

Thermoluminescence from CO-doped solid Ar

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Abstract. Cameron bands luminescence from a new thermoluminescence (TL) system—CO-doped solid Ar—has been investigated using selective excitation by synchrotron radiation and thermally stimulated luminescence methods. The photoexcitation and TL emission spectra of the Cameron bands are measured. The activation energies and the frequency factors of charge traps are determined by numerical fitting of the TL emission spectrum.

1. Introduction

Solid Ar with its simple crystal and electronic structures is an attractive model system suitable for fundamental research into energy relaxation and charge separation [1]. The excitation of the solid Ar electron subsystem is accompanied by clearly manifested processes of localization of electronic excitation energy, leading to the formation of self-trapped excitons [1] and holes [2] as well as stable neutral [3] and charged [4] defect centres. Solid Ar is widely used as an inert matrix to isolate atoms, molecules, radicals and ions and to study chemical reactions [5]. However, only recently was the phenomenon of thermoluminescence from pure [6,7] and doped [8,9] solid Ar found upon cathode, photo- and x-ray irradiation.

Because of the fast electronic relaxation by the intersystem crossing to the lowest excited a $^3\Pi$ state [10] and the pronounced Cameron band emission in CO-doped rare gas solids [11,12], carbon monoxide can be used as a sensitive luminescent impurity. On the other hand, CO has a positive electron affinity [13], which makes it possible to use the CO-doped solid Ar for the charge separation and TL investigations. Finally, CO is the most common residual gas component adsorbed on cryogenic parts of vacuum systems [14] and, therefore, it is possible to develop a Co–Ar TL dosimetric system. The paper reports the first observation of thermoluminescence of Cameron bands from CO-doped solid Ar and numerical fitting of the TL emission spectra.

2. Experimental details

The samples were grown from a high-purity vapour phase in special cryogenic cells. The gases were pre-mixed in an ultra-high-vacuum gas-handling system. Following [10] we used gas mixtures with the CO concentration of

0.1 at%, in which case the spectra were representative of well-isolated CO molecules and the interactions between the CO molecules were not responsible for the processes discussed in this paper. Because of strong enhancement of Ar and CO evaporation at temperatures above 27 K, the temperature range of the measurements was 5–27 K.

The thermoluminescence experiments were performed in a molecular spectroscopy laboratory of the Verkin Institute at Kharkov. For the thermoluminescent measurements we used samples with thicknesses of no more than 0.1 mm. For such thin crystals we did not take into account the temperature gradient from the heater strip to the emitting surface of the sample [17]. The samples were excited by an electron beam of energy $E_e = 1000$ eV insufficient to form defects by elastic collisions. The electron beam current was $j_e \leq 100 \mu\text{A cm}^{-2}$. The time of irradiation was 600 s. Luminescence analysis with $\Delta\lambda = 4$ nm was carried out with a 1 m near-normal incidence monochromator VMR-2. The signals were recorded with a photomultiplier (FEU-142) operating in a single-quantum mode. Thermoluminescence from CO-doped solid Ar was excited by warming up the sample after turning off the liquid helium flow in the cryostat [6]. TL emission signals of various wavelengths were recorded in a scanning mode to obtain the TL emission spectra.

The selective excitation measurements were carried out at the SUPERLUMI experimental station at the Hamburger Synchrotronstrahlungslabor HASYLAB. The selective photon excitation was performed with $\Delta\lambda = 0.25$ nm. The excitation spectra were measured with a 0.5 m Pouey monochromator ($\Delta\lambda = 2$ nm) equipped with a solar-blind photomultiplier. In the excitation spectrum, the luminescence intensity is measured as a function of the photon energy of the exciting light and then normalized with respect to the intensity of the incident exciting radiation. Both set-ups were described recently in detail [15,16].

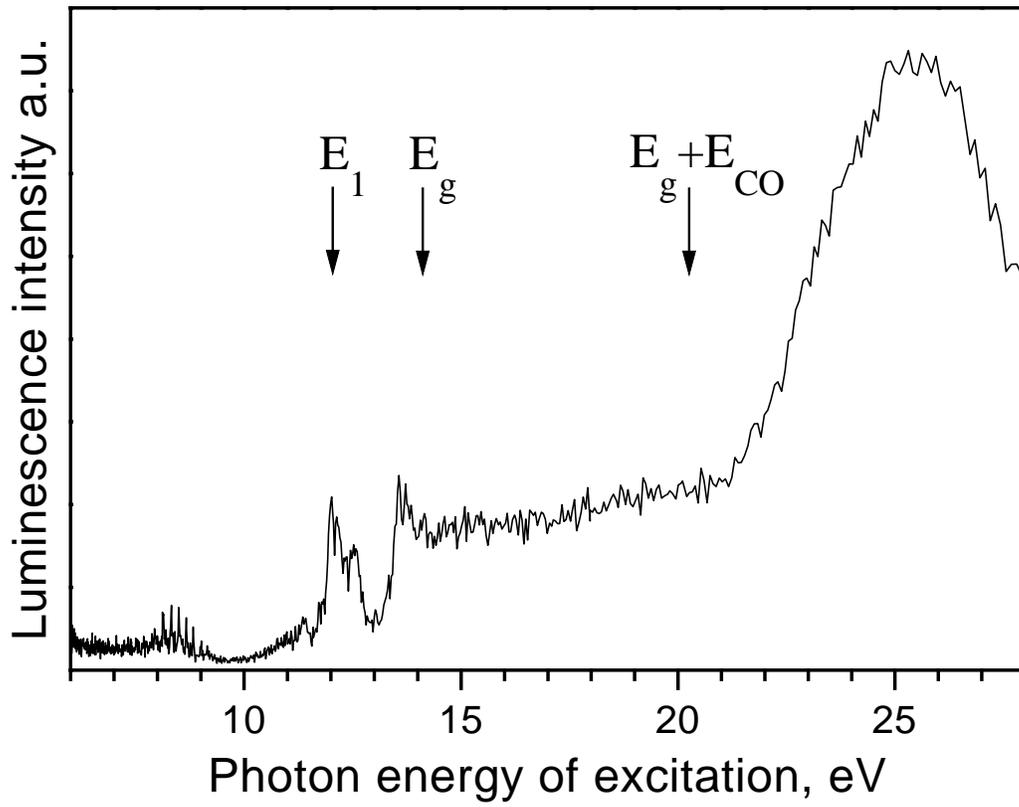


Figure 1. The luminescence excitation spectrum of 219.5 nm Cameron band at $T = 5$ K.

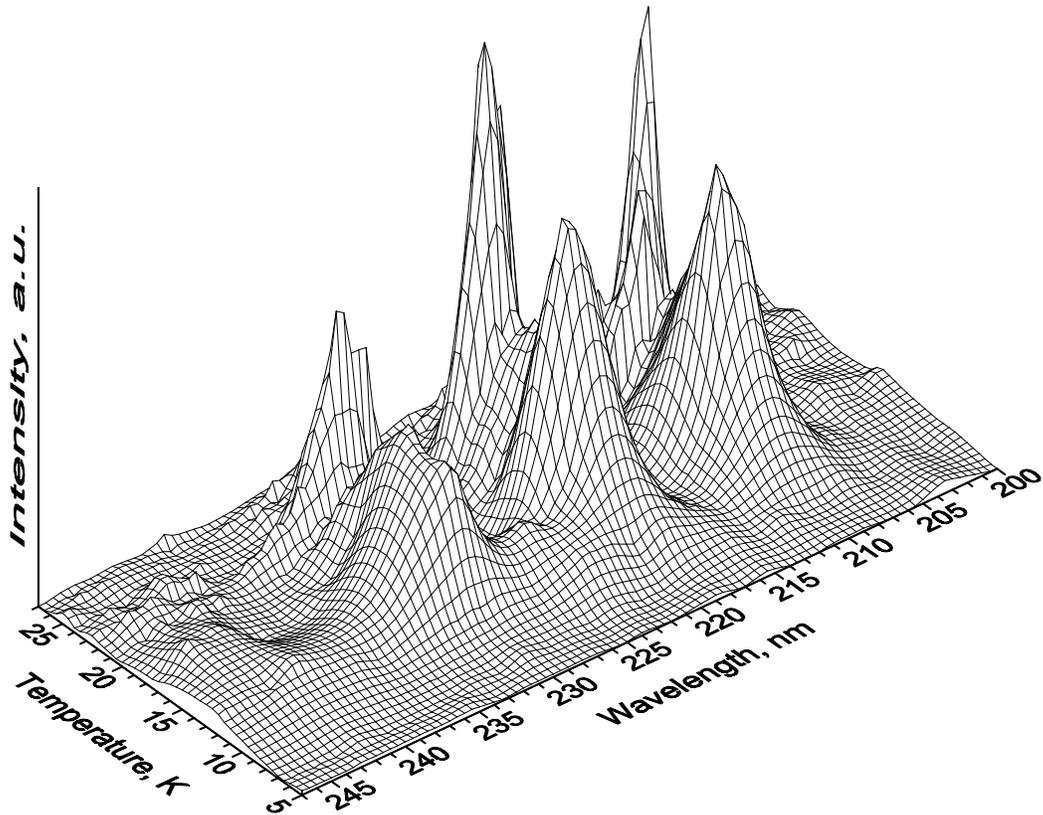


Figure 2. The thermoluminescence emission spectrum of Cameron bands from CO-doped solid Ar.

3. Results and discussion

The photon excitation spectra of Cameron bands demonstrate that the emission is sensitive to the processes of generation of electron–hole pairs in the matrix and to charge and energy transfer to the impurity. Figure 1 shows the excitation spectrum of the $a^3\Pi(v' = 0) \rightarrow X^1\Sigma^+(v'' = 1)$ luminescence band ($\lambda_{emission} = 219.5$ nm). $E_{CO} = 5.957$ eV denotes the energy of the lowest electronic triplet $X^1\Sigma^+(v = 0) \rightarrow a^3\Pi(v = 0)$ transition [10]. The weak lines at 8 eV correspond to direct photoexcitation of the matrix isolated CO by spin-allowed singlet transitions $X^1\Sigma^+ \rightarrow A^1\Pi$. The features in the range 12–14 eV correspond to the excitation of the impurity molecule by free excitons of the matrix. E_1 denotes the energy of the lowest ($\Gamma(3/2) n = 1$) exciton. Above the threshold at the band gap energy $E_g = 14.16$ eV the excitation spectrum yields an effective population of the impurity emitting states via generation of free electron–hole pairs. A second threshold at $E_{th} = E_g + E_{CO}$ is significantly lower than the threshold for creation of excitons $E_g + E_1$ [18]. The ‘hot’ photoelectrons with energies above E_{th} can be scattered inelastically by the impurity to a lower state and then, during relaxation, can excite another impurity. As a result two excited CO can be obtained per absorbed photon. With such a high sensitivity of the CO emission to the existence of electrons in the conduction band of solid Ar, the intensity of the thermoluminescence obtained from CO-doped solid Ar is sufficient to allow one to perform the TL emission spectrum measurements.

Figure 2 shows the TL emission spectrum of the Cameron bands ($a^3\Pi(v' = 0) \rightarrow X^1\Sigma^+(v'' = 0 \dots 3)$). The total number of photons detected within 450 s of the thermoluminescence readout was about 5000, corresponding to about 10^{-4} of the total number of photons detected every second in the luminescence under electron beam irradiation. The full width at half maximum (FWHM = 4 nm) of these bands was determined only by a slit apparatus function of the monochromator. The relative intensities of the bands in the Cameron system corresponded to those obtained from the photoexcitation measurements [12].

In the previous work [6] we performed a kinetic analysis of the glow curve for pure solid Ar. Using the McKeever *et al* estimation of the validity of first-order kinetics [19], we approximated the charge escaping and recombination by the first-order kinetic equation

$$I_{TL} = -\frac{dn}{dt} = ns \exp\left(-\frac{E_a}{kT(t)}\right) \quad (1)$$

where I_{TL} is the TL intensity, n the number of trapped electrons, s the frequency factor, E_a the activation energy, k the Boltzmann constant and T the absolute temperature. The solution of (1) for a constant heating rate $dT/dt = \beta$ is [20]

$$I_{TL}(T) = n_0 s \exp\left(-\frac{E_a}{kT}\right) \times \exp\left[-\frac{s}{\beta} \int_{T_0}^T \exp\left(-\frac{E_a}{kT'}\right) dT'\right] \quad (2)$$

Table 1. Kinetic parameters for CO-doped solid Ar.

Peak	T_m (K)	s (s^{-1})	E_a (meV)
1	11.92	7×10^3	12.0
2	15.41	5×10^3	14.3
3	17.17	4×10^3	16.8
4	18.97	4×10^3	19.2
5	21.10	1×10^6	30.5
6	22.71	1×10^{12}	61.0
7	24.87	1×10^6	37.0

where T_0 and n_0 are the initial temperature and concentration of trapped electrons, respectively.

Under non-linear sample heating conditions the kinetic equations can be solved numerically [21]. In our experiments the temperature variation under heating was approximated by the sixth-order interpolation polynomial $T(t) = \sum_{i=0}^6 a_i t^i$ with coefficients $a_0 = 5.22445$, $a_1 = -1.9396 \times 10^{-2}$, $a_2 = 2.54677 \times 10^{-3}$, $a_3 = -2.06914 \times 10^{-5}$, $a_4 = 7.39862 \times 10^{-8}$, $a_5 = -1.2566 \times 10^{-10}$ and $a_6 = 8.2617 \times 10^{-14}$. We used the computer program [6] to calculate the TL emission spectrum of Cameron bands from CO-doped solid Ar by the fourth-order Runge–Kutta method:

$$n(t + \tau) = n(t) + \frac{1}{6}(k_1 + 2k_2 + 2k_3 + k_4) \quad (3)$$

where $k_1 = \tau f(t, n(t))$, $k_2 = \tau f(t + \tau/2, n(t) + k_1/2)$, $k_3 = \tau f(t + \tau/2, n(t) + k_2/2)$, $k_4 = \tau f(t + \tau, n(t) + k_3)$, $f(t, n(t)) = n(t)s \exp[-E_a/(kT(t))]$ and $\tau = 10^{-4}$ s. The analysis of thermally stimulated luminescence and conductivity of doped Ar solids confirms the applicability of the first-order kinetics to solid Ar [9].

Figure 3 shows the calculated TL emission spectrum. The section of this spectrum along $\lambda = 210$ nm and its deconvolution on seven first-order peaks are shown in figure 4. Table 1 contains the trapping parameters and peak temperatures T_m which were found to be most suitable for fitting the TL emission spectrum. On the basis of analysis of the dependence of the glow curve on the irradiation dose [6] and comparing our data with data on thermal desorption spectrometry [22], we subdivide these seven peaks into three groups: (i) peaks 5–7 at 20–25 K, (ii) peaks 2–4 at 15–19 K and (iii) peak 1 at 11.92 K. We assume that these groups correspond to three types of traps: (i) vacancies as electron traps; (ii) Frenkel pairs, which can be considered as binary traps for electrons on vacancies and holes on interstitial atoms simultaneously after ionization of excitons on such defects; and (iii) peak 1 at 11.92 K corresponds to some kind of surface traps. This has been discussed in detail in [6] and we refrain from repeating those arguments here.

Peaks 1–4 are characterized by extremely low values of the frequency factors. This may be due to various reasons. Conditions for the emergence of pseudo-first-order kinetics may be realized when the electron and the hole formed as a result of ionization of an atom by irradiation do not go beyond the Onsager radius and participate in the geminate recombination [23]. On the other hand, the presence

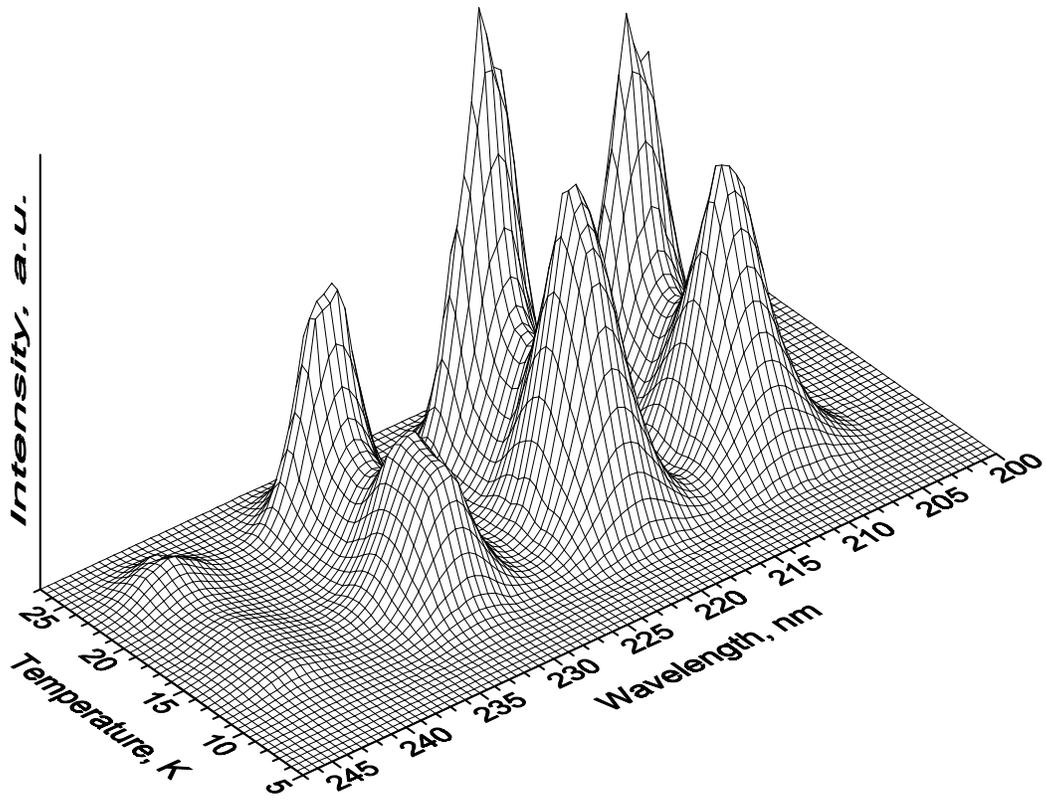


Figure 3. The calculated TL emission spectrum of Cameron bands.

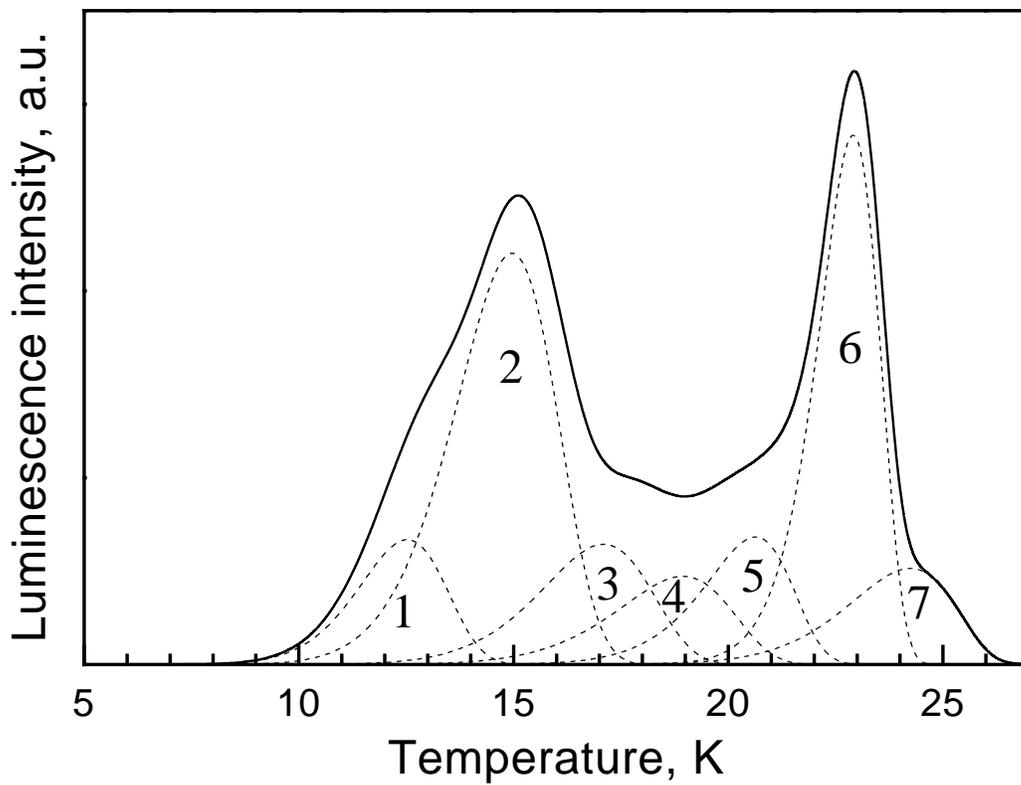


Figure 4. The section of the calculated TL spectrum along $\lambda = 210$ nm and its deconvolution into first-order peaks.

of a set of traps assumes the possibility of recapture of carriers released from shallow traps by deeper traps [24, 25]. Moreover, the electrons need not enter the conduction band at all and may recombine as a result of thermally assisted tunnelling or localized transitions [20]. Finally, a situation is possible in which the activation energies of the traps are distributed continuously within a finite range [9, 26] and the superposition of glow peaks formed by each trap results in a broad peak whose frequency factor will be much lower than the frequency factors of the superposition components. In any case, the condition for the fitting of the glow curve by the first-order kinetic equation is satisfied insofar as the concentration of active traps is much lower than that of the CO impurities responsible for the final relaxation of the liberated carriers [25].

4. Conclusion

Thermoluminescence emission spectra of Cameron bands have been obtained from CO-doped solid Ar. All TL peaks of pure solid Ar are presented in these spectra. Carbon monoxide is shown to be a sensitive luminescent impurity, which collects emission in a definite energy range of the Cameron bands and can be used as a probe to study the electronic energy storage at charge separation. Numerical computation of the measured TL emission spectrum in terms of seven first-order peaks may be considered as the first step in the analysis of the thermoluminescence of CO-doped solid Ar and further investigations are highly desirable.

Acknowledgments

Financial support by the BMFT (grant 05650 GUB) and of PECO-Project is gratefully acknowledged.

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