will argue, therefore, that the accord between theory and experiment presented in Ref. 3 cannot be taken as evidence that phonons rather than spin excitations are the most important source of relaxation.

I begin by outlining the factors which enter into a calculation of the relaxation of crystal field transitions. Following Lovesey and Staub let us consider a transition between two eigenstates $|a\rangle$ and $|b\rangle$ of the lowest energy $J$ multiplet of a lanthanide ion in a crystal field. For simplicity let $|a\rangle$ be the ground state. The lifetime of the $|a\rangle \to |b\rangle$ transition is finite because of coupling to electronic or vibrational degrees of freedom in the host system. Relaxation from $|b\rangle$ back to $|a\rangle$ can take place either directly or indirectly, the latter proceeding via an intermediate lanthanide energy level $|\gamma\rangle$. If $|\gamma\rangle$ is higher in energy than $|b\rangle$ then for the indirect transition to take place the 4f ion must be able to absorb energy from the host, and this can be done if the temperature $T$ is large enough to generate a significant thermal population of excitations in the host with energies equal to the difference in energy between $|a\rangle$ or $|b\rangle$ and $|\gamma\rangle$. The density of host excitation states at the relevant energy will clearly be relevant in determining the importance of a given relaxation channel, whether direct or indirect, and a further factor is the size of the transition matrix elements connecting the states involved. The relevant matrix elements for the models under consideration are those of the quadrupolar operators $Q_{\alpha}$ in the case of magnetoelastic coupling, and of the total angular momentum operators $J_{\alpha}$ in the case of exchange coupling. Here $\nu$ is a symmetry label, and $\alpha = x, y, z$.

In principle there are as many indirect relaxation channels as there are intermediate states $|\gamma\rangle$, but because there often exists a wide variation in the sizes of the transition matrix elements the effectiveness of each channel varies considerably. In Ref. 3 it was argued that inclusion of only 3 states ($|a\rangle$, $|b\rangle$ and a single $|\gamma\rangle$) allows the relaxation calculation to be simplified while retaining all the essential features.

On the basis of this 3-level approximation Lovesey and Staub derived an expression (Eq. (6.7) of Ref. 3) for the temperature dependence of the transition linewidth, and fitted their model to the experimental linewidth data for Tb$^{3+}$, Ho$^{3+}$, and Tm$^{3+}$ in superconducting YBa$_2$Cu$_3$O$_{6+x}$ assuming a Debye density of states to describe the lattice vibrations. The calculation for Ho$^{3+}$ is reproduced in Fig. 1 together with the data from Boothroyd et al. 5. The energy of the $|a\rangle \to |b\rangle$ transition is 0.5 meV, and the value of the intermediate level $|\gamma\rangle$ used to generate the calculated curve is 11.8 meV.

From the quality of the agreement shown in Fig. 1 it is tempting to be satisfied with the use of the 3-level
model, and indeed for the Tb$^{3+}$, and Tm$^{3+}$ systems there are sound physical arguments based on the energies of the excited crystal field levels and size of the quadrupole matrix elements to suggest that the totality of intermediate levels can reasonably be approximated by a single level. These arguments are discussed in Ref. [6]. In the case of Ho$^{3+}$, however, the validity of the 3-level approximation is considerably harder to justify because there are no fewer than 6 crystal field levels in the energy range 1–12 meV several of which have substantial quadrupole matrix elements connecting them to levels |a⟩ or |b⟩. Hence, these levels will contribute to the measured relaxation of the 0.5 meV |a⟩ → |b⟩ transition through indirect processes.

These considerations make it worthwhile extending the magnetoelastic model to include an arbitrary number of intermediate levels. For simplicity we will take level |a⟩ to be the ground state and level |b⟩ the first excited state, and re-label these states as |0⟩ and |1⟩ respectively. In this simplification all other intermediate levels |γ⟩ are higher in energy than |1⟩, as occurs in the experimental systems considered here, but it is straightforward to treat other sequences of levels. Let ωγ be the energy of |γ⟩ relative to the ground state (ℏ = 1). Generalising the results of Ref. [6] we can express the linewidth (half width at half maximum) in the magnetoelastic model as

\[ \Gamma_{ME} = \sum_{\nu} \Gamma_{\nu}, \]

where,

\[ \Gamma_{\nu} = c_{\nu}^2 |\langle 0|Q_{\nu}|1 \rangle|^2 \frac{Z_{\nu}(\omega_1)}{\omega_1 \coth(\beta \omega_1/2)} + \sum_{\gamma > 1} (c_{\nu}^\prime)^2 |\langle 0|Q_{\nu}|\gamma \rangle|^2 \frac{Z_{\nu}(\omega_\gamma)}{\omega_\gamma} n(\omega_\gamma) + \sum_{\gamma > 1} (c_{\nu}^\prime)^2 |\langle 1|Q_{\nu}|\gamma \rangle|^2 \frac{Z_{\nu}(\omega_\gamma - \omega_1)}{\omega_\gamma - \omega_1} n(\omega_\gamma - \omega_1). \] (1)

Here, χ''(ω) is the imaginary part of the local dynamical susceptibility at the position of the paramagnetic ion. To model the normal state of the superconductors we take χ''(ω) ∝ ω for reasons discussed in Ref. [5].

With Eqs. (1) and (2) written in this form it is easy to see that there exists a simple mapping between ΓME and Γν, as was pointed out in Ref. [6]. Eq. (1) becomes Eq. (3) if we replace the c2 constants by 2ΓME, the Qν by the Jν operators, and the function Zν(ω)/ω by χ''(ω).

Having stated the basic formulae I will now proceed to a comparison of the temperature dependence of the linewidth predicted by the two models for the case of Ho$^{3+}$ in YBa$_2$Cu$_3$O$_{6+x}$. For this purpose I will make the same simplifications as made in Ref. [6], namely to use the Debye density of states \( Z(\omega) = 3\omega^2/\omega_D^3 \) with \( \omega_D = 80 \) meV for Zν(ω), independent of ν, and to treat all the magnetoelastic coupling constants as equal and mode-independent. The quadrupole matrix elements are calculated from the Ho$^{3+}$ wavefunctions derived from the established model for the crystal field. This means there is only one unknown parameter c which can be adjusted to match the experimental linewidth data in the temperature range over which the superconductor is in the normal state (T ≳ 100 K).

Fig. 2(a) displays the curve obtained from the magnetoelastic model including the first 8 levels of the crystal field split J = 8 ground state of Ho$^{3+}$ together with the same data as on Fig. 1. In principle one could include all \( 2J + 1 = 17 \) levels in the calculation, but we prefer to apply a cut-off after level 8 (11.8 meV) because there is a large gap to level 9 (at 58 meV) at which energy the measured phonon density of states [1] is much smaller than that calculated from the Debye model. This, together with the small thermal occupancy at energies of 58 meV and above, means that the contribution to the relaxation from levels 9–17 will in reality be negligible. A comparison of the calculated curves in Fig. 1 and Fig. 2(a) reveals a very significant difference between the 3-level and the 8-level approximations. The shape of ΓME(T) calculated in the 3-level approximation has too much curvature in the temperature range 10–100 K relative to the more complete calculation. The reason for this difference, as anticipated earlier, is the neglect in the 3-level approximation of 5 of the 6 levels in the energy range 1–12 meV. These levels become thermally accessible as the temperature is raised and cause a significant amount of relaxation through indirect transitions.

What is clear from Fig. 2(a) is that the experimental points deviate systematically from the calculated curve for temperatures below T ≈ 100 K. This deviation is emphasised in Fig. 2(b) by plotting Γ/ΓME, the ratio of the experimental linewidths to the theoretical linewidths derived from the 8-level magnetoelastic model. Figs. 2(a) and (b) can be compared with the corresponding results for the spin exchange coupling model shown in Figs. 2(a) and (d) of Ref. [6] which exhibit a similar deviation.

The important point to emphasise, therefore, is that if only 3 levels are included in the relaxation calculation
then the predicted curve follows the experimental points very well, as illustrated by Fig. 1, but as more intermediate levels are included the experimental linewidths fall significantly below the calculated curves both for the magnetoelastic model and for the spin exchange coupling model (the deviation being somewhat larger for the latter model). The apparent agreement between experiment and theory suggested by Fig. 1 cannot, therefore, be used as evidence to favour the magnetoelastic model over the exchange coupling model as claimed by Lovesey and Staub. Indeed, if anything, the failure of the magnetoelastic model to describe the data depicted in Figs. 2 provides further support for the spin exchange model because in this scenario the anomalous reduction in linewidth below $T_c$ is explained by the opening of a gap (the superconducting and/or pseudogap) in the electronic excitation spectrum of the CuO$_2$ layers.

The second point I wish to make concerns the magnitude of the magnetoelastic coupling constant. As indicated on Figs. 1 and 2(a) the value of $c^2$ needed to fit the experimental data changes from 1.93 meV$^3$ to 0.268 meV$^3$ as the number of intermediate levels is increased from 3 to 8. This sensitivity to the number of levels included in the model is significant if the coupling constants for different lanthanides are to be compared. For example, in the magnetoelastic model proposed in Ref. 1 $c$ is proportional to the Stevens factor $\alpha$ of the lanthanide ion, and so the strength of the paramagnetic relaxation for one lanthanide ion can be scaled onto another. In Ref. 1 linewidth data for Tb$^{3+}$ and Ho$^{3+}$ in superconducting YBa$_2$Cu$_3$O$_{6+\delta}$ were found to be consistent with the predictions of this scaling hypothesis when analysed with the 3-level model. Mindful of the sensitivity of $c^2$ to the number of intermediate levels included in the relaxation calculation I re-analysed the linewidth data for Tb$^{3+}$ with a 13-level model and found $c^2 = 11.5$ meV$^3$ (the equivalent value from the 3-level model is 24 meV$^3$). My estimate for the ratio $c^2$(Tb)/$c^2$(Ho) is 11.5/0.268 = 43, which compares with the scaling prediction $c^2$(Tb)/$c^2$(Ho) = 20.7, a factor 2 difference. Hence, the validity of the claim in Ref. 1 that the scaling of the linewidths supports the magnetoelastic model for the paramagnetic relaxation is once again seen to be dependent on how many crystal field levels are included in the calculation.

I will finish with some brief comments on the two mechanisms, magnetoelastic or exchange coupling, proposed to explain the paramagnetic relaxation of lanthanides in YBa$_2$Cu$_3$O$_{6+\delta}$. It has not been the intention here to criticise the magnetoelastic model itself. Indeed, the theory provided by Lovesey and Staub, summarised in Eq. 4 above, is an important contribution that permits progress to be made in the disentanglement of different sources of relaxation. Rather, the purpose of making this Comment is to illustrate the pitfalls of comparing a minimal model with experimental data. The inclusion of more relaxation channels has dramatically changed the quality of agreement with the data, and one cannot accept the analysis in Ref. 1 as evidence in favour of phonon damping. My opinion is that a true assessment of whether phononic processes provide an important mechanism can only be made when more is known about the phonon density of states and magnetoelastic coupling strengths for individual phonon modes.

In my opinion one of the strongest arguments for the exchange coupling interpretation is the evidence in many of the measurements for an anomalous reduction in linewidth at a temperature at or above $T_c$, an effect first observed in the non-cuprate system La$_{1-x}$TB$_x$Al$_2$. Such an anomaly cannot be produced by phonon damping. The absence of any anomaly in other measurements can perhaps be explained by the size of the effect. In most cases where the crystal field transition probed is below 1 meV the reduction in linewidth is found to be typically 0.02 meV, e.g. Fig. 2(a). This is smaller than the error bar on the data around $T_c$ in Refs. 1 and 2 which are for quasielastic transitions, and so it would not have been possible to observe such an anomaly with the experimental sensitivity available.

It is hoped that the continuing debate over phonon versus spin fluctuation damping will stimulate a better understanding of paramagnetic relaxation mechanisms for lanthanide ions in correlated electron systems, and that the formulae summarised here may facilitate progress in this area.

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The 3-level model can only be justified for Ho$^{3+}$ if the effect of indirect relaxation involving all levels apart from level $|8\rangle$ at 11.8 meV is negligible. This would require a large enhancement in $Z_\nu(\omega)$ over the Debye density of states for energies around 11.8 meV due to a particular phonon branch with the correct symmetry to couple $|8\rangle$ to $|0\rangle$ and/or $|1\rangle$, and a substantial magnetoelastic coupling between this mode and the lanthanide ion. As there are many phonon branches of different symmetry close to 11.8 meV, this coincidence seems unlikely.

Given in addition that the relaxation in Tb$^{3+}$ is dominated by indirect transitions to a pair of levels near 40 meV, in contrast to Ho$^{3+}$ where only levels below 12 meV are involved, and that the ratio $Z(40 \text{ meV})/Z(12 \text{ meV})$ is certain to be less than that given by the Debye model, the ratio $c^2(\text{Tb})/c^2(\text{Ho})$ is likely to be still larger.

In fact, a magnetoelastic model for the linewidth of crystal field excitations due to phonon damping very similar to that of Lovesey and Staub was discussed earlier by K.W. Becker and P. Fulde, *Crystal Field Effects in Metals and Alloys*, edited by A. Furrer (Plenum Press, New York, 1977), p. 284.

FIG. 1. Temperature dependence of the intrinsic linewidth of the ground-state-to-first-excited-state (0.5 meV) crystal field transition of Ho$^{3+}$ in Ho$_0$Y$_{0.9}$Ba$_2$Cu$_3$O$_7$. The points are the experimental data from Ref. 5 and the line is calculated from the magnetoelastic model of Lovesey and Staub with inclusion of 3 crystal field levels.

FIG. 2. (a) The same plot as shown in Fig. 1 but with 8 crystal field levels included in the magnetoelastic model calculation and a reduction in the $c^2$ coefficient from 1.93 meV$^3$ to 0.268 meV$^3$. (b) Temperature dependence of the reduced linewidths obtained by dividing the data by the theoretical curve in (a).