A magneto-elastic model for the relaxation of lanthanide ions in YBa$_2$Cu$_3$O$_{7-\delta}$ observed by neutron scattering

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Abstract

The 4f electrons attached to a lanthanide ion substituting for Y in YBa$_2$Cu$_3$O$_{7-\delta}$ are described with a crystal-field potential (symmetry D$_{2h}$) and a magneto-elastic interaction, linear in the normal modes of vibration of the paramagnetic ion and anions. The most significant matrix elements of the interaction are determined using selection rules and wavefunctions for the crystal-field states. Applied to Tb^{3+}, Ho^{3+} and Tm^{3+}, calculations for the ground state and first excited state indicate that the dynamic properties of the lanthanide ions are adequately described by the simple addition of one crystal-field state, leading to a three-state model similar to the one introduced by Orbach for the interpretation of electron paramagnetic resonance signals from a lanthanide ion in dilute concentration in a salt.

The cross-section for inelastic scattering of neutrons by an ion is derived by constructing a pseudo-spin model (spin = 1) and treating the magneto-elastic interaction as a perturbation on the three crystal-field states. In the case of Tb^{3+}, the energy of the first excited state relative to the ground state is found to be very much smaller than the energy of any other state, the scattering of neutrons is thus a quasi-elastic process and the width in energy or, alternatively, the relaxation rate is proportional to $\{\exp(\Delta/k_BT) - 1\}^{-1}$, where T is the temperature and Δ is the energy of the third, intermediate crystal-field state at which the density of phonon states is very significant. The value of Δ suggested by the calculation and the law predicted for the temperature dependence of the relaxation rate are in accord with measurements, on metallic and non metallic samples. An equally impressive account is given of data published on the relaxation rate of Ho^{3+} in metallic YBa$_2$Cu$_3$O$_{7-\delta}$, and the relaxation rate is predicted to be different from zero at zero temperature. The relaxation rate and cross-section for Tm^{3+} are predicted to be significantly different from those for Tb^{3+} and Ho^{3+}.

1. Introduction

Several groups of researchers claim that charge carriers in ceramic superconductors are probed in an investigation of the valence electrons of substitutional paramagnetic ions, offering information on the carriers obtainable by no other means. For the claim to be valid, an essential requirement is that the potent source of relaxation for the impurity states is the interaction of valence electrons with host carriers, and thermal vibrations of the host ions at most cause a minor perturbation. Following this line of thought, the observed variation with temperature of the relaxation rate of 4f impurity states is described as anomalous for not following the temperature dependence predicted by a realistic model of the exchange scattering of impurity and host electrons. The anomaly is attributed to an energy gap associated with the onset of a state of superconductivity, and statements made about the opening as well as the symmetry of the energy gap.

Features of a ceramic superconductor, and we have in mind $YBa_2Cu_3O_{7-\delta}$, diminish the density of host charge-carriers relative to an ordinary metallic host and, consequently, their efficacy in producing the foregoing scenario is impaired. There is a finer balance between Coulomb and electron-lattice interactions than might immediately be recognized and their relative roles in the mechanisms of relaxation bear scrutiny, using experimental and theoretical techniques. For $\delta = 1.0$ the material is a good semiconductor. The addition of oxygen injects a few charge carriers to the CuO_2 planes, and paramagnetic ions that substitute for Y sandwich between two planes. The onset of a superconducting state further diminishes the density of these few charge carriers available to expedite relaxation of the 4f state. Couched in terms of a mechanism for relaxation, the ability of charge carriers to absorb energy is reduced by the opening of a gap in their energy spectrum.

The balance between the Coulomb and electron-lattice interactions as the source of relaxation of 4f electrons has shifted to favour the electron-lattice interaction in light of experiments by Staub et al. [1] on metallic and non-metallic materials. These investigators have shown that, the relaxation rate of the lowest energy state of Tb^{3+} substituted for Y in $YBa_2Cu_3O_{7-\delta}$ follows temperature according to a law familiar in the interpretation of electron paramagnetic resonance (EPR) signals from magnetic salts. Here, the potent source of relaxation is modulation of the orbital motion of the valence electrons by thermally activated relative displacements between the paramagnetic ion and anions. The mechanism of relaxation is particularly effective with lanthanide ions for the spin-orbit interaction is large, and the valence states are adequately labelled by the total angular momentum. Staub et al. [1] find that the temperature dependence of the relaxation rate is the same

in metallic (δ = 0.03) and non-metallic (δ = 0.9) samples, and at low temperatures the law is $\exp(-\Delta / k_B T)$ where T is the temperature and the energy Δ is the energy of a known electronic state of Tb^{3+}. In the literature on EPR the law is associated with the name of Orbach, following his investigation of a two-phonon process enlisting an intermediate state of the valence electrons, with an energy Δ, to provide a substantial density of lattice vibrations and a fast relaxation process [2].

In the studies of ceramic superconductors we have described the investigative tool is the inelastic scattering of neutrons. Peaks in the spectrum, viewed as a function of the energy of the scattered neutrons, provide the energies of the valence states of the impurity ion, and the widths of the peaks are controlled by the relaxation of the states. The technique of neutron-electron spectroscopy has a long history [3,4]. With modern sources of neutrons and spectrometers it is possible to investigate processes on a scale of energy from μeV to a few eV.

In this paper we report our findings for the spectrum of inelastically scattered neutrons using a model of the paramagnetic ion built from a local (crystal field) potential and a magneto-elastic interaction. A review of previous work on this model and models in which the Coulomb interaction and virtual mixing of electrons are dominant mechanisms is found in reference [5]. Hitherto, the expression reported in [5] for the relaxation rate produced by the Coulomb interaction has been adopted as the basis for the interpretation of the spectrum of inelastically scattered neutrons [4, 6].

The crystal-field potential in our model takes account of the electron-electron Coulomb potential, spin-orbit coupling, and the interaction of the valence electrons with (static) anions. The modulation of the orbital motion of the valence electrons by thermally activated vibrations in the local potential is described by a magneto-elastic interaction linear in the normal modes of vibration of the anions. For the spatial coordinates of the valence electrons in the interaction we use an operator equivalent quadratic in the operators of total angular momentum.

The model applied to Tb^{3+} bolsters the interpretation of quasi-elastic neutron data in terms of a lattice-driven relaxation process given by Staub et al. [1]. First, we establish that the magneto-elastic interaction strongly couples the two states of Tb^{3+} lowest in energy to states at about 40 meV, which coincide with substantial weight in the phonon density of states. Secondly, the calculated relaxation rate behaves as a function of temperature like $\{\exp(\Delta/k_B T) - 1\}^{-1}$. In addition, we

report similar investigations of Ho^{3+} and Tm^{3+}, and predict that these ions display features due to the magneto-elastic interaction not found with Tb^{3+}. Our findings are gathered in section 7.

2. Point group symmetry and selection rules

The lanthanide ion substitutes Y in $YBa_2Cu_3O_{7-\delta}$ and its environment in the highly oxygenated materials has the symmetry D_{2h}. All four representations of this group are one dimensional. The unit representation is denoted by A. The remaining representations are denoted by B_1, B_2 and B_3, and the corresponding base functions transform as z, y and x, respectively [7]. Direct products of the representations obey A x B_j = B_j , B_j x B_j = A, B_1 x B_2 = B_3 plus the two products obtained by cyclic permutations of the numbers. These results are used in establishing selection rules for matrix elements. Let Γ_β be the representation that corresponds to the symmetry of the operator in the matrix element, and let the 4f wavefunctions transform as Γ_α and Γ_γ . The matrix element in question can be different from zero if the representation Γ_α x Γ_β x Γ_γ contains A.

For an ion with an integer value of the total angular momentum, J, a rhombic field removes the $(2J + 1)$ - fold degeneracy. The rotation group with $J = 6$ (appropriate for Tb^{3+} and Tm^{3+}) contains A four times, and B_1, B_2 and B_3 are each contained three times. For $J = 8$ (Ho^{3+}) the rotation group contains A five times and each B_j four times.

3. Magneto-elastic interaction

Our discussion of the influence of lattice vibrations on the magnetic properties of the substitutional impurity is based on a magneto-elastic interaction proportional to the normal modes of vibration of the anions that surround it. A normal mode that transforms according to the representation Γ_ν is denoted by $u(\Gamma_\nu)$. In the interaction operator the spatial coordinates of the 4f-electrons are represented by quadrupole operators $Q(\Gamma_\nu)$. The rotation group with angular momentum $l = 2$ contains the represention A twice and each B_j once, and the five quadrupole operators are taken to be,

$$Q(A_\alpha) = J_x^2 - J_y^2 , \; Q(A_\beta) = 3J_z^2 - J(J+1), Q(B_1) = J_x J_y + J_y J_x, Q(B_2) = J_x J_z + J_z J_x,$$

and, (3.1)

$$Q(B_3) = J_y J_z + J_z J_y.$$

The magneto-elastic interaction operator is taken to be,

$$\mathcal{H}' = -\sum_{\Gamma_\nu} \zeta(\Gamma_\nu) u(\Gamma_\nu) Q(\Gamma_\nu). \tag{3.2}$$

Here, the coupling parameter $\zeta(\Gamma_\nu)$ has the dimension of energy/length. The order of magnitude of ζ is obtained from, $\delta\zeta \sim e^2 \overline{r^2} \alpha(J)/\delta^3$. In this expression, r is the radial coordinate of a 4f electron and the mean value of r^2 is about 0.2Å^2, δ is the distance between the magnetic ion and an anion, and $\alpha(J)$ is a Stevens factor which has the values $-1/99$, $1/450$ and $1/99$ for Tb^{3+}, Ho^{3+} and Tm^{3+}, respectively. Using the expression, the order of magnitude of $\delta\zeta$ is found to be a few meV.

4. Crystal-field model

A parametric description of the states of 4f-electrons in a crystal must account for the electron-electron repulsion, spin-orbit coupling, and crystal-field interaction. The method used to establish our model of a lanthanide ion in $YBa_2Cu_3O_{7-\delta}$ has recently been reviewed by Staub and Soderholm [8]. In view of this, we shall here present with little discussion results for the energy levels and wavefunctions of the ions of immediate interest.

$Tb^{3+}(^7F_6)$ The energy levels are listed in Table 1. Important features of the energy levels are that the two states lowest in energy are very well separated from the remaining 11 states, and the separation in energy of the two states is only a few μeV. The wavefunctions are quite simple and thus admit an interpretation based on the geometric properties of spherical harmonics. Additions to the principal components of the wavefunctions, listed in Table 1, are small.

A measure of the purity of the wavefunctions is obtained by comparing matrix elements of the quadrupole operator calculated using the principal components and the complete wavefunctions. Some matrix elements of $Q(\Gamma_\nu)$ made with the complete wavefunctions are given in Table 2, and using the principal components, listed in Table 1, we find,

$$\langle a|Q(B_3)|g\rangle = -\langle b|Q(B_2)|g\rangle = \langle a|Q(B_2)|h\rangle = \langle b|Q(B_3)|h\rangle = -11\sqrt{3}.$$

In this instance, the error introduced by using the principal components in place of the complete wavefunctions is 4%, and we accept this as tolerable.

The wavefunction of a non-degenerate state can be chosen to be purely real, and we have made this choice for the principal components listed in Table 1. In consequence, matrix elements of the angular momentum operator J_α, where α denotes a Cartesian component, are zero or purely imaginary and matrix elements of $Q(\Gamma_v)$ are zero or purely real. Diagonal matrix elements of J_α are zero.

Turning to the relative magnitudes of the matrix elements of $\langle a|Q(\Gamma_v)|\gamma\rangle$ and $\langle b|Q(\Gamma_v)|\gamma\rangle$ we note that large contributions to the magneto-elastic interaction are made by the states $\gamma = g$ and h. In addition, the density of phonon states at which these states occur is large. The finding of Brüesch and Bührer [9] is that, for $YBa_2Cu_3O_7$, the density of phonon states weighted by the eigenvectors of the oxygen ions is substantial in an energy interval in the range 20 - 40 meV and, again, from 55 meV out to near the maximum phonon frequency. The density of states weighted by the eigenvectors of the copper ions is substantial in a narrow range of energies, estimated to be 15 - 25 meV.

$Ho^{3+}(^5I_8)$ The wavefunction of the ground state belongs to the representation B_1. The next level is at an energy 0.51 meV above the ground state and it belongs to the representation B_2. We find $\langle a|Q(B_3)|b\rangle = -18.39$, whereas the corresponding matrix element for Tb^{3+}, and allowed by the selection rule, is zero, to a good approximation.

Nearly half the states lie in the interval 0 - 11.20 meV, and the rest are in the interval 55 - 75 meV. It is notable that some matrix elements $\langle a|Q(\Gamma_v)|\gamma\rangle$ and $\langle b|Q(\Gamma_v)|\gamma\rangle$ have very different magnitudes, as illustrated by the following examples:

$$\langle a|Q(B_2)|c\rangle = -27.79, \langle b|Q(B_1)|c\rangle = 2.75, \langle a|Q(B_3)|h\rangle = -25.62, \langle b|Q(A_\alpha)|h\rangle = -28.22,$$

$$\langle a|Q(B_1)|j\rangle = -27.38, \langle b|Q(B_2)|j\rangle = 2.64 \text{ and } \langle a|Q(B_2)|l\rangle = -6.26, \langle b|Q(B_1)|l\rangle = 17.78$$

The energies of the states $|c\rangle$, $|h\rangle$, $|j\rangle$ and $|l\rangle$ are 1.90, 11.20, 58.79 and 62.27 meV, respectively.

A common feature of the wavefunctions of Ho^{3+} and Tm^{3+} is that the wavefunctions contain several components each with substantial weight. In this respect, the properties of Ho^{3+} and Tm^{3+}, and Tb^{3+} are very different.

$Tm^{3+}(^3H_6)$ The wavefunction of the ground state belongs to the representation B_1. The next two states highest in energy belong to the representation B_3 (14.05 meV) and B_2 (14.93 meV). The matrix elements of the quadrupole operator between these states and the next two states are found to be:

$$\langle a|Q(B_2)|b\rangle = -0.04$$
$$\langle a|Q(B_3)|c\rangle = 0.95, \langle b|Q(B_1)|c\rangle = 31.96, \langle a|Q(B_1)|d\rangle = 26.81, \langle b|Q(B_3)|d\rangle = -3.86$$
$$\langle a|Q(B_1)|e\rangle = 0.0, \langle b|Q(B_3)|e\rangle = 5.17, \text{ and } \langle c|Q(B_2)|d\rangle = 4.01.$$

The large size of the matrix elements $\langle a|Q(B_1)|d\rangle$ and $\langle b|Q(B_3)|d\rangle$ and the fact that the energy of the state $|d\rangle$, at 25.31 meV, lies in an energy interval where the phonon density of states is substantial is evidence in favour of this state being active in the lattice modulation of the states $|a\rangle$ and $|b\rangle$. Note that if the transition probed in the neutron scattering experiment is $|a\rangle \rightarrow |c\rangle$, instead of the transition $|a\rangle \rightarrow |b\rangle$ which is slightly lower in energy, the similar magnitudes of the matrix elements $\langle b|Q(B_3)|d\rangle$ and $\langle c|Q(B_2)|d\rangle$ indicate no significant change in the influence on the transition of the magneto-elastic interaction.

5. A three-state model

To calculate the cross-section for the inelastic scattering of neutrons by one of the ions described in the previous section we construct a model designed to capture their essential features. The model contains the ground state and the first excited state, at an energy ε relative the ground state. A third state, at an energy Δ relative to the ground state, is coupled to each of these states by

the magneto-elastic interaction (3.2) which, as we have seen, can couple the two lowest-energy states. In the next section we provide expressions for the cross-section for the transition from the ground state to the state at an energy ε. Here we formulate the three-state model we have described.

A natural algebra for the model is provided by the spin operators and associated quadrupole tensors of a spin with magnitude $S = 1$. We map the three crystal-field states, labelled a, b and γ, and the interaction between the states to the square matrices of these operators taken in their Cartesian basis representation. Diagonal components of the interaction (3.2) are not included in the model, since they only shift the energies of the states and our work is focused on their relaxation.

The spin operators satisfy familiar relations like $\mathbf{S}\cdot\mathbf{S} = 2$, and commutation relations $[S_x, S_y] = iS_z$ and two more obtained by a cyclic permutation of the Cartesian labels. Less familiar, perhaps, are the quadrupole tensors, $T_{\alpha\beta}$. The identity matrix, spin and quadrupole matrices form a complete basis for the representation of an arbitrary square matrix of dimension three.

The three states of the crystal field are represented by,

$$\mathcal{H}_0 = \Delta T_{xx} + (\Delta - \varepsilon)\, T_{yy}. \tag{5.1}$$

An alternative form for $\mathcal{H}_0$ is obtained by using $S_\alpha^2 = T_{\alpha\alpha} + (2/3)I$. The off-diagonal matrix elements of $\mathcal{H}'$, equation (3.2), in the space of the three states are represented by,

$$\mathcal{H}_1 = -2\langle a|\mathcal{H}'|b\rangle T_{xy} - 2\langle a|\mathcal{H}'|\gamma\rangle T_{xz} - 2\langle b|\mathcal{H}'|\gamma\rangle T_{yz}, \tag{5.2}$$

where ($\alpha \neq \beta$),

$$T_{\alpha\beta} = \tfrac{1}{2}(S_\alpha S_\beta + S_\beta S_\alpha) = T_{\beta\alpha}.$$

The lattice displacements that appear in (5.2) are described by the Hamiltonian $\mathcal{H}_2$, which is taken to be harmonic.

The technique used to investigate the statistical mechanics of the quantum system described by the Hamiltonian $\mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2$ is the same as the perturbative technique used in [10] to investigate anharmonic lattice vibrations. Results for the cross-section and relaxation rate presented in the next section are correct at the first level of approximation in the perturbation expansion.

6. Neutron scattering cross-section

The interaction of a neutron with the electrons in the valence state of a lanthanide ion can be described by the operator for the total angular momentum of the ion, J_α. Should the beam of neutrons be deflected through a large angle the operator becomes more complicated but this situation does not concern us.

For the three ions investigated in section 4 we find for $\langle a | J_\alpha | b \rangle$ the results $-6i\delta_{\alpha,z}$ (Tb^{3+}), $3.93i\ \delta_{\alpha,x}$ (Ho^{3+}) and $3.96i\ \delta_{\alpha,y}$ (Tm^{3+}). The selection rule on the Cartesian label follows immediately on noting that, for D_{2h} symmetry, J_x, J_y and J_z transform like the representations B_3, B_2 and B_1, respectively.

In the space of the three states included in our model the matrix element $\langle a | J_\alpha | b \rangle$ is represented by the operator S_z, e.g. for Ho^{3+} we need to obtain the evolution with time, t, of the operator $-3.93\ S_z(t)$. The cross-section is proportional to the power spectrum of the correlation function $\langle S_z(0)S_z(t) \rangle$, where the angular brackets denote a thermal average with respect to all the quantum variables that occur in the total Hamiltonian.

From now until Section 7 we use reduced units in which $\hbar = k_B = 1$.

The two lowest-energy states of Tb^{3+} are separated in energy by a few μeV, and relevant states to which they are coupled by the magneto-elastic interaction occur at a much higher energy. Thus, the energy scales in our model satisfy $\varepsilon << \Delta$, and we report a result for $\varepsilon = 0$. Taking this limit for ε greatly simplifies the expression for the cross-section, as we will soon see when we investigate our model for $\varepsilon \neq 0$ which is appropriate for Ho^{3+} and Tm^{3+}.

For $\varepsilon = 0$ we find,

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, \exp(-i\omega t) \langle S_z S_z(t) \rangle = \tfrac{1}{\pi} \omega \{1 + n(\omega)\} \frac{\chi(T)\,\Gamma(T)}{\omega^2 + \Gamma^2(T)}. \tag{6.1}$$

In this expression, ω is the energy transferred from the beam of neutrons to the sample, and the distribution function,

$$n(\omega) = \left\{ \exp(\omega/T) - 1 \right\}^{-1}. \tag{6.2}$$

The quantity $\chi(T)$ is the isothermal susceptibility of the ion. It is related to a sum rule on the power spectrum; the latter divided by ω and integrated over ω from $-\infty$ to $+\infty$ has the value $\chi(T)/2$.

Neglecting the influence on the susceptibility of the magneto-elastic interaction one finds, $\chi(T) = (T[1 + \tfrac{1}{2}\exp(-\Delta/T)])^{-1}$. In the limit $(\Delta/T) \ll 1$ one gets $\chi(T) \rightarrow (2/3T)$, which is consistent with the Curie susceptibility of a free ion with spin $= 1$.

Our result for the relaxation rate is correct to the leading-order in the magneto-elastic interaction and it is,

$$\Gamma(T) = \frac{3\pi r n(\Delta)}{2M\,\Delta} \left\{ \zeta^2(B_2) \langle a|Q(B_2)|\gamma \rangle^2 Z_{B_2}(\Delta) + \zeta^2(B_3) \langle b|Q(B_3)|\gamma \rangle^2 Z_{B_3}(\Delta) \right\}. \tag{6.3}$$

Here, r is the number of ions in a unit cell and M the mass of an anion. The symmetry representation labels are appropriate for $|\gamma\rangle = |h\rangle$, and they appear in the opposite order for $|\gamma\rangle = |g\rangle$. Lastly, $Z_\Gamma(\omega)$ is the phonon density of states weighted by the symmeterized eigenvectors of the anions, namely,

$$Z_\Gamma(\omega) = \tfrac{1}{3rN} \sum_{j\mathbf{q}} \left| \varepsilon_{j\mathbf{q}}(\Gamma) \right|^2 \delta(\omega - \omega_{j\mathbf{q}}), \tag{6.4}$$

where N is the number of unit cells in the crystal, $\mathbf{jq}$ are labels for the eigenstates (j takes $3r$ values), $\omega_{\mathbf{jq}}$ is the phonon dispersion, and $\varepsilon_{\mathbf{jq}}(\Gamma)$ is the symmeterized eigenvector for the anion. A feature of (6.3) is the absence of a cross-term involving the product of matrix elements belonging to different symmetry representations; the cross-term is zero, at the level of approximation employed in deriving (6.3).

The dependence of $\Gamma(T)$ on the temperature comes solely from the distribution function $n(\Delta)$ defined by (6.2). For $(\Delta/T) \ll 1$ we have $n(\Delta) = (T/\Delta)$ and in the opposite limit $n(\Delta) = \exp(-\Delta/T)$. Note that the prefactor $n(\Delta)/(\Delta)$ in (6.3) decreases rapidly with increasing Δ.

For the case when $\varepsilon > 0$ the isothermal susceptibility is,

$$\chi(T) = \frac{2[n(E) - n(\Delta)]}{\varepsilon[n(\Delta) + n(E) + 3n(\Delta)n(E)]} \,, \tag{6.5}$$

where $E = \Delta - \varepsilon$. The Curie susceptibility is obtained from this expression in the limit of a very high temperature, and the previous expression for $\chi(T)$ is recovered on taking the limit $\varepsilon = 0$.

The power spectrum defined in (6.1) is for $\varepsilon > 0$,

$$\frac{1}{\pi}\omega\{1 + n(\omega)\}\chi(T)\frac{\omega_o^2 M_1(T,\omega)}{[\omega^2 - \omega_o^2 + \omega M_2(T,\omega)]^2 + [\omega M_1(T,\omega)]^2} \,. \tag{6.6}$$

Several comments about this expression are in order. First, the resonance frequency, ω_o, depends on the magneto-elastic interaction. The functions $M_1(T, \omega)$ and $M_2(T, \omega)$ result from the interaction, and if the interaction is reduced to zero the functions go to zero and $\omega_o = \varepsilon$. It is apparent that $M_1(T, \omega)$ contributes a width in energy to the resonance near $\omega = \varepsilon$, and $M_2(T, \omega)$ contributes a shift in energy from the bare resonance energy. We shall not investigate the question of the magneto-elastic interaction giving rise to an excitation created from crystal-field and phonon states, which has the nature of a bound state. Our result for $M_1(T, \omega)$ is given in an appendix, together with an expression for $M_2(T, \omega)$ in terms of $M_1(T, \omega)$. The correction to the resonance frequency created at

leading order by the interaction is also in the appendix. The expression (6.6) satisfies the sum rule referred to following (6.1).

Given the use of perturbation theory to describe the influence of the magneto-elastic interaction is perfectly legitimate, the relaxation rate observed by inelastic neutron scattering is $M_1\,(T,\,\varepsilon) = \Gamma(\,T\,)$. From the expression for $M_1\,(T,\,\omega)$ given in the appendix,

$$\Gamma(T) = \left(\frac{3\pi r}{M}\right)\left\{\ \tfrac{1}{\varepsilon}\coth(\varepsilon/2T)\left[\ \left(\zeta\langle a|Q|b\rangle\right)^2 Z(\varepsilon)\ \right]_\Gamma + \right.$$

$$\left(\zeta\langle b|Q|\gamma\rangle\right)^2_{\Gamma'}\frac{n(\Delta-\varepsilon)}{(\Delta-\varepsilon)}\ \left[Z(\Delta-\varepsilon)+Z(\varepsilon-\Delta)\right]_{\Gamma'} +\left(\zeta\langle a|Q|\gamma\rangle\right)^2_{\Gamma''}\frac{n(\Delta)}{\Delta}Z_{\Gamma''}(\Delta)\left.\right\}.$$

(6.7)

Here, we have indicated that ζ, Q and $Z(\omega)$ depend on a symmetry representation, which is possibly different in each of the three terms. We have allowed for $(\Delta - \varepsilon) \lessgtr 0$, the two possible signs coming from the two possible orderings with respect to energy of the states $|b\rangle$ and $|\gamma\rangle$. On taking the limit $\langle a|Q|b\rangle = 0$ and $\varepsilon = 0$ the expression (6.7) reduces to twice (6.3) and the power spectrum (6.6) reduces to the result in (6.1), as required for this limit.

In (6.7) the phonon density of states contributes at three energies, namely, $\varepsilon, |\Delta-\varepsilon|$ and Δ. The energies $|\Delta-\varepsilon|$ and Δ are the energies of the normal modes of the three-state, pseudo-spin model defined in the previous section, and ε is the energy at which the model is probed. In the limit when the temperature is large compared to these energies $\Gamma(\,T\,)$ is proportional to the temperature. Evidently, one can have $\Gamma(0) \neq 0$. A relaxation rate different from zero at absolute zero is an outcome of $\langle a|Q|b\rangle \neq 0$. Also, if $\varepsilon > \Delta$ there is a contribution to $\Gamma(0)$ proportional to $\langle b|Q|\gamma\rangle^2$. In the event ε satisfies $\varepsilon << T$ and $\varepsilon << \Delta$, the relaxation rate is the sum of a term proportional to T and a term proportional to the distribution function $n\,(\Delta)$.

A feature of our expression for $\Gamma(\,T\,)$ is that it does not vanish if $\langle a|Q|\gamma\rangle$ or, alternatively, $\langle b|Q|\gamma\rangle$ is set to zero, so $\Gamma(\,T\,)$ is not the relaxation rate identified by Orbach. There is a case for not referring to the width in energy of the neutron spectrum as a relaxation rate, and to reserve this name for intrinsic or, alternatively, natural line widths. Intrinsic relaxation arises when two or more

states are mixed and quasi-discrete, with $1/\Gamma$ a measure of the time over which the state of interest can be detected. By nature, intrinsic relaxation exists in the absence of an external probe. In the case of Orbach relaxation, the states $|a\rangle$ and $|b\rangle$ are mixed through the agency of a third state to which they individually have a direct interaction.

We draw attention to the similarity between the expression (6.7) and the relaxation rate discussed in reference [5], due to the Coulomb interaction between crystal-field states and conduction electrons. The similarity is to be expected, of course. On comparing the two expressions for $\Gamma(T)$ one can identify the dissipative part of the susceptibility of the electrons with $Z(\omega)/\omega$, and the operator for the total angular momentum, J_α, with the quadrupole operator in the magneto-elastic interaction. Most importantly for the present discussion, in the two cases the dependence of $\Gamma(T)$ on temperature arises from the same functions. In applications of the expressions, the essential difference between the two cases of electron and phonon mediated relaxation is caused by the actual magnitudes of the matrix elements of J_α and Q. As we have seen, these matrix elements are quite different, e.g. for Tb^{3+} $\left|\langle a|J_z|b\rangle\right| = 6$ and $\left|\langle a|Q(B_1)|b\rangle\right| = 0$, and the values of $\Gamma(T)$ in the two cases turn out to be quite different.

7. Discussion

In this section we gather our findings and discuss the ramifications for the three lanthanide ions Tb^{3+}, Ho^{3+} and Tm^{3+}.

Tb^{3+} The separation between the ground state and first excited state satisfies $\varepsilon \ll \Delta$ and the scattering of neutrons is a quasi-elastic process. The power spectrum and relaxation rate, $\Gamma(T)$, are found in (6.1) and (6.3). In $\Gamma(T)$ the matrix elements of the quadrupole operator in the magneto-elastic interaction have equal magnitudes. Assuming the coupling parameter in the interaction, ζ, and the phonon density of states, Z, are common to the two terms one finds for the relaxation rate,

$$\Gamma(T) = 2178\pi r \frac{(\hbar\zeta)^2}{M\Delta} Z(\Delta) n(\Delta), \tag{7.1}$$

where the distribution function is $n(\Delta) = \{\exp(\Delta/k_B T) - 1\}^{-1}$. In arriving at the numerical factor the states $|g\rangle$ and $|h\rangle$ are included equally in the relaxation process.

The experimental data for $\Gamma(T)$ collected by Staub et al. [1] follow the temperature law (7.1) with $\Delta = 39.5$ meV, which is totally consistent with the energy of the crystal-field states we use to derive (7.1), cf. Table 1. A fit to the experimental data gives a value 8.7 meV for the coefficient of $n(\Delta)$. While not in a position to give a totally independent argument to arrive at this value, knowledge gathered on the crystal-field potential and lattice dynamics of $YBa_2Cu_3O_{7-\delta}$ show that the experimentally derived figure is achievable [8, 9, 11]. The coupling parameter and parameters in the crystal-field potential should be viewed in the same way, and a value for ζ derived from fitting to experimental data. (By way of orientation to the magnitude of the quantities in the coefficient of $n(\Delta)$ in (7.1) one finds, for $\delta = 2.4$Å, $\zeta \sim (2 \text{ meV})/\delta$ and the order of magnitude of $Z(\Delta)$ is $3\Delta^2/E_D^3$ with a Debye energy $E_D \sim 2\Delta$. Collecting these figures, the coefficient of $n(\Delta)$ in (7.1) is ~ 4 meV.)

Ho^{3+} The crystal-field state favoured for the third state in the pseudo-spin model has an energy $\Delta = 11.20$ meV. Matrix elements of the magneto-elastic interaction between this state and the two states lowest in energy, separated by $\varepsilon = 0.51$ meV $\equiv 5.9$K, are large and very similar in size. Also, the matrix element of the interaction taken between these two states is large. However, looking at expression (6.7) for the relaxation rate, its contribution to $\Gamma(T)$ is brought down by $Z(\varepsilon)$ which is likely to be as much as three orders of magnitude smaller than $Z(\Delta)$. Hence, except at a very low temperature, $k_B T \ll \Delta$, $\Gamma(T)$ is well represented by the second and third terms in (6.7), and these reduce to provide the estimate,

$$\Gamma(T) \cong 4358 \pi r \frac{(\hbar\zeta)^2}{M\Delta} Z(\Delta) n(\Delta). \tag{7.2}$$

The available data on $\Gamma(T)$ for Ho^{3+} in metallic $YBa_2Cu_3O_{7-\delta}$ is described very well by (7.2) with $\Delta = 11.2$ meV.

The coefficient of $n(\Delta)$ determined from experimental data is 0.16 meV. It is satisfying to find that a similar value is obtained by scaling the value of the coefficient for Tb^{3+}, namely,

8.7 meV. The scaling is done by taking account of the Stevens factor in ζ, the numerical coefficient, Δ, and $Z(\Delta)$ which is assumed to be proportional to Δ^2; taking all these factors into account we arrive at 0.2 meV for the coefficient of $n(\Delta)$ in the relaxation rate of Ho^{3+}.

As the temperature approaches zero the relaxation rate approaches the value,

$$\Gamma(0) = \frac{3\pi r}{M\varepsilon}\left[\left(\hbar\zeta\langle a|Q|b\rangle\right)^2 Z(\varepsilon)\right]_{B_3} = \frac{1015\pi r}{M\varepsilon}\left[\left(\hbar\zeta\right)^2 Z(\varepsilon)\right]_{B_3}, \qquad (7.3)$$

where $\varepsilon < \Delta$. In this expression, the order of magnitude of $Z(\varepsilon)$ is $3\varepsilon^2/E_D^3$ and the Debye energy $E_D \sim 80$ meV. Assuming the density of states is quadratic, the coefficient of $n(\Delta)$ determined experimentally, 0.16 meV, leads to the estimate $\Gamma(0) \sim 1.7$ μeV.

Tm^{3+} For this ion we find $\varepsilon = 14.05$ meV. With regard to the matrix elements of the magneto-elastic interaction there is essentially no coupling of the two states lowest in energy, in contrast to Ho^{3+}. If the crystal-field state at $\Delta = 25.31$ meV is taken to be the third state in the pseudo-spin model there are contributions to $\Gamma(T)$ weighted by Z_{B_1} (25.31) and Z_{B_3} (11.26), and these are accompanied in the relaxation rate by quite large matrix elements of the interaction. Should we take the state at 14.93 meV as the third state in the model the phonon density of states contributes at this energy and 0.88 meV; the density of states at 0.88 meV is comparatively small, and the density of states at 14.93 meV is accompanied by a comparatively small matrix element. These observations lead us to predict that $\Gamma(T)$ is essentially determined by the crystal-field state with energy $\Delta = 25.31$ meV. In this instance, the dependence on temperature is a weighted sum of the distribution functions n (25.31) and n (11.26), and $\Gamma(0) = 0$.

Acknowledgement

Appendix

The functions M_1 (T, ω) and M_2 (T, ω) in (6.6) are, respectively, the real and imaginary parts of a dynamic self-energy, and they are related through the dispersion formula,

$$M_2(T,\omega) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{du M_1(T,u)}{(\omega - u)}, \tag{A1}$$

where P denotes the principal part of the integral. M_1 (T, ω) is an even function of the frequency, and M_2 (T, ω) is an odd function. We provide results for M_1 (T, ω) that are correct at the first level of approximation in the magneto-elastic interaction. The relaxation rate discussed in the main text $\Gamma(T) = M_1$ (T, ε) where ε is the energy of the excitation in the three-state, pseudo-spin model, defined in section 5, which is probed by neutron scattering, i.e. ε is the difference in the energies of the states we have labelled a and b.

We find $M_1(T,\omega)$ is a sum of three terms proportional to $\langle a|Q(\Gamma_v)|b\rangle^2$, $\langle b|Q(\Gamma_v)|\gamma\rangle^2$ and $\langle a|Q(\Gamma_v)|\gamma\rangle^2$. The first term is,

$$\left(\frac{3\pi r}{M\varepsilon}\right) \coth(\varepsilon/2T) \left\{ \left(\zeta \langle a|Q|b\rangle\right)^2 [Z(\omega) + Z(-\omega)] \right\}_\Gamma. \tag{A2}$$

Here, ζ, Q and Z depend on the symmetry representation, Γ, which is attached as a subscript to the brackets in which they appear. The function $Z(\omega)$ is the phonon density of states weighted by the symmeterized eigenvectors of the anions.

The next term in M_1 (T, ω) is,

$$\left(\frac{3\pi r}{4M\varepsilon}\right) \exp(-\Delta/T)[1 + n(\varepsilon)] \left(\zeta \langle b|Q|\gamma\rangle\right)^2_\Gamma$$

$$\left\{ \left(\frac{[1 + n(\Delta - \omega)](\omega + \varepsilon)^2}{\omega n(\omega)(\Delta - \omega)} [Z(\Delta - \omega) + Z(-\Delta + \omega)]_\Gamma \right) + (\omega \to -\omega) \right\}. \tag{A3}$$

Inside the curly brackets the second contribution is obtained from the first by changing the sign of ω, i.e. it is proportional to $(\omega - \varepsilon)^2$ and does not appear in $\Gamma(T)$. Lastly, the term proportional to $\langle a|Q|\gamma\rangle^2$ is obtained from (A3) by (i) replacing Δ by $(\Delta - \varepsilon)$ and (ii) replacing $(\omega \pm \varepsilon)^2$ by $(\omega \mp \varepsilon)^2$.

In addition to creating a width to the resonance peak in the cross-section for scattering by a paramagnetic ion, the magneto-elastic interaction changes ε and makes it a function of temperature. The position of the peak in the cross-section depends on $\varepsilon(T)$ and $\Gamma(T)$, and it is given by the formula $\{\varepsilon^2(T) - \Gamma^2(T)/2\}^{1/2}$.

The magneto-elastic interaction acts to repel two crystal-field levels, and increases their separation in energy. Hence, there is an increase in energy between a and γ and between b and γ, and $\varepsilon(T)$ is the difference between the two energies.

In giving our expression for $\varepsilon(T)$ it is convenient to introduce two integrals,

$$Y_\Gamma(T,\varepsilon) = \varepsilon P \int \frac{du.Z_\Gamma(u)\coth(u/2T)}{u(\varepsilon^2 - u^2)},$$

and,

$$F_\Gamma(T,\omega) = P \int \frac{du.Z_\Gamma(u)}{(\omega^2 - u^2)}\left\{\frac{\omega}{u}\coth(u/2T) - 1\right\}.$$

In the limit of a high temperature the two integrals approach the same value, namely,

$$2T\omega \, P \int \frac{du.Z_\Gamma(u)}{u^2(\omega^2 - u^2)}.$$

For a Debye density of states, $3u^2/E_D^3$, we find the integral has a value,

$$\left(3T / E_{\mathrm{D}}^3\right)\ln\left(\frac{E_{\mathrm{D}} + \omega}{\left|E_{\mathrm{D}} - \omega\right|}\right).$$

The singularity at E_{D} in this expression is an artifact of the Debye density of states.

Our expression for $\varepsilon(T)$ is,

$$\varepsilon(T) = \varepsilon + \frac{3r}{M}\left\{\left(\zeta\langle a|Q|b\rangle\right)_{\Gamma}^2 Y_{\Gamma}(T,\varepsilon) - \tfrac{1}{2}\left(\zeta\langle b|Q|\gamma\rangle\right)_{\Gamma'}^2 F_{\Gamma'}(T,\Delta-\varepsilon) + \tfrac{1}{2}\left(\zeta\langle a|Q|\gamma\rangle\right)_{\Gamma''}^2 F_{\Gamma''}(T,\Delta)\right\}. \qquad \text{(A.4)}$$

In this expression, ε is the energy of the state b relative to the state a obtained from the crystal-field potential. The integrals in the correction to ε caused by the magneto-elastic interaction do not vanish at zero temperature. In the limit of a high temperature the integrals approach a common value which is proportional to the temperature, and the sign of the correction is determined by the relative sizes of the matrix elements of the quadrupole operator and the coupling parameters.

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Table 1

States of $Tb^{3+}(^{7}F_{6})$ in a crystal-field potential of D_{2h} symmetry. The principal component of the wave function is shown which is chosen purely real. $|M\rangle \equiv |J = 6, M\rangle$. The normalization factor $1/\sqrt{2}$ is included with a principal component in carrying out a reported calculation.
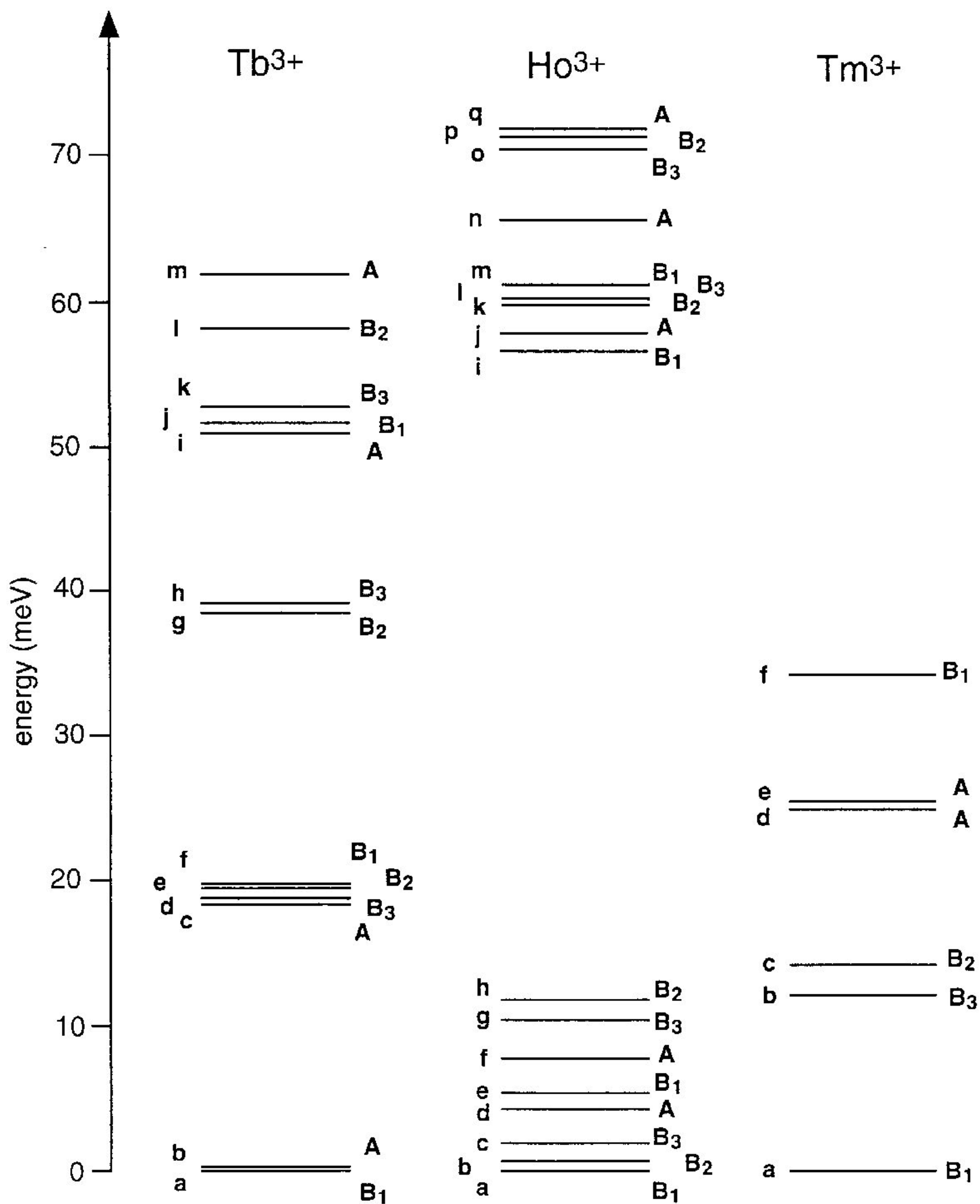
Energy (meV)	Symmetry	Label	Principal component
0.0	B_1	a	$i(-|6\rangle + |-6\rangle)$
0.007	A	b	$-(|6\rangle + |-6\rangle)$
18.48	A	c	$-|0\rangle$
18.64	B_3	d	$-i(|1\rangle + |-1\rangle)$
19.35	B_2	e	$(-|1\rangle + |-1\rangle)$
19.87	B_1	f	$i(-|2\rangle + |-2\rangle)$
38.35	B_2	g	$(-|5\rangle + |-5\rangle)$
39.45	B_3	h	$i(|5\rangle + |-5\rangle)$
50.99	A	i	$(|2\rangle + |-2\rangle)$
51.79	B_1	j	$i(-|4\rangle + |-4\rangle)$
52.62	B_3	k	$i(|3\rangle + |-3\rangle)$
58.54	B_2	l	$(-|3\rangle + |-3\rangle)$
61.21	A	m	$(|4\rangle + |-4\rangle)$

Table 2

Some matrix elements of the quadrupole operator $Q(\Gamma_v)$ for states of Tb^{3+} in a crystal-field potential of D_{2h} symmetry, e.g. $\langle a|Q(\Gamma_v)|d\rangle = 0$ for $\Gamma_v \neq B_2$ and $\langle a|Q(B_2)|d\rangle = -4.15$. For $\langle a|Q(\Gamma_v)|b\rangle$ one obtains $\langle a|Q(B_1)|b\rangle = 0.03$, and all other matrix elements are zero. All the off-diagonal matrix elements of $Q(A_\beta)$ not zero by a selection rule are similarly very small in magnitude.

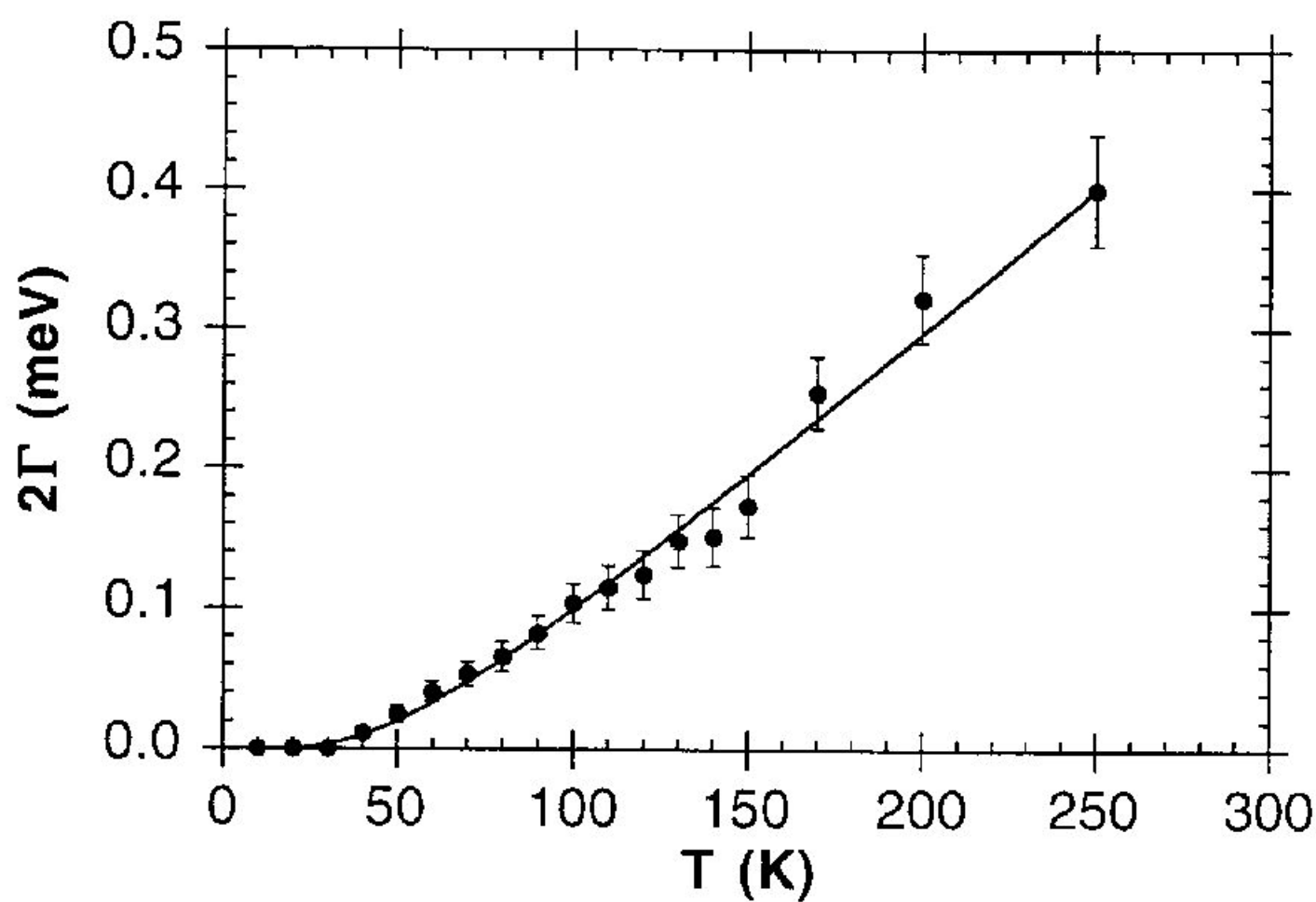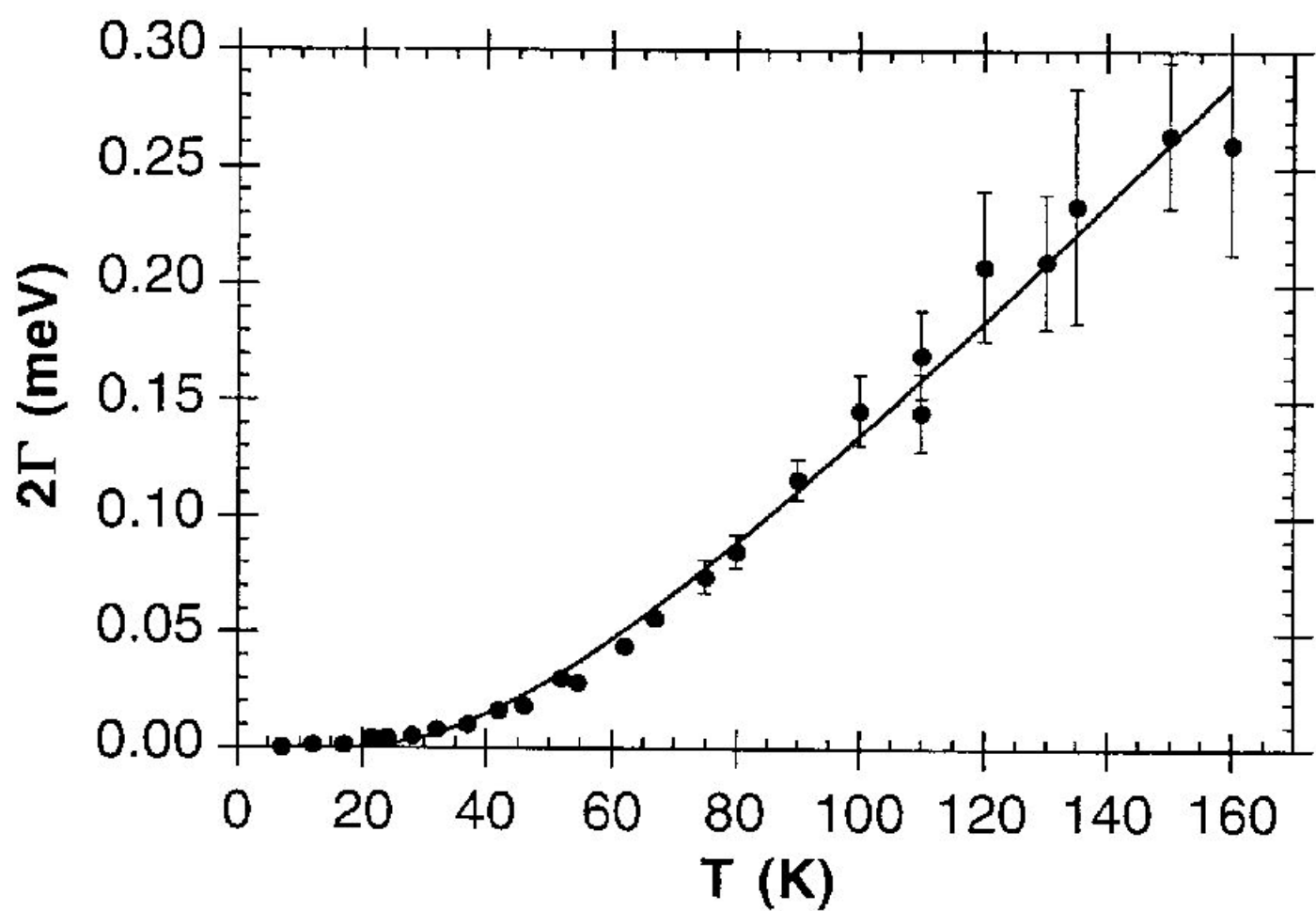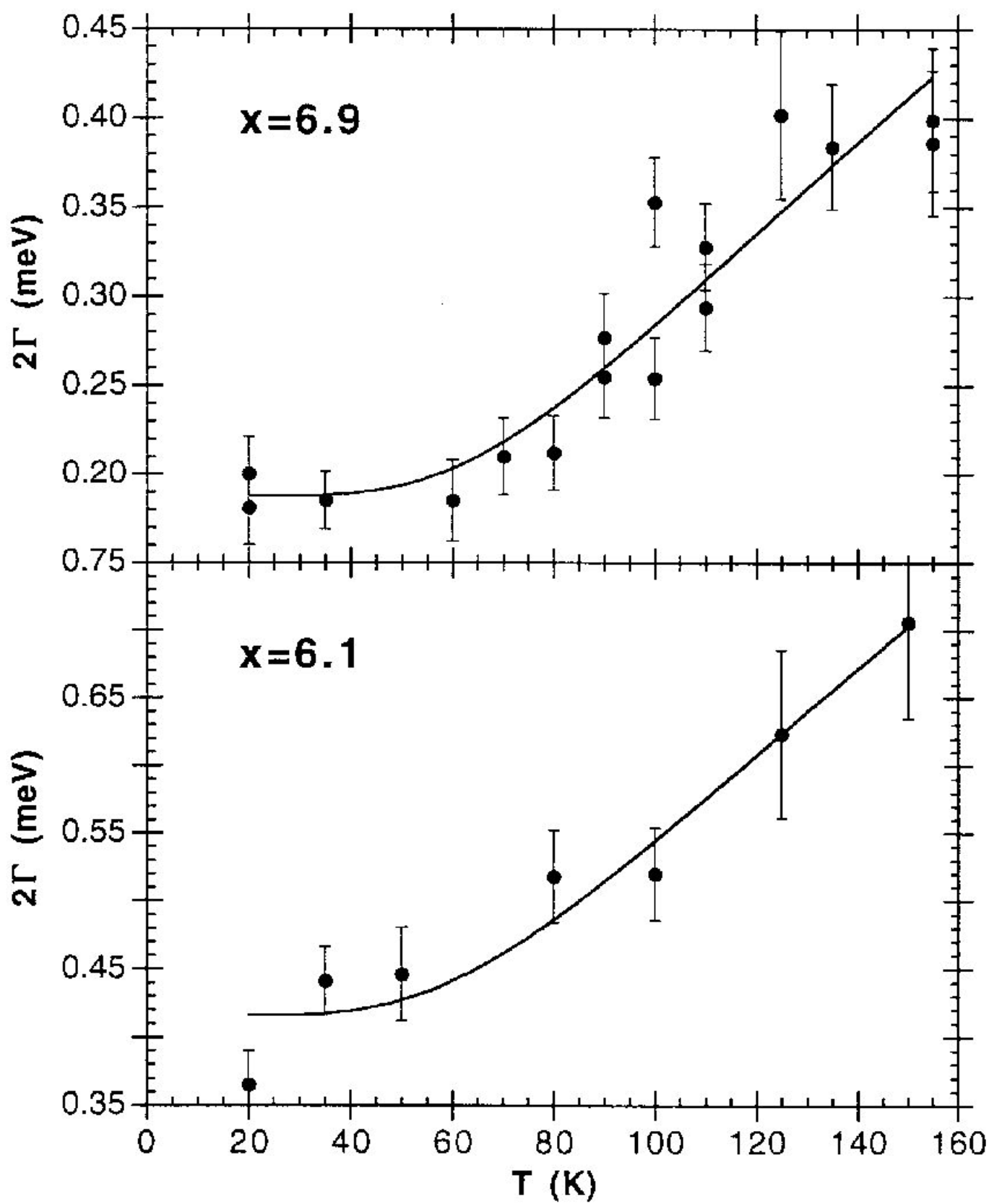|	$\langle a|$	$\langle b|$
$|c\rangle$	$Q(B_1)$, 3.20	$Q(A_\alpha)$, −3.19
$|d\rangle$	$Q(B_2)$, − 4.15	$Q(B_3)$, − 4.15
$|e\rangle$	$Q(B_3)$, 3.23	$Q(B_2)$, − 3.23
$|f\rangle$	$Q(A_\alpha)$, 0.39	$Q(B_1)$, 0.39
$|g\rangle$	$Q(B_3)$, − 18.32	$Q(B_2)$, 18.32
$|h\rangle$	$Q(B_2)$, − 18.38	$Q(B_3)$, − 18.38

Fig. 1

Fig. 2

Fig. 3

Fig. 3