SPECTRAL ENERGY TRANSFER IN RUBY
A. Attar, E. Duval, M. Montagna, A. Monteil, G. Viliani

To cite this version:
A. Attar, E. Duval, M. Montagna, A. Monteil, G. Viliani. SPECTRAL ENERGY TRANSFER IN RUBY. Journal de Physique Colloques, 1985, 46 (C7), pp.C7-99-C7-102. <10.1051/jphyscol:1985719>. <jpa-00224968>

HAL Id: jpa-00224968
https://hal.archives-ouvertes.fr/jpa-00224968
Submitted on 1 Jan 1985

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.
L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
SPECTRAL ENERGY TRANSFER IN RUBY

A. Attar, E. Duval, M. Montagna+, A. Monteil and G. Viliani+

Spectroscopie des Solides, Université Lyon I, 69622 Villeurbanne, France
+Dipartimento di Fisica, Università di Trento, 38050 Povo, Trento, Italy
and
Centri Interuniversitario di Struttura della Materia.

Abstract: The 1-phonon assisted non-radiative transfer in ruby is re-examined in the light of recent experimental results. It is shown that constructive (instead of destructive) interference among 1-phonon processes may occur.

I - INTRODUCTION

There are two main problems concerning non-radiative transfer in ruby which are not resolved yet: (i) Does fast spatial resonant transfer take place in crystals with more than 0.2 Cr% concentration? (ii) Which is the nature of the phonons (or of other energy quanta) which induce spatial-spectral transfer in the 5-30 °K range, whose temperature dependence is linear /1/?

In this communication we will be interested in spatial-spectral non-radiative transfer. Selzer et al /1/ observed the transfer rate in the 5-30 °K range to be both proportional to T and energy-mismatch-independent. This behaviour is characteristic of 1-phonon assisted processes. However, Holstein et al /2/ estimated the 2-phonon process to dominate over 1-phonon process by one to three orders of magnitude in the considered temperature range. There are two reasons why 1-phonon processes should be weak: (1) Since the inhomogeneous R1 line is relatively sharp (<1 cm\(^{-1}\)), the wavelength of the phonons which assist transfer is much larger than the inter-ionic distance, giving rise to completely destructive interference among the different possible 1-phonon processes; (2) The density of states for phonons of \(\nu\) cm\(^{-1}\) energy is much smaller than for 29 cm\(^{-1}\) phonons, which is the splitting between the 2 and 2\(\xi\) states and which corresponds to the energy of the phonons that are involved in resonant 2-phonon processes /2/.

However, recent experimental results show that reason (1) is not valid: on the contrary, constructive interference may take place among different 1-phonon processes.

II - RECENT EXPERIMENTAL RESULTS

1-Splitting of the R1 line under uniaxial stress /3/

In Fig.1 we show the projection of the \(\alpha\)-Al\(_2\)O\(_3\) lattice on a (2110 plane; the \(x_1\) axis is parallel to the \(C_3\) crystal axis, the \(x_3\) axis to the \(C_3\) axis. As shown in the paper by Monteil et al /3/, the sites which are symmetric under a \(\pi\)-rotation around \(C_2\) (i.e. A and B), are inequivalent with respect to \(\sigma_{12}\) or \(\sigma_{13}\) uniaxial stress; the sites which are inversion-symmetric (i.e. A and B' or B and A') are equivalent with respect to any stress. Therefore, the Al\(^{3+}\) (or Cr\(^{3+}\)) sites lying between two adjacent
The splitting $\delta E$ is induced by interaction with a deformation transforming as the $E$ irreducible representation of the trigonal group. This interaction is non-diagonal within the states $E, 2A_2$ or within the states $E, 2T_2$. The matrix elements of the crystal field of $E$-symmetry have opposite signs in the different $\sigma$-sublattices if due to $\sigma_{12}$ or $\sigma_{13}$ stress, while they have the same sign for $(\sigma_{11} - \sigma_{22})$ or $\sigma_{23}$ stress. The simultaneous presence of $\sigma_{12}$ and $\sigma_{13}$ and of $(\sigma_{11} - \sigma_{22})$ and $\sigma_{23}$ gives rise to the splitting $\delta E$.

2-Spectral transfer under uniaxial stress /5/

When a uniaxial stress is applied which induces splitting of the $R_1$ line, the transfer rate is observed not to be energy-mismatch-independent at short times after excitation; the transfer rate is higher on the tails of the excitation line and of its satellites splitted by 0.38 cm$^{-1}$ (see Fig. 2). This fact is explained by assuming that nearby ions belonging to different $\sigma$-sublattices are put out of resonance by the stress. This implies that the interference among different transfer processes cannot be destructive.

III - ONE-HOPON ASSISTED SPECTRAL TRANSFER INDUCED BY $E$-TYPE INTERNAL STRAINS

The above-mentioned experimental results show that $E$ internal strains may play an important role. The interaction of electrons with such strains mixes the states $E$ and $2A_2$ (or $E$ and $2T_2$); therefore, $E$-phonons (considered as a perturbation) act at first order and may induce 1-phonon transfer. According to Holstein et al /6/
the probability of spectral transfer between Cr ions at sites (1) and (2) is proportional to the squared difference of the electron-phonon interactions for the two ions:

\[ W_{21} \propto |g(2) - g(1)|^2 \]

If the crystal is isotropic, \( g(2) \sim g(1) \), and \( W_{21} \sim 0 \), as mentioned in the Introduction: this is the destructive interference effect. However, for two ions belonging to different stress sublattices, in the presence of suitable symmetry, interference may be constructive. Let us show this by re-adapting Holstein et al's /6/ calculation in order to take into account the existence of different stress sublattices. We consider first the effect of static strains. The static-strain-mixed wavefunctions for ions 1 and 2 which are placed in different stress sublattices will be:

\[
\begin{align*}
|E_1^+\rangle & = \alpha |\bar{E}\rangle + \beta(1+\gamma) |2\bar{A}\rangle \\
|E_1^-\rangle & = \alpha' |\bar{E}\rangle + \beta(1+\gamma) |2\bar{A}\rangle
\end{align*}
\]

where \( \alpha, \alpha' \sim \gamma; \) \( \beta \) is the mixing induced by \( (\sigma_{12} - \sigma_{22}) \) or \( \sigma_{23} \) static strains which act in the same way on the two sites; \( \gamma \) is the mixing induced by \( \sigma_{12} \) or \( \sigma_{13} \) static strains which act in different ways on the two sites.

Now, phonons of \( E(T_2) \) symmetry /7/ may induce 1-phonon assisted transfer. The new relevant matrix elements are:

\[
\begin{align*}
\langle 1,\bar{E}, n_{sq} | H_{ph} | 1,2\bar{A}, n_{sq} \rangle & = \beta'(1+\gamma') \langle n_{sq} |1\rangle | \varepsilon(1) | n_{sq} \rangle \\
\langle 2,\bar{E}, n_{sq} | H_{ph} | 2,2\bar{A}, n_{sq} \rangle & = \beta'(1-\gamma') \langle n_{sq} |1\rangle | \varepsilon(2) | n_{sq} \rangle
\end{align*}
\]

where \( \beta' \) and \( \gamma' \) are the same as \( \beta \) and \( \gamma \), but for phonons. Carrying out the calculation we obtain for the 1-phonon transition probability:

\[
W(1) = \frac{2\pi |J'|^2}{K(\Delta E_{12})^2} \sum_{sq} (48\beta'(\gamma+\gamma'))^2 |\langle n_{sq} |1\rangle | \varepsilon | n_{sq} \rangle |^2 \delta(\omega - \Delta E_{12})
\]

where \( J' \) is of the order of \( J \), which is the matrix element of the electronic interaction, and \( \Delta E_{12} \) is the energy-mismatch between the transferring ions.

We are now in position to evaluate the order of magnitude of the ratio \( W(1)/W(res) \).
where \( W(\text{res}) \) is the 2-phonon resonant transfer probability \(/6/\). The quantities \( \beta', \gamma' \) depend on the particular phonon being considered; \( \gamma' \) is a measure of the relative importance of the phonon components which act differently in different stress sublattices, with respect to those which act in the same way: we will assume therefore \( \gamma' \approx 1 \). \( \beta' \) is a measure of the electronic interaction between the states \( \bar{E} \) and \( 2A \), and is the same as the quantity \( A \) in Eq. (2.33) of Ref. 6; finally, \( \gamma \) is also assumed to be unity.

For an energy mismatch of the order of a few tenths of cm\(^{-1}\), we obtain \( \Delta \approx 0.1 \), which corresponds to deformations of the order of \( 10^{-2} \approx 10^{-3} \). It is then easy to obtain:

\[
\frac{W(1)}{W(\text{res})} = \frac{|J'|^2}{K} \frac{4i' (\gamma + \gamma')}{1 + \exp(\Delta E_{12}/kT)} (\Delta E_{12}/\Delta)^3 \left( n(\Delta E_{12})/n(\Delta) \right)
\]

where \( \Delta = 29 \text{ cm}^{-1} \), and \( K \) is of the order of \( J/6 \). Taking \( \Delta E_{12} = 1 \text{ cm}^{-1} \), in the range \( 5^\circ K < T < 40^\circ K \) we may approximate \( n(\Delta E_{12}) \approx \exp(\Delta/kT) \), and \( n(\Delta) \approx \exp(\Delta/kT) \); moreover, assuming \( |J'|/K \approx 1 \), \( W(1) \) and \( W(\text{res}) \) turn out to be comparable at \( 5^\circ K \); a further factor \( \approx 10 \) in favour of \( W(1) \) may be obtained by considering destructive interference effects on \( W(\text{res}) \), that have been neglected here. However, \( W(\text{res}) \) dominates as soon as the temperature is increased above about \( 10^\circ K \).

IV - CONCLUSIONS

We have discussed the recent experimental results which indicate that the anisotropic structure of ruby plays a fundamental role in determining the characteristics of non-radiative spectral transfer. More precisely, we have discussed the effects of internal strains of given symmetry; these strains in principle make 1-phonon assisted transfer allowed between two ions belonging to different stress sublattices. We have also set up a very simplified model to take into account the crystal anisotropy, in order to estimate the relative importance of 1- and 2-phonon assisted processes. We find that at low temperature (\( T \approx 5^\circ K \)) the 1-phonon process may be the dominant one, especially if we take into account the destructive interference which takes place among different 2-phonon processes; these results are in agreement with the experimental findings of Selzer et al.\(/1/\). Even though our model is not able to completely explain the data of Ref. 1 (i.e. the linear \( T \)-dependence up to \( \approx 30^\circ K \)), it cannot be excluded that anisotropy plays an even more important role than here considered, also in view of the oversimplifications inherent to our model.

REFERENCES