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

A. T. Boothroyd

Department of Physics, Oxford University, Oxford, OX1 3PU, United Kingdom

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 generalizing 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.

In a recent paper,[1] 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[2–9] 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 three 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 three-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. 1 cannot be taken as evidence that phonons rather than spin excitations are the most important source of relaxation.

I begin by outlining the factors that 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 $|a\rangle \rightarrow |b\rangle$ 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 importance of a particular relaxation channel will depend on the density of host excitation states at the relevant energy and on the size of the transition matrix elements connecting the states involved. For the models under consideration the relevant matrix elements are those of the quadrupolar operators Q_ν in the case of magnetoelastic coupling and of the total angular momentum operators J_α in the case of exchange coupling. Here, ν 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. 1 it was argued that inclusion of only three 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 three-level approximation Lovesey and Staub derived an expression [Eq. (6.7) of Ref. 1] 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 $|a\rangle \rightarrow |b\rangle$ transition is 0.5 meV, and the value of the intermediate level $|\gamma\rangle$ used to generate the calculated curve is 11.8 meV.

It is tempting to interpret the good agreement shown in Fig. 1 as justification for use of the three-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 sizes of the quadrupole matrix ele-
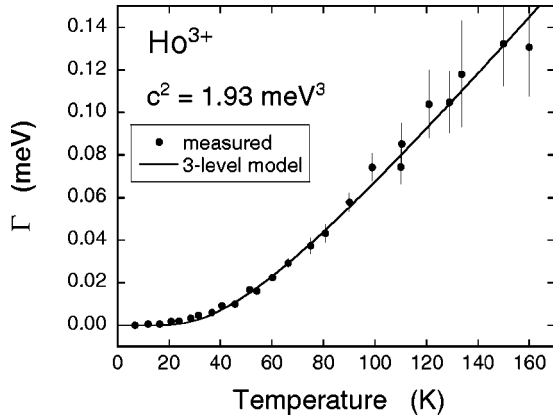
FIG. 1. Temperature dependence of the intrinsic linewidth of the ground-state-to-first-excited-state (0.5-meV) crystal-field transition of Ho^{3+} in $Ho_{0.1}Y_{0.9}Ba_2Cu_3O_7$. The points are the experimental data from Ref. 5 and the line is calculated from the magnetoelastic model of Lovesey and Staub (Ref. 1) with inclusion of three crystal-field levels.

ments to suggest that the totality of intermediate levels can reasonably be approximated by a single level. These arguments are outlined in Ref. 1. In the case of Ho^{3+}, however, the validity of the three-level approximation is much harder to justify because there are no fewer than six crystal-field levels in the energy range 1–12 meV. Several of these additional levels have substantial quadrupole matrix elements connecting them to levels $|a\rangle$ and/or $|b\rangle$, and so they can contribute to the measured relaxation of the 0.5-meV $|a\rangle \rightarrow |b\rangle$ 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 $|a\rangle$ to be the ground state and level $|b\rangle$ the first excited state, and relabel these states as $|0\rangle$ and $|1\rangle$, respectively. In this simplification all other intermediate levels $|\gamma\rangle$ are higher in energy than $|1\rangle$, as occurs in the experimental systems considered here, but it is straightforward to treat other sequences of levels as well. Let ω_γ be the energy of $|\gamma\rangle$ relative to the ground state ($\hbar = 1$). Generalizing the results of Ref. 1 we can express the linewidth (half width at half maximum) in the magnetoelastic model as

$$\Gamma_{ME} = \sum_\nu \Gamma_\nu,$$

where

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

$$(1)$$

$Z_\nu(\omega)$ is the density of phonon modes of symmetry ν at energy ω, $n(\omega) = 1/(e^{\beta\omega} - 1)$, and $\beta = 1/k_B T$. The constants c_ν, c_ν', and c_ν'' are proportional to the magnetoelastic coupling constants and depend upon the symmetry of the modes.

The corresponding expression for the linewidth due to damping by spin excitations mediated via an isotropic exchange interaction J_{Ex} is[5]

$$\Gamma_{Ex} = \sum_\alpha \Gamma_\alpha \qquad (\alpha = x, y, z),$$

where

$$\Gamma_\alpha = 2J_{Ex}^2 |\langle 0|J_\alpha|1\rangle|^2 \chi''(\omega_1) \coth(\beta\omega_1/2)$$
$$+ \sum_{\gamma>1} 2J_{Ex}^2 |\langle 0|J_\alpha|\gamma\rangle|^2 \chi''(\omega_\gamma) n(\omega_\gamma)$$
$$+ \sum_{\gamma>1} 2J_{Ex}^2 |\langle 1|J_\alpha|\gamma\rangle|^2 \chi''(\omega_\gamma - \omega_1) n(\omega_\gamma - \omega_1).$$

$$(2)$$

Here, $\chi''(\omega)$ 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 $\chi''(\omega) \propto \omega$ for the 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 Γ_{ME} and Γ_{Ex}, as was pointed out in Ref. 1. Equation (1) becomes Eq. (2) if we replace the c^2 constants by $2J_{Ex}^2$, the Q_ν by the J_α operators, and the function $Z_\nu(\omega)/\omega$ by $\chi''(\omega)$.

Having stated the basic formulas 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 $YBa_2Cu_3O_{6+x}$. For this purpose I will make the same simplifications as made in Ref. 1, namely, to use the Debye density of states $Z(\omega) = 3\omega^2/\omega_D^2$ with $\omega_D = 80$ meV for $Z_\nu(\omega)$, 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+} wave functions derived from the established model for the crystal field.[10] This means there is only one unknown parameter c that can be adjusted to match the experimental linewidth data in the temperature range over which the superconductor is in the normal state ($T \gtrsim 100$ K).

Figure 2(a) displays the curve obtained from the magnetoelastic model including the first eight levels of the crystal-field-split $J = 8$ ground state of Ho^{3+} together with the same data as in Fig. 1. In principle one could include all $2J + 1 = 17$ levels in the calculation, but we prefer to apply a cutoff 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[11] 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
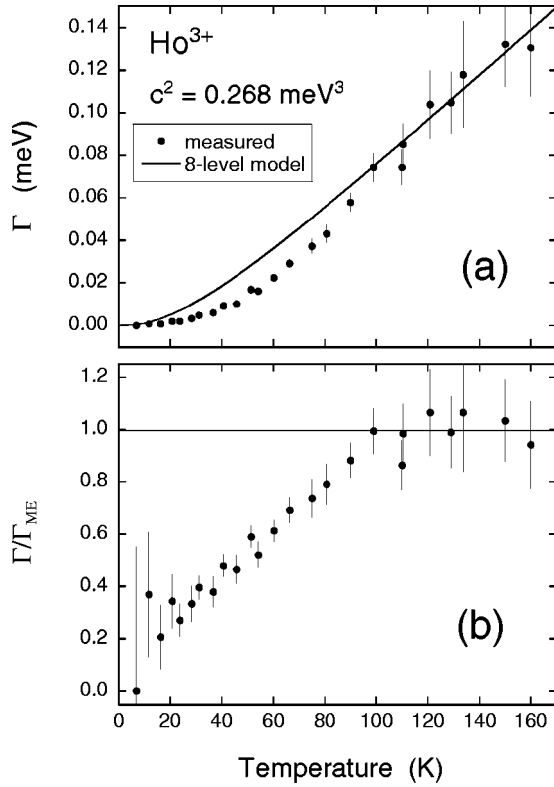
FIG. 2. (a) The same plot as shown in Fig. 1 but with eight crystal-field levels included in the magnetoelastic model calculation and a reduction in the c^2 coefficient from 1.93 meV^3 to 0.268 meV^3. (b) Temperature dependence of the reduced linewidths obtained by dividing the data by the theoretical curve in (a).

three-level and the eight-level approximations. The shape of $\Gamma_{ME}(T)$ calculated in the three-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 three-level approximation of five out of the six 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 $T \approx 100$ K. This deviation is emphasized in Fig. 2(b) by plotting Γ/Γ_{ME}, the ratio of the experimental linewidths to the theoretical linewidths derived from the eight-level magnetoelastic model. Figures. 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. 5, which exhibit a similar deviation.

The important point to emphasize, therefore, is that if only three 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 slightly larger for the latter model). The apparent

agreement between experiment and theory suggested by Fig. 1 cannot, therefore, be used as evidence to favor the magnetoelastic model over the exchange-coupling model as claimed[12] by Lovesey and Staub. Indeed, if anything, the failure of the magnetoelastic model to describe the data depicted in Fig. 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 three to eight. 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 α 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 $YBa_2Cu_3O_{6+x}$ were found to be consistent with the predictions of this scaling hypothesis when analyzed with the three-level model. Mindful of the sensitivity of c^2 to the number of intermediate levels included in the relaxation calculation I re-analyzed the linewidth data[7] for Tb^{3+} with a 13-level model and found $c^2 = 11.5$ meV^3 (the equivalent value from the three-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 $\alpha^2(Tb)/\alpha^2(Ho) = 20.7$, a factor 2 difference.[13] 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 $YBa_2Cu_3O_{6+x}$. It has not been the intention here to criticize the magnetoelastic model itself. Indeed, the theory provided by Lovesey and Staub, summarized in Eq. (1) above, is an important contribution that permits progress to be made in the disentanglement of different sources of relaxation.[14] 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 favor of phonon damping. A true assessment of whether phononic processes provide an important mechanism can only be made when more is known about the 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[2–6,9] for an anomalous reduction in linewidth at a temperature at or above T_c, an effect first observed[15] in the intermetallic system $La_{1-x}Tb_xAl_2$. Such an

anomaly cannot be produced by phonon damping. The absence of any anomaly in some measurements of cuprate superconductors[7,8] 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). The data around T_c in Refs. 7 and 8 (for quasielastic transitions) have error bars that are larger than 0.02 meV, and so with this experimental sensitivity it would have been difficult to observe such an anomaly.

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 formulas summarized here may facilitate progress in this area.

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[12] The three-level magnetoelastic model can only be justified for Ho^{3+} if indirect relaxation via level $|7\rangle$ at 11.8 meV dominates over that from all other levels. This outcome would require the existence of a particular phonon mode ν with $\omega_\nu \simeq 11.8$ meV, having (i) the correct symmetry to couple $|7\rangle$ to $|0\rangle$ and/or $|1\rangle$, (ii) a large enhancement in $Z_\nu(\omega \simeq 11.8$ meV) over the Debye density of states, and (iii) a substantial magnetoelastic coupling with the lanthanide $4f$ electrons. As there are many phonon branches with different symmetries at low energies in $YBa_2Cu_3O_{6+x}$ (Ref. 11) it seems unlikely that one mode will dominate in this way.

[13] Given in addition that the relaxation in Tb^{3+} is dominated by indirect transitions to a pair of crystal-field levels near 40 meV, in contrast to Ho^{3+} where only levels below 12 meV are involved, and that the actual ratio $Z(40$ meV$)/Z(12$ meV$)$ is certain to be less than that calculated from the Debye model, the ratio $c^2(Tb)/c^2(Ho)$ is likely to be even larger than 43, making the discrepancy with the scaling prediction worse.

[14] 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.

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