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Optical Spectroscopy

Optical Spectroscopy is a classification for a range of experimental techniques which involve using ultraviolet, visible, or infrared light to conduct spectroscopy experiments. Spectroscopy is the analysis of the light spectrum which is either absorbed or emitted by a particular sample. The light is separated by wavelength, allowing a quantitative analysis of the particular frequencies absorbed and emitted, which can show up as faint lines or gaps. The intensity of those lines can also then be measured. These gaps correspond to energy transitions in the material, since $E = \hbar\omega$, allowing investigations of the characteristics of that material. This paper will look at various kinds of optical spectroscopy, and discuss the results of a recent paper performing optical spectroscopic experiments on a perovskite sample.

Optical spectroscopy might be considered to be the earliest form of spectroscopy, originating with Newton, who demonstrated the use of a prism to separate a light signal into the spectrum of visible light that made it up, although the ability of a prism to produce a rainbow had been known since ancient times [4]. It is from Newton calling the resulting rainbow a spectrum that spectroscopy derives its name [4]. Later, spectroscopy was advanced by the use of a diffraction grating to replace the prism, allowing a greater degree of spectral resolution and quantification of the wavelengths [4]. Modern spectroscopy uses photomultipliers to measure the intensity of the spectral signal resulting from the diffraction grating, allowing a clear analysis of the spectrum [2].

There are many different kinds of optical spectroscopy, depending on both the source of the light and the analysis of the spectrum. One method of optical spectroscopy which is commonly used in condensed matter applications is photoluminescence spectroscopy. In a photoluminescence experiment, a sample is exposed to a source of light, such as a laser, and the resulting luminescence

from the sample is recorded [3]. Photoluminescence occurs as a result of the relaxation and recombination of electron-hole pairs after an excitation from a light source [3]. A laser pulse first creates these electron hole pairs by exciting electrons out of their ground state and into a conduction band [3]. The system then relaxes, and then the electron falls back into the ground state and recombines with the hole [3]. The recombination occurs when the electron falls back into the valance band, so this causes a photon emission [3]. Photoluminescence in samples occurs in two main groups: fluorescence, in which the luminescence does not persist in absence of the excitation source, and phosphorescence, in which the luminescence can continue for a significant amount of time after the excitation source is removed [1]. Because the photoluminescence of the sample from an excitation will be dependent upon the band structure of the sample, and thus its composition, photoluminescence provides a way to characterize the defects in the material and their concentration [1].

The photoemissions from a sample resulting from photoluminescence make up the light source upon which the spectroscopy is performed. A standard photoluminescence spectroscopy experiment using a fixed excitation energy, and measures the intensity of the resulting signal at various emission frequencies [1]. A simple modification of the photoluminescence experiment involves fixing the energy of the photoluminescence from the sample and instead measuring the intensity as a function of the excitation energy [3]. This is called photoluminescence excitation spectroscopy. Photoluminescence excitation spectroscopy is closely associated with absorption, rather than emission, since it is expected that the signal will be strongest at a point corresponding to the excitation energy absorbed in order to make the transition that leads to photoluminescence [3].

The paper under consideration, *Optical Spectroscopy of Two Dimensional Layered $(C_6H_5C_2H_4-NH_3)_2-PbI_4$ Perovskite*, discusses the results of photoluminescence and photoluminescence excitation spectroscopy experiments on a perovskite sample which consists of layered 2 dimensional planes of

organic and inorganic molecules [2]. Photoluminescence experiments were performed for various temperatures and excitation laser powers, and photoluminescence excitation experiments were performed to explore the intensity dependence of the peaks as a function of excitation energy [2]. Note that measurements made as a function of power involve varying the excitation beam intensity, while measurements made as a function of excitation energy involve varying the excitation frequency.

In the photoluminescence experiment at 10 K, two peaks can be observed, one at 2.355 eV, labeled S1, and one at 2.337 eV, labeled S2 [2]. The paper discusses various explanations given in the literature for these spectral lines, including excitons bound to impurities, bi-excitons, or three peaks being present [2]. An exciton is a quasi particle made from an electron-hole pair, and a bi-exciton is refers to a pair of correlated excitons [1]. In order to eliminate some of these possibilities, Gauthron et al. consider the results of the photoluminescence experiments as a function of excitation power [2]. It can clearly be seen that the intensity of both peaks exhibit a linear dependence on the excitation power, so, as Gauthron et al. points out, explaining the 2.337 line in terms of excitons bound to defects and bi-excitons are both ruled out [2]. This is because excitons bound to defects would saturate, and so would display a dependence that is sublinear. Meanwhile bi-excitons clearly require a superlinear behavior, since it is intuitive that the dependence would be of the form:

$$I \propto n_{bi} \propto n_{ex}(n_{ex} - 1) \approx n_{ex}^2$$

where I is the bi-exciton intensity, n_{bi} is the number of bi-excitons, and n_{ex} is the number of excitons, recalling that bi-excitons are pairs of correlated excitons.

Gauthron et al. examined the results of photoluminescence excitation spectroscopy experiments looking at both the 2.337 eV and 2.355 eV emissions, and found them to be exactly similar [2]. This further indicates that the one of the lines is not due to bi-excitons, since bi-excitons would be expected exhibit a different absorption or photoluminescence excitation profile. Since the

measurements were exactly similar it suggests that the two lines are due to the same excited states, as it is indicative of matching absorption [2]. Gauthron et al. also note that the 14 meV separation in energy of the S1 and S2 lines is approximately the optical phonon energy of PbI_2 of 13.7 meV, and so suggest that S2 may be a phonon replica of S1 [2].

When the photoluminescence spectrum was examined with respect to temperature, Gauthron et al. found that the integrated intensity of the peak S1 remained stable between 10 and 100K, but dropped off sharply as $e^{E_a/kT}$ where the activation energy E_a was found to be 30 to 80 meV depending on the sample being measured [2]. Gauthron et al. suggest that the wide variance in activation energy may be due to the excitation of some other non-radiative carrier, which would thus not contribute to the photoluminescence [2]. In addition, the S1 peak exhibited substantial broadening as the temperature was increased [2]. Gauthron et al. attribute this broadening to exciton interaction with phonons, and fitted the full width at half maximum of the peak with respect to temperature using a phenomenological model often used in inorganic quantum well compounds of the form

$$\Gamma = \Gamma_0 + aT + \frac{\Gamma_{LO}}{e^{\hbar\omega_{LO}/kT} - 1} + \Gamma_{imp}e^{-E_a/kT}$$

where Γ is the full width at half maximum with respect to temperature T , Γ_0 is the full width at 0 K, the second and third terms represents the effect of the acoustic and optical phonons, respectively, with Γ_{LO} representing the exciton-phonon coupling and $\hbar\omega_{LO}$ representing the energy of the optical phonons, which is fitted using the value from PbI_2 of 13.7 meV. The fourth term accounts for the contribution of exciton scattering from impurities and the activation energy E_a was chosen to be 60meV [2]. Gauthron et al. note that the model requires the assumption that the variation in the exciton's wavefunction be smooth on several unit cells, and that the approach ignores the thermal variation of the optical phonon

energy [2]. As a result of fitting the experimental data to this model, Gauthron et al. obtain numerical values for $\Gamma_0 = 17 \pm 1 \text{ meV}$, $a = 0.03 \pm 0.01 \text{ meV K}^{-1}$, and $\Gamma_{LO} = 70 \text{ meV}$ [2].

Gauthron et al. compared the shift between the S1 line and the lower energy photoluminescence excitation line, which would indicate the shift between the absorption and the emission energies, corresponding to the difference created when the exciton relaxes before recombination [2]. They note that in inorganic quantum wells the shift is usually due to excitons being localized within potential minima induced by disorder, but as temperature increases and the thermal energy fluctuations overpower the potential, the trapping weakens and the shift disappears as temperature increases [2]. However, in the perovskite under study, they observe that the shift remains constant with respect to temperature at about 10 meV [2]. They also note that in lead halides such as PbI_2 , strong coupling between excitons and phonons causes the excitons to become self-trapped [2]. That is to say, the excitons correlate with phonons to cause the surrounding potential to localize the exciton, and within such compounds this interaction is stronger than the ambient thermal fluctuations. This exciton-phonon coupling can be treated as together as a quasi-particle called a polaron, and as such, Gauthron et al. conclude that the S1 line would be best described with a polaron model [2].

The study by Gauthron et al. serves as a useful example of the applications of optical spectroscopy, and in particular photoluminescence spectroscopy, in characterizing the properties of a material. Owing to the ease and applicability of the technique, it is clear that, despite its ancient origins, optical spectroscopy will remain useful and relevant in modern condensed matter physics.

References:

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