Reply to "Comment on 'Magnetoelastic model for the relaxation of lanthanide ions in $YBa_2Cu_3O_{7-\delta}$ observed by neutron scattering'"

Stephen W. Lovesey[1] and Urs Staub[2]
[1]*ISIS Facility, Rutherford Appleton Laboratory, Oxfordshire OX11 0QX, United Kingdom*
[2]*Swiss Light Source, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland*
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The influence of lattice vibrations and charge fluctuations on the lifetime of crystal-field states is discussed in the context of experimental studies of lanthanide ions in $YBa_2Cu_3O_{7-d}$. Apart from *S*-state ions, lattice vibrations always provide a channel for relaxation and, through the agency of an intermediate-energy crystal-field state, a significant contribution to the lifetime. In consequence, it is an unsafe practice to interpret the measured lifetime of lanthanide ion crystal-field states in terms of scattering by charge carriers ignoring a lattice contribution. Certainly, it is a bad practice when the host material is a poor metal, like $YBa_2Cu_3O_{7-d}$, and the density of charge carriers is small.

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A closer inspection of the points of criticism raised by Boothroyd[1] shows that they can be easily rebutted. In substantiating our opinion, we start with the reminder that lanthanide ions with nonzero orbital angular momentum in a solid are known to interact strongly with the electric field created by neighboring ions. The electric field, also called the crystal-field potential, is responsible for several well-established properties of lanthanide materials, including magnetic anisotropy and magnetostriction. Hence, apart from *S*-state ions, e.g., gadolinium, *a priori* the ion-lattice interaction is required in the model Hamiltonian used to describe the properties of lanthanide ions in solids. The experimental observations of immediate interest involve the energy levels of the static, time-independent crystal-field potential. These levels are modulated by vibrations in the crystal field which can be expressed in terms of phonon degrees of freedom. Strongly effective modulations are caused by relative displacements between the lanthanide and neighboring ions and involve optical phonons.

One manifestation of modulations on the static crystal field is their role in the relaxation of disturbances to magnetic properties of lanthanide materials. Another channel in relaxation is the interaction between charge carriers and a lanthanide ion. Of course, in insulating materials this interaction is negligible compared to the one involving lattice vibrations because the density of carriers is essentially zero. The opposite extreme is a good metal [as, e.g., Tb:$LaAl_2$ (Ref. 2), where the relaxation by charge carriers is likely dominating], and in general both interactions with the magnetic ion are potentially strong channels of relaxation. The actual materials in question are high-T_c superconductors and these are not good metals: the few charge carriers present in the materials are created by doping. In consequence, for such materials it requires an exceptionally large exchange coupling in the charge-carrier interaction to make the interaction comparable in size to the omnipresent interaction involving lattice vibrations. Set against this, and without any justification, the scenario of researchers[3–5] is that it is legitimate in the interpretation of data on crystal-field widths to include only relaxation through charge carriers and to completely ignore relaxation through lattice vibrations.

In reviewing the strength of the coupling between the lanthanide ion impurity and charge carriers in the doped materials of interest, we first cite the well-established fact that lanthanide impurities are a weak disturbance to the superconducting properties. The finding is the opposite to that with normal superconductors doped with magnetic ions and, clearly, the finding is strong evidence that in the doped materials coupling between the magnetic ion and charge carriers is extremely weak. A quantitative measure of the coupling strength is obtained from electron paramagnetic resonance experiments on gadolinium in dilute concentration in a europium compound.[6] The exchange coupling between the Gd spin magnetic moment and charge carriers is found to be at least two orders of magnitude smaller than those observed in metals.

The view expressed in the foregoing paragraphs, that modulations to the crystal field caused by lattice vibrations must be included as a channel of relaxation for crystal-field states, is backed up by a model calculation.[7,8] Applied to several sets of data gathered on different samples, the model calculation shows that the interaction involving lattice vibrations is probably the dominant channel of relaxation. For certain, it is unsound to completely ignore the relaxation of the crystal-field states by lattice vibrations and attribute observed relaxation rates solely to charge carriers.

A calculation of the relaxation rate due to lattice vibrations is quite a demanding undertaking, since it requires a full knowledge of the crystal field and a full knowledge of the lattice vibrations; the latter includes eigenvectors, frequencies, and the density of states and from this knowledge values of the coupling constants. On closer inspection, however, less detailed knowledge is sufficient to obtain an estimate of the relaxation rate Γ. Two factors contrive to reduce the required information. First, significant contributions to Γ are made by vibrations that give large contributions to the density of phonon states. In particular, low-energy (acoustic) vibrations do not play a significant role in Γ (such vibrations appear in the so-called direct phonon relaxation rate, which is too small to be observed in the experiments under discussion). Second, in the calculation of Γ the phonon density of states is sampled at energies corresponding to the crystal-

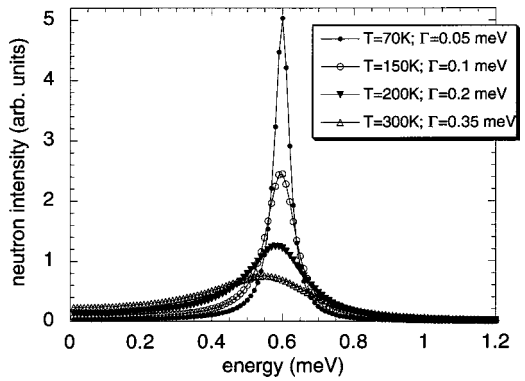

FIG. 1. Model calculation for the $\Gamma_3^{(1)} \rightarrow \Gamma_4^{(1)}$ transition using the theoretical predictions of the neutron cross section for a transition broadened by relaxation (Ref. 7). The following approximation has been used: $M_1(T,\omega)=2\Gamma$, and correspondingly, $M_2(T,\omega)=0$. Values for Γ and the excitation energy (a single crystal-field level) are taken from Ref. 4. Note that the line shape does not depend on the source of relaxation, i.e., it is independent of the model. The lines are a guide to the eye.

field levels and of these few vibrational states some can be discounted because associated matrix elements of the deformation operator are very small. (In our calculation, the operator is taken to be the quadrupole operator and the magnitude of its matrix elements for Tb, Ho, and Tm vary strongly from one crystal-field level to another.) Moreover, in the expression for Γ there is an energy-dependent weighting which enhances contributions with the lowest energy. For the three lanthanide ions we examine, it is found that on taking account of all features just mentioned Γ is largely controlled by the agency of one crystal-field state; this finding leads to a three-state model comprised of the two states probed in the inelastic-scattering event and the agent state. In fitting the calculated expression for Γ to experimental data we assume that there is one coupling constant, denoted by ζ. In this instance, the expression for Γ contains one parameter, which is the product of ζ^2 and the magnitude of the phonon density of states at the energy of the agent state. We obtain impressive accounts of data published on the relaxation rates of Tb, Ho, and Tm and the parameter for each ion determined by fitting is physically reasonable and internally consistent.

To achieve a yet more realistic model for Γ a number of aspects are to be addressed. In order to make real progress in this direction the aspects must be introduced in a systematic and consistent manner. For example, to go beyond what we have done in addressing the relative importance of the crystal-field levels as agents in Γ one must examine how their contribution depends on the magnitude of the density of states and the dependence of the associated coupling constant on energy and the corresponding combination of eigenvectors. By not following such a line of rigorous enquiry, Boothroyd[1] is unreasonably including the low-energy acoustic-phonon modes in the calculation of Γ for holmium. As we have mentioned, such modes are not significant in Γ because the associated density of phonon states is very small [smaller than extrapolated from the density of states at 12.5 meV (Ref. 9) by the Debye model], and acoustic modes do not create relative displacements of ions that are strongly effective modulations which result in large coupling constants (the ions move locally in phase). These crucial factors are absent in the calculations reported in the Comment.[1] Instead, each level is assigned the same coupling constant, and the phonon density of states is replaced by the Debye model, which is inadequate for an assessment of the relative importance of crystal-field levels as agents in Γ. The largely arbitrary extension[1] of our calculation is incomplete, which allows Boothroyd to obtain these unrealistic results.

There are two small points to note. First, assuming an anomalous reduction of Γ, it may as well reflect a small change of the phonon density of states due, e.g., to a slight change of a phonon branch, as the singularities in the phonon density of states can be very sharp. Second, note that Γ in Y:$HoBa_2Cu_3O_7$ (Ref. 3) is found to be two times larger at 150 K than in $HoBa_2Cu_3O_7$,[10] which cannot be due to the change of the interaction strength with charge carriers (the same *f* ion and the same crystalline-electric-field potential) and the same density of states, but could be understood by the differences of the phonon density of states due to the replacement of Y by the heavier Ho.

We conclude by noting other points of concern in the interpretation of inelastic-neutron-scattering experiments to extract information from the relaxation rate on charge carriers. (A) Determining Γ demands more of the data analysis than determining just the position in energy of an excitation. A Lorentzian line shape is not valid universally and there is evidence that a damped harmonic oscillator is better for low-energy states, as illustrated in Fig. 1 for the case of $HoBa_2Cu_4O_8$.[4] In addition, the experimental data is not built from single excitations, and data analysis requires extremely accurate knowledge of the origin and temperature dependence of the substructures.[3–5] (B) Notwithstanding the very real difficulties to be faced in properly analyzing data to precisely extract Γ, one might view the finding of an isotope effect in the width of a crystal-field level[4,5] as evidence of the role of lattice vibrations in the relaxation of a crystal-field state.

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