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Two-photon spectroscopy of point defects

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Résumé. — Les informations experimentales de la spectroscopie à deux photons dans les impuretés et les défauts dans les solides sont ici résumées. Les résultats les plus importants sont la mesure de la probabilité d'absorption et l'attribution de la symétrie des transitions. Les effets non linéaires sont importants aussi dans d'autres cas comme la création des centres colorés dans les cristaux d'halogénures alcalins.

Abstract. — The experimental results on two-photon spectroscopy in impurities and defects in solids are reviewed. The main results are the measurement of absorption cross sections and in some cases the assignment of the symmetry of the transitions. Nonlinear effects can be of importance also in the process of colour centre formation in alkali halides crystals.

1. Introduction. — Two-photon spectroscopy has recently become a powerful tool for the investigation of the optical properties of solids. Two-photon effects, predicted theoretically by Maria GoeppertMayer in 1931 [1], have been experimentally verified by Kaiser and Garret in 1961 [2], soon after the discovery of the laser.

It was immediately realized that, due to the different selection rules, the information obtained with the two-photon spectroscopy is complementary to that obtained from the conventional one-photon spectroscopy [3, 4, 5]. However the intrinsic experimental difficulties, due to the small probability of this second order effect [6], have prevented up to now a widespread application of the two-photon technique. These limitations are particularly severe in the study of the electronic properties of localized defects in solids and most of the work on two-photon spectroscopy was devoted to intrinsic absorption in insulators and semiconductors (for a comprehensive review see [7]). Indeed in the study of point defects one deals with a number of absorbing centres of the order $10^{17}$ cm$^{-3}$ and therefore the two-photon absorption coefficients are at least four order of magnitude smaller than those measured in band-to-band absorption in solids with $10^{21}$ electrons cm$^{-3}$. Because of these difficulties two-photon absorption in localized defects has been mostly studied monitoring the absorption through its subsequent luminescence. The main advantage of the detection of the two-photon absorption by luminescence is the much greater sensitivity, limited only by the noise of the signal. In this way however one actually measures a two-photon excitation spectrum and the interpretation of the results of this indirect method is less straightforward because of the possibility of non-radiative decays or photoinduced reactions among the defects.

Another limitation of most of the experiments performed up to now in localized defects has been the use of only one or two laser lines at fixed frequency as sources of both photons. In this way two-photon effects rather than two-photon spectra have been observed. It is evident that only a spectrum over a sizable energy range can yield complete information on the positions of the excited states of the defects. The use of tunable lasers as excitation sources promises to be most valuable in this respect.

2. Two-photon effects of impurities in solids. — The first two-photon excitation was detected via luminescence by Kaiser and Garret in CaF$_2$ doped with Eu [2]. Two photons from a ruby laser (1.78 eV) simultaneously absorbed produced a blue fluorescence (~ 2.9 eV) whose intensity increased with the square of the laser power (Fig. 1). This quadratic behaviour is the most evident signature that a two-photon process takes place. Two-photon absorption coefficient of impurities in alkali halides was calculated for NaCl : Ag$^+$ by Gold and Hernandez [8] and measured in a similar system (KCl : Ag$^+$) by the pioneering work of Frölich and coworkers [9]. The A-band of KCl : Ag$^+$ is due to the transition of the Ag$^+$ ion $4d^{10} \rightarrow 4d^9 5s$. This transition is parity allowed for the absorption of two photons. In this experiment the fundamental (1.78 eV) and the second harmonic frequency (3.56 eV) of a ruby laser provided the required energy. The excitation frequency is fixed ($\nu_1 + \nu_2 = 5.34$ eV) but the relative polarization of the two beams can be varied. The angular dependence of the luminescence intensity (see Fig. 2)
1. Quadratic dependence of the blue fluorescence of CaF₂ : Eu²⁺ upon the intensity of the exciting laser beam (see ref. [12]).

Luminescence intensity of KCl : Ag⁺, excited in the A-band, as a function of the angle between the polarization of the two lasers beams (see ref. [9]).

allows the determination of the symmetry ($\Gamma_3 + \Gamma_5$) of the excited states involved in the A-band transition.

Using two photons of the same laser as excitation source one can gain in intensity, but one cannot change independently the polarization of the two beams. However by choosing different directions of incidence and by polarizing the laser beam linearly and circularly, one can perform a complete analysis of the symmetry of the levels involved in the transition. An experiment of this kind has been done in CaF₂ : Eu²⁺ at five different wavelengths [10]. The absorption of the Eu²⁺ ion (around 3.5 eV) is attributed to the transition 4f' ($^8S_{7/2}$) → 4f' (F)5d where the final level of the d electron is split by the cubic crystalline field. The transition probability for two identical photons can be decomposed into contributions of $\Gamma_1$, $\Gamma_3$ and $\Gamma_5$ symmetry. The experimental results rule out the $\Gamma_5$ contribution and help to study the symmetry of the levels originating within the F-d multiplet.

3. Two-photon effects in colour centres. — Two-photon effects in colour centres are still more difficult to observe than those in impurities because of the intrinsic instability of these defects that during the experiment can be ionized, can aggregate or annihilate, also at low temperature. Probably because of this instability some results are not very reproducible and some are not yet clearly understood. In γ-irradiated NaF we have measured the two-photon absorption at a particular wavelength (1.06 μm) [11]. Two luminescence bands, identified by their excitation spectra as due to $F_3^-$ and $I_3^-$ centres (see Fig. 3), increase with the square of the laser power. Assuming the same quantum yield of the emissions excited either by one or by two photons, we have evaluated the absorption cross section at 1.06 μm. We found $\sigma_{F_3^-} = 6.5 \times 10^{-49}$ cm² s photon⁻¹ centre⁻¹ and $\sigma_{I_3^-} = 5.5 \times 10^{-48}$ cm² s photon⁻¹ centre⁻¹ respectively. These values are somewhat uncertain because we could not check the absolute values against some known nonlinear cross section (e.g. Raman cross section [12, 13]) but we believe they are correct within a factor of two.

Two other bands are observed in figure 3 around 510 nm and 775 nm. No precise assignment for the origin of these emissions could be made. The green emission (at energy higher than twice the laser energy) decays with time of excitation at a rate that increases with the laser intensity. It can be probably attributed to a radiative recombination of interstitial-vacancy pairs in the irradiated crystals. Indeed this luminescence is absent in additively coloured NaF. The green band decreases also on increasing the temperature. A nonradiative process, with an activation energy of ~ 35 meV, becomes more probable than the emission.
Two-photon spectroscopy has been also observed in additively coloured KCl containing only F centres. The emission contains two peaks at 700 nm and 900 nm; the latter is superimposed on a pronounced emission tail continuing up to the laser wavelength (Fig. 4). We have interpreted the broad emission tail as *hot fluorescence* [14]. The 900 nm peak is somewhat reminiscent of the two photon excited emission observed by De Martini et al. [15]. Same differences may be due to the different laser pulse duration. Our spectra change markedly if we record the emission at increasingly longer delay times after the laser pulse. In the same system Vassiliev et al. [16] reported on two-photon absorption of F centres followed by ionization. The effect was monitored through the F' centres formation.

4. **Nonlinear effects in localized defects.** — The results reported in the previous paragraphs, although too incomplete to yield two-photon spectra, are nevertheless aimed at the knowledge of the spectroscopic properties of defects such as the symmetry and the energy of states with the same parity of the ground state.

Nonlinear effect have also been used for production and control of point defects in alkali halides. The weak absorption coefficient in the two photon process assures colouration or photocromic processes much more uniform than those obtainable with one photon. With a N₂ laser (3.68 eV) one can colour alkali halides with gap smaller than 7.36 eV such as KI, KBr, NaBr [17] or doped KCl : I, KCl : Br [18] but not wider gap materials such as pure KCl or NaCl. The induced absorption spectrum, as shown in figure 5, is practically the same as that produced in pure X-rayed samples and the refore must be an intrinsic process. The same conclusions were reported by Bradford et al. [19] who coloured KCl by two photons of 4.68 eV (fourth harmonic of a mode-locked YAG : Nd laser).

Two laser photons were used by Mollenauer et al. [20] to produce uniform F centre colouration or to colour only selected regions of the crystals exploiting the controlled optics of the laser beam. KCl crystals containing substitutional hydrogen ion H⁻ (U centres) are transparent to the fourth harmonic of the YAG : Nd laser. Absorption of two such a photons however, generates electron-hole pairs that induce the U → F conversion.
Another nonlinear effect we have recently found is the second harmonic generation in a cubic crystal (NaCl) containing anisotropic defects lacking inversion symmetry [21]. These defects are produced in crystals coloured at high pressure of Na vapor, and annealed at 480 °C. At this temperature the quasi-colloidal X band is destroyed and the isolated duplications brought recently forward by Frolich [21] are really astonishing [22] (see Fig. 7) and it is quite likely the in the next few years two-photon absorption spectroscopy could yield a wealth of new experimental results in the study of point defects in solids.

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References