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LUMINESCENCE PROPERTIES OF RARE GAS SOLIDS

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Abstract

The VUV luminescence spectra of rare gas solids consist of free exciton and self trapped exciton emission and give insight into exciton-phonon interaction. Detailed information about the emitting states is obtained from recent time resolved investigations. The special advantages of synchrotron radiation excitation for photoluminescence studies are discussed.

1. Introduction

Since the first paper on the intrinsic emission of rare gas solids (RGS)|1| this new field of luminescence research has gained considerable interest|2,3|. RGS are model substances for Van der Waals solids. The special properties of exciton-lattice interaction enable co-existence of different centres. The luminescence spectra are similar in solid, liquid, and dense gaseous rare gases thus linking together concepts of ordered and disordered condensed phases with atomic and molecular aspects. Moreover, rare gases are promising candidates for vacuum ultraviolet (VUV) lasers|4|.

Initially, luminescence of RGS was excited by α-particles, electrons or x-rays. Photoluminescence experiments were scarce due to the lack of suitable VUV light sources until synchrotron radiation was used|5|.

2. Luminescence bands under stationary excitation conditions

The luminescence spectra of RGS (Fig. 1) range from ∿ 7 eV to ∿ 17 eV. Emission lines of free excitons (FE) co-exist with Stokes shifted lines of an atomic type self trapped exciton (a-STE) and broad bands of a molecular type self trapped exciton (m-STE). The decay of vibrationally excited (hot luminescence) and vibrationally relaxed m-STE is established. Systematic trends of co-existence and relative intensities are deduced progressing from Xe to Ne. The trends and energetic positions are summarised in Fig. 2.

FE luminescence is very weak (Xe|6-8|, Kr|8,9|, Ar|3|). The small Stokes shifts (compared to absorption of n = 1 excitons, arrows in Fig. 1) are due to reabsorption. Besides the n = 1 exciton the forbidden J = 2 exciton shows up in emission as well. In Kr, luminescence of the n' = 1 spin orbit split exciton has been established|9|. The main contribution is STE emission. The vibrationally relaxed m-STE dominates in the heavier rare gases. Vibrationally excited m-STE shows up weakly in Kr[9], Ar[3] but is strong in Ne[10,11]. A similar trend holds for a-STE luminescence (Kr[9], Ar[3]). In Ne[10] it is the main emission and resolves into narrow lines under higher resolution which could be assigned to different atomic states involved.

The general features mentioned above are found independent of the nature of excitation. Details of the spectra (relative intensities etc.) sensitively depend on preparation of the samples[12].

3. Properties of the luminescence centres

The m-STE bands (relaxed) are nearly identical with the second continua of the gaseous phase which result from the decay of the lowest excited electronic states, $^{3,1}\Sigma_u^+$, to the repulsive ground state, $^1\Sigma_g^+$, of rare gas molecules R_2^*. Therefore the m-STE bands are ascribed to rare gas molecules embedded in and influenced only little by the surrounding lattice[1,13].

Two mechanism for the creation of centres were proposed[14].

(i) Self trapping of the valence hole and capture of the conduction electron.

(ii) Direct self trapping of free excitons via exciton-phonon interaction.

Exciton phonon interaction was analysed recently[15,17]. In RGS, only deformation potential interaction with acoustic phonons has to be taken into account (optical phonons are absent in fcc-RGS). Using a trial wavefunction for the exciton with a variational parameter, α, which describes the spatial extension, the total energy of the exciton interacting with the lattice was minimised. If the lattice relaxation energy, E_{LR}, exceeds the half width of the exciton band, B, self trapping can occur. This condition is fulfilled in RGS.

The result for the total energy $E(\alpha)$ (measured from the energy of the free exciton)

$$E(\alpha) = B\alpha^2 - E_{LR}\alpha^3$$

predicted the existence of a potential barrier between the FE state and the STE[15]. This potential barrier enables the simultaneous existence of FE emission and STE emission.

E_{LR} may have different values for different geometrical configurations of the relaxed lattice. At least two configurations[15] may co-exist (Fig. 3).

(i) Uniaxial relaxation and localization of the exciton at a pair of nearest neighbours (110-direction). This is very effective in RGS as molecular formation $R^* + R \rightarrow R_2^*$ is very effective. The binding energy is the main contribution to E_{LR}. The potential curves of this centre (m-STE) are described by the internuclear distance of the atomic pair, Q_m

(ii) Formation of a cavity around the exciton which is localized at one single atom (a-STE). The nearest neighbour distance, Q_a, may be used as the configuration coordinate.

The self trapping process is due to thermal activation and/or tunneling through the barrier. The heights of the barriers (Fig. 3) are different for the two species of STE and were estimated in [3,17]. The barriers control the co-existence of different luminescence bands and their relative intensities.

Though the models for the centres (Fig. 3) describe the general features quite well some limitations must be mentioned. Due to the use of a trial wavefunction no detailed picture of the potential curves is obtained. At least in the m-STE it is known from gas phase data[18] that several excited bonding and antibonding R_2^* -states exist which may severely influence the self trapping process. Attempts to investigate these states by transient absorption have been made recently[19].

E_{LR} of the a-STE is generally smaller than for the m-STE because no chemical bond (molecular formation) is involved. Excluding self trapping in this configuration, E_{LR} may get even smaller than B for heavier RGS (Xe[17]). The value for the Xe a-STE potential barrier[3,17] seems to be by far overestimated. In Kr, the band at 9.7 eV has been interpreted as a-STE emission[9] though it is slightly red shifted compared with the emission of free atoms. This interpretation is still questionable because traces of Xe impurities may lead to extrinsic emission at similar energy[12].

The tendency for hot luminescence of the m-STE in light RGS reflects the fact that the vibrational quantum of the centres increases with decreasing atomic number. The order of multiphonon processes for vibrational relaxation reaches ∿ 18 in Ne[13]. Following excitation, excited Ne goes into the 3rd vibrational level. The shape of the bands at 14 eV and 16.5 eV is attributed to the Franck-Condon factors for transitions from $v = 3$ to the repulsive ground state[11].

4. Time resolved luminescence spectroscopy

Time resolved experiments are restricted so far to the relaxed m-STE band. In Fig. 3, the detailed structure of the emitting states was not included. In the crystal field, $^{3,1}\Sigma_u^+$ states split into more levels (Fig. 4)[20]. Due to the steep repulsive ground state these levels are not identified in stationary state experiments. They show up in time resolved luminescence spectra (ordinary decay curves and time correlated luminescence spectra).

In the decay curves, following pulsed e^--excitation, a nearly constant short component of a few ns is found[9,21] together with one or more long components (Xe, optical excitation[22], Kr and Ar[9]) which are temperature dependent (Fig. 4).

Time correlated luminescence spectra (Fig. 4) show the following behaviour. Collecting the ns-component with a time window inside the excitation pulse gives a peak position at higher energy than the long components measured separately. The energy splitting, ΔE, is attributed to the splitting between Γ_3' ($^1\Sigma_u^+$, fully allowed) and the centre of the other states ($^3\Sigma_u^+$, partly forbidden). It is much smaller than early estimates[18]. In the case of Xe, it is in agreement with gas phase data[23].

The temperature independent ns component is attributed to the Γ_3' ($^1\Sigma_u^+$) state and may approximately be the radiative lifetime[9]. The states associated with $^3\Sigma_u^+$ interact strongly (splittings comparable with phonon energies). Satisfactory model calculations are missing for extracting the radiative lifetimes. It seems necessary to extend the measurements to much lower (Kr) and higher temperatures (Ar).

5. Aspects of synchrotron radiation excited luminescence of RGS

SR is a very promising excitation source for luminescence experiments in the VUV mainly for two reasons.

(i) The intense spectrum of SR is a smooth continuum extending from the IR to the x-ray range. In the VUV and soft x-ray range it is superior to all other continuous light sources and allows for monochromatic excitation with any desired photon energy.

(ii) SR is pulsed. The storage ring DORIS at Hamburg offers 130 ps pulses (repetition rate between 480 MHz and 1 MHz). With delayed coincidence technique, rise and decay times between ∿ 50 ps and some μs can be measured[24,25].

The highlights of SR excited experiments on RGS may be summarised as follows.

(i) Selective excitation of excitons (avoiding the production of electron-hole pairs) has clearly established that free excitons are directly self trapped in all RGS[2,5].

(ii) Luminescence yields were measured as a function of excitation energy. Within the excitonic range of excitation, migration of excitons was investigated. It seems to be of diffusive type. Diffusion lengths deduced from surface quenching experiments range between ∼ 1000 Å (Xe) and ∼ 50 Å (Ar)[26,27]. In the range of band-to-band transitions inelastic scattering of photoelectrons with valence electrons leads to a stepwise increase of the luminescence yield. The steps give evidence for creation of free electronic polaron complexes by the excitation process itself[28].

(iii) In RGS doped with rare gas atoms, electronic relaxation of Wannier and Frenkel type exciton states has been investigated. Results are presented in another contribution of this volume[25].

(IV) It has been demonstrated that SR is also an appropriate source for energy transfer experiments. Host-guest and guest-guest transfer was studied in RGS doped with organic molecules (e.g. benzene[29], toluene and mesitylene[30]). Of special interest are systems like $Kr:N_2O$ as potential condensed laser media. Comparison of the luminescence yields of pure RGS and doped RGS gave insight into the formation of KrO^* laser molecules after host excitation[31].

The last two points mentioned touch the wide field of matrix isolation spectroscopy which will benefit very much from SR as an excitation source in the future.

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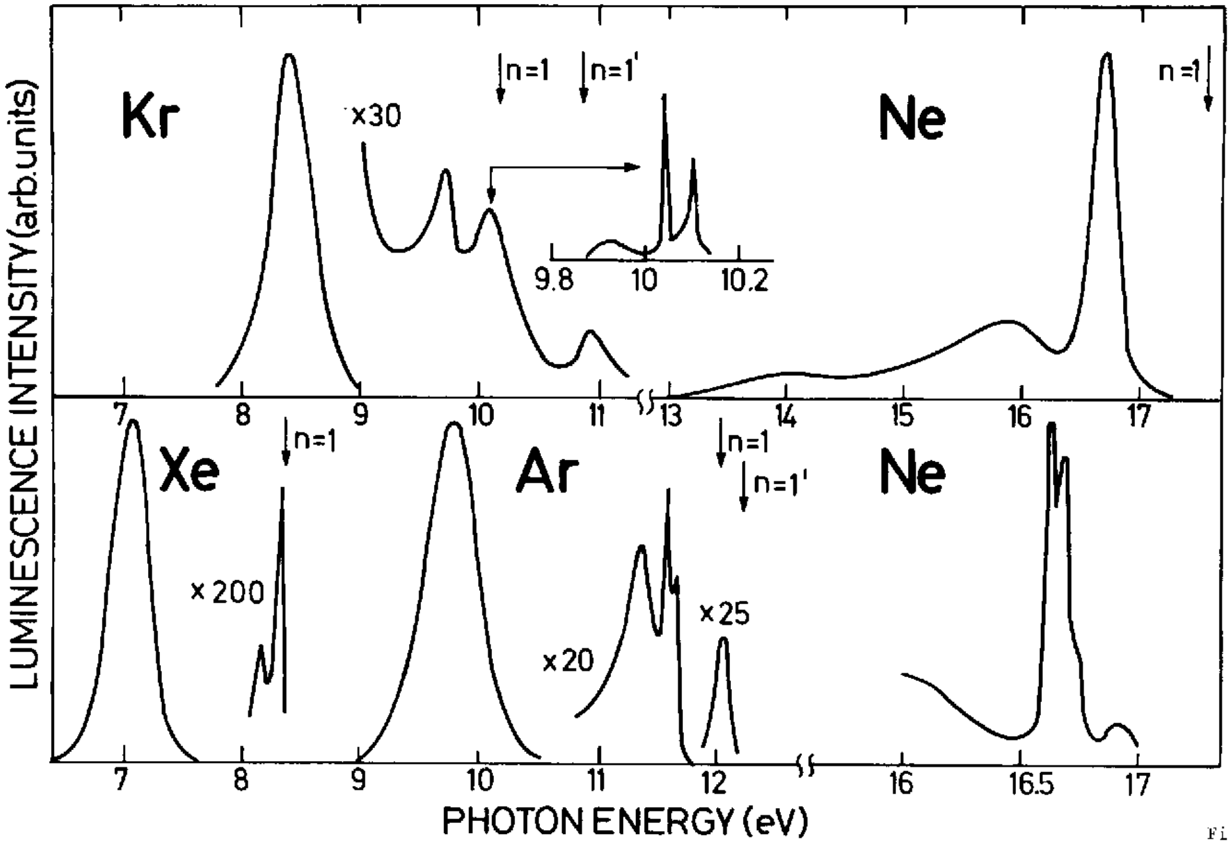
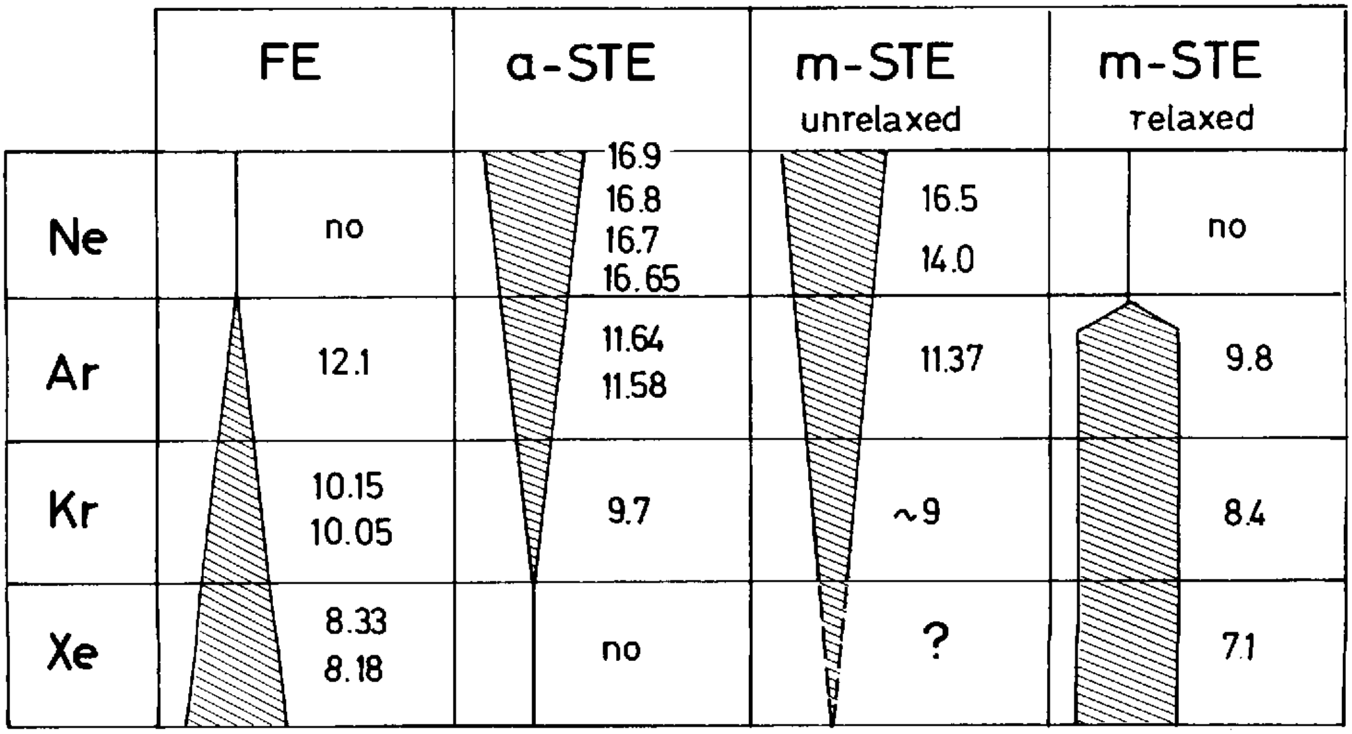


Fig. 1



	FE	a-STE	m-STE unrelaxed	m-STE relaxed
Ne	no	16.9 16.8 16.7 16.65	16.5 14.0	no
Ar	12.1	11.64 11.58	11.37	9.8
Kr	10.15 10.05	9.7	~9	8.4
Xe	8.33 8.18	no	?	7.1

Fig. 2

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Figure captions

Fig. 1 Typical luminescence spectra of RGS. Ne, x-ray excited, 5 K (upper curve), 11 K (lower curve)|10|. Ar, e^--excited (spectra above 11 eV, 4.5 K|3|); optical excitation (9.8 eV band, 5 K|2|). Kr, e^--excited (low resolution curve 5 K|9|, high resolution insert 40 K|8|). Xe, e^--excited (above 8 eV, 4 - 60 K|7|); optical excitation (7.1 eV band|2,5|).

Fig. 2 Trends and energetic positions of different luminescence bands of RGS. Hatched areas qualitatively give the importance when progressing from lighter to heavier elements. The energies (in eV) are extracted from the references of Fig. 1.

Fig. 3 Qualitative scetch of potential curves of the m-STE and a-STE and simplified representation of the centres. Estimates of the heigths of the potential barriers from|3|.

Fig. 4 Results of time resolved luminescence spectroscopy of RGS (relaxed m-STE bands) and level schema of the m-STE. The intensities of the time correlated luminescence spectra (full curves: ns-components, dashed curves: long decay components) are given in arbitrary units. References see text.

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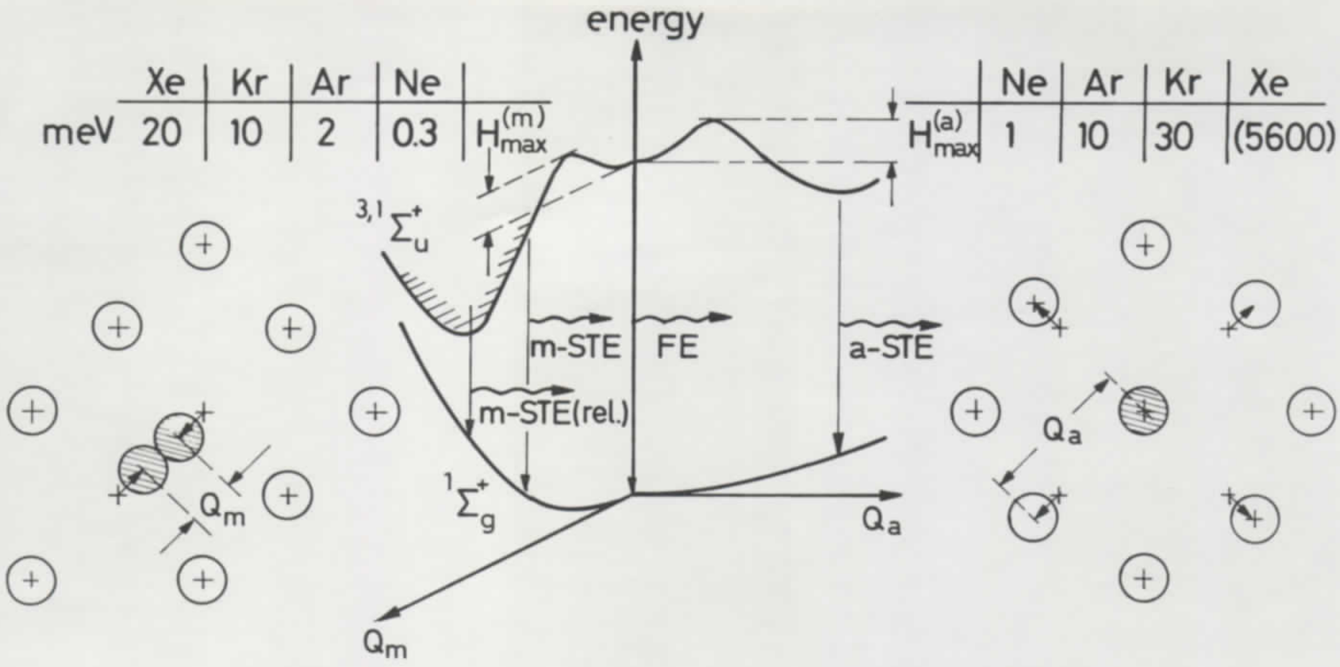

Fig. 3

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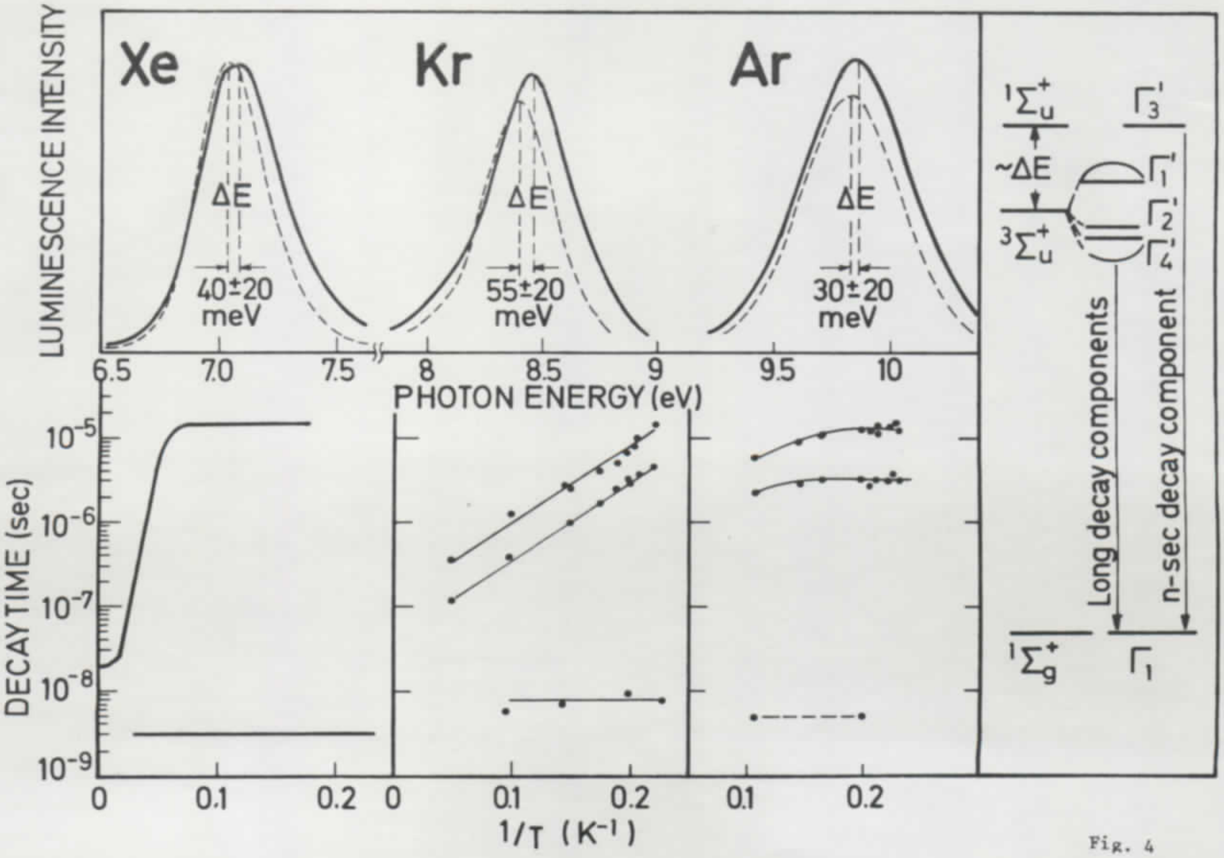

Fig. 4