



## Photoelectron scattering in CO doped solid Ar

A.N. Ogurtsov <sup>a,1</sup>, E.V. Savchenko <sup>a</sup>, J. Becker <sup>b</sup>, M. Runne <sup>b</sup>, G. Zimmerer <sup>b</sup>

<sup>a</sup> Verkin Institute for Low Temperature Physics & Engineering, 47 Lenin Avenue, 310164 Kharkov, Ukraine

<sup>b</sup> II. Institut für Experimentalphysik der Universität Hamburg, 22761 Hamburg, Germany

Received 20 August 1997; in final form 7 November 1997

### Abstract

Inelastic photoelectron scattering in CO doped solid Ar has been investigated using the method of luminescence excitation spectroscopy. The threshold energies for multiplication of electronic excitations under selective excitation by synchrotron radiation have been measured. For specially selected radiative decay channels, different kinds of photoelectron scattering are observed. The observation of multiple electronic excitation is of particular interest. © 1997 Elsevier Science B.V.

### 1. Introduction

In rare gas solids the energy loss rate of photoelectrons with energies above the band gap energy is mainly determined by electron–electron scattering [1]. The scattering of a “hot” photoelectron by a valence electron results in the formation of an additional electron–hole pair which can be bound or free. Such processes of multiplication of excitations with well-defined thresholds lead to prominent structures in the photoluminescence excitation spectra. Since the pioneering work by Möller et al. [2], the influence of inelastic electron–electron scattering processes on the quantum efficiency of intrinsic photoluminescence has been the subject of continuous interest as a powerful tool to investigate the relaxation mechanisms in pure solid Xe, Kr and Ar [3–5]. Solid argon doped with carbon monoxide is exten-

sively used to investigate intra- and intermolecular energy relaxation into the impurity subsystem (see e.g. Ref. [6]). Due to the fast electronic relaxation by the intersystem crossing to the lowest excited  $^3\Pi$  state [7] and the pronounced Cameron band emission [8,9], carbon monoxide can be used as a sensitive luminescent probe to detect electronic relaxation at an impurity. This Letter reports the observation of the influence of photoelectron scattering on the luminescence of CO doped solid Ar.

### 2. Experiment

The experiments were performed at the SUPERLUMI experimental station of the Hamburger Synchrotronstrahlungslabor HASYLAB at DESY. The apparatus was designed for time and spectrally resolved luminescence under selective photon excitation in the vacuum-ultraviolet spectral range and was described in detail in Ref. [10]. The samples were grown from a high purity vapor phase in a special cryogenic cell [11] under isobaric ( $P = 80$  Pa) condi-

<sup>1</sup> Corresponding author.

tions with a constant rate of cooling of 0.1 K/s in the temperature range 60–50 K. The gases were pre-mixed in an ultrahigh vacuum gas-handling system. Following Ref. [7] we used gas mixtures with a CO concentration 0.1 at. % in which case the spectra are representative for well-isolated CO molecules. In this way, bulk, completely clear samples were obtained with a thickness up to few mm. The samples were therefore “optically thick” throughout the whole range of photon energy of excitation covered in the present Letter. The photoelectrons were generated by synchrotron radiation. Selective photon excitation was performed with  $\Delta\lambda = 0.25$  nm. Both in luminescence and excitation spectra, the luminescence was spectrally dispersed with the 0.5 m Pouey monochromator ( $\Delta\lambda = 2$  nm) equipped by a solar-blind photomultiplier. In the excitation spectra, the luminescence intensity was measured as a function of the photon energy of the exciting light and then normalized to the intensity of the incident exciting radiation. The excitation spectra of spectrally selected luminescence bands, shown in this Letter, are given in relative units. They are not corrected for the wavelength-integrated intensity of the respective radiative decay channel. Therefore, it is not possible to sum up the excitation spectra in order to obtain the excitation spectrum of total luminescence. Solid argon exhibit strong effects of neutral and charged defect formation induced by electronic transitions [12,13]. Therefore all measurements were carried out after saturation of dose effects [13] at steady concentrations of point defects and ionic centers.

### 3. Results and discussion

The dynamics of photoelectrons in CO doped solid Ar are determined by the hierarchy of characteristic energies of the electronic states involved: the energy  $E_{\text{CO}} = 5.96$  eV of the lowest electronic transition  $X^1\Sigma^+ \rightarrow a^3\Pi$ , the energy of free excitons  $E_{\text{ex}} = 12.06$  eV and the band gap energy  $E_{\text{g}} = 14.16$  eV. The Letter focuses on the dynamics of photoelectrons at excitation well above  $E_{\text{g}}$ .

The quantum efficiency of solid Ar luminescence is about 50% [14–16]. The luminescence spectrum of CO doped solid Ar under band-to-band excitation is presented in Fig. 1. It consists of several pro-

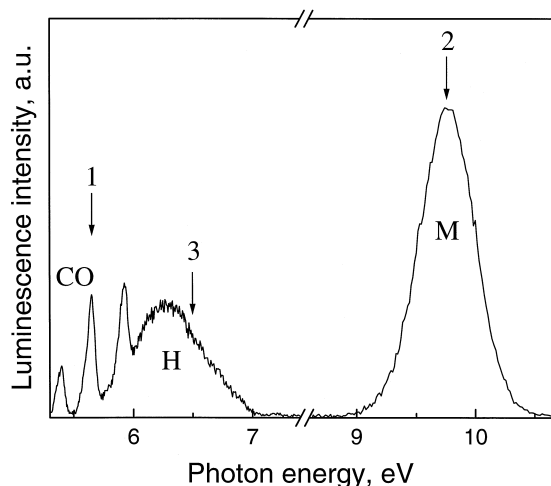


Fig. 1. Luminescence of CO doped solid Ar, excited with  $h\nu = 14.2$  eV at  $T = 5$  K. Arrows indicate the photon energies at which excitation spectra in Fig. 2 were measured.

nounced features: a vibrational progression of the Cameron system of CO, *H*-band and *M*-band emissions due to the Ar matrix. The *M*-band originates from the radiative decay of molecular trapped excitons and is formed by the  $^{1,3}\Sigma_u^+ \rightarrow ^1\Sigma_g^+$  transitions in quasi-exciters  $\text{Ar}_2^*$  [14]. Its internal structure was recently analyzed [17]. The *H*-band originates from the radiative decay of intrinsic ionic centers like  $\text{Ar}_2^{+*}$ , which are the subject of active current investigations [13,18,19]. Such centers are assumed to be formed in a two-step process: trapping of holes followed by excitation of a trapped hole by excitons [19]. The matrix isolated molecules of carbon monoxide emit a  $^3\Pi \rightarrow X^1\Sigma^+$  Cameron bands.

The excitation spectra of bands *M* (curve 2) and *H* (curve 3) of solid Ar and the  $a^3\Pi(\nu' = 0) \rightarrow X^1\Sigma^+(\nu'' = 1)$  luminescent band from the Cameron system of CO (curve 1) are shown in Fig. 2. The emitting photon energies (denoted in Fig. 1 by arrows) were chosen in such a way as to discriminate the above types of emissions. The excitation spectra show that both types of host emission as well as CO emission are observed following primary creation of electron–hole pairs with photon energies  $h\nu \geq E_{\text{g}}$ . At higher photon energies of excitation, the excitation spectra of the Cameron band and the *M*- and *H*-bands exhibit a distinct threshold behavior at the energies  $E_1 = 21$ ,  $E_2 = 26$  and  $E_3 = 30$  eV, respec-

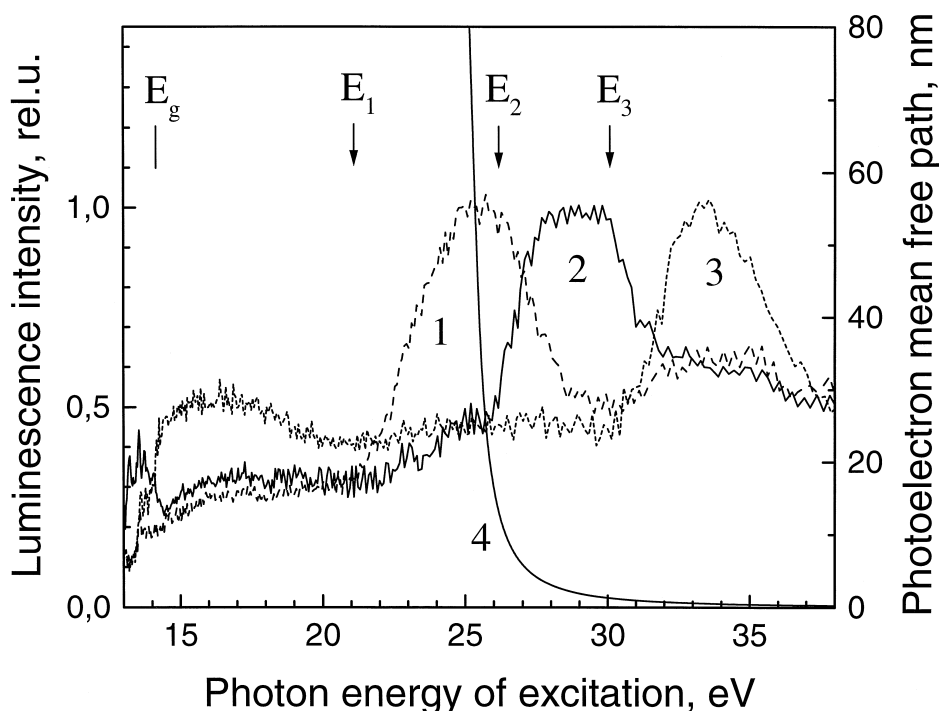


Fig. 2. Excitation spectra of luminescence of CO doped solid Ar at luminescence photon energies indicated in Fig. 1 by arrows (curves 1, 2, 3). All spectra are rescaled to their values at the maxima. Curve 4 - mean free path of photoelectrons in solid Ar [1].

tively. This behavior can be explained in the following way. The incident photon with energy  $E > E_1$  produces an electron-hole pair. The “hot” photoelectron can be scattered inelastically by a CO impurity to a lower state. The remaining electron-hole pair is able to excite another CO molecule by energy transfer, as is obvious from the excitation spectrum at lower photon energy of excitation. As a result, for photon energies above threshold  $E_1$ , the number of excited CO molecules per absorbed photon is roughly doubled. The threshold photon energy can be estimated using a simplified theory for a system with two parabolic energy bands, the extrema of which are located at the  $\Gamma$  point of the Brillouin zone [20]:

$$E_1^{\text{th}} = E_g + E_{\text{CO}}(1 + m_e/m_h) \quad (1)$$

With the literature values [21] of the effective masses of electrons ( $m_e = 0.48 m_0$ ) and holes ( $m_h = 5.3 m_0$ ), threshold energy is  $E_1^{\text{th}} = 20.7$  eV.

The mean free path of photoelectrons with energies  $E \approx E_1$  exceeds the lattice constant by some hundreds. Curve 4 in Fig. 2 represents the energy

dependence of the mean free path  $L(E)$  of photoelectrons in solid Ar. It can be well approximated by [1]:

$$L(E) = C(E - E_g)^{1/2}(E - E_{\text{sc}})^{-2} \quad (2)$$

where  $C = 100 \text{ \AA eV}^{3/2}$  and  $E_{\text{sc}} = 24.5$  eV are parameters. With an increase in the excitation energy, the mean free path of photoelectrons decreases rapidly and at the second characteristic energy  $E_2$  it is comparable to the lattice constant. The energy  $E_2^{\text{th}} = E_g + E_{\text{ex}}$  is the threshold for creation of excitons [2]. It is well-pronounced in the excitation spectrum of the  $M$ -band. In this case an electronic polaron complex is formed. It consists of an electron-hole pair “dressed” by an electronic polarization cloud and an additional exciton. This second kind of multiplication of electronic excitations was proposed by Devreese et al. [22]. The value of the mean free path of the photoelectrons is crucial for the branching between both processes. The energy transfer to

the impurity requires a large value. As soon as the mean free path of the photoelectrons is shortened to a value comparable with the lattice constant, energy transfer to CO gets less efficient whereas “multiplication” of the number of electronic host excitations *via* electronic polaron complex formation becomes pronounced. This explains the behavior of the excitation spectra around  $E_2$ .

Further increase in the energy of incident photons results in the result that the processes of photoelectron creation and scattering may take place at neighbouring atoms or even at the initially excited atom itself. The generation of secondary electron–hole pairs during photoelectron scattering leads to the formation of intrinsic ionic centers. The threshold photon energy for the formation of the secondary electron–hole pair is given by an equation similar to (1):

$$E_3^{\text{th}} = E_g + E_g(1 + m_e/m_h) \quad (3)$$

This energy  $E_3^{\text{th}} = 29.6$  eV is close to the measured threshold  $E_3$ . The competition between the generation of ionic centers and excitons reflects in the anticorrelation of the excitation spectra of the *H*- and *M*-bands above  $E_3$ .

The data obtained suggest that in CO doped solid Ar three types of photoelectron scattering exist: (i) long-range photoelectrons are scattered inelastically by the impurity molecules, (ii) short-range photoelectrons with energies about  $E_2$  form electronic polaron complexes, (iii) photoelectrons with energies above  $E_3$  can create intrinsic ionic centers as a result of the formation of secondary electron–hole pairs during scattering. To confirm this interpretation, however, theoretical calculations of the cross-sections for such many body effects are called for.

## Acknowledgements

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

## References

- [1] N. Schwentner, E.E. Koch, J. Jortner, *Electronic Excitation in Condensed Rare Gases*, Springer Tracts in Modern Physics, vol. 107, Springer, Berlin, 1985.
- [2] H. Möller, R. Brodmann, G. Zimmerer, U. Hahn, *Solid State Commun.* 20 (1976) 401.
- [3] M. Hävecker, M. Runne, G. Zimmerer, *J. Electron. Spectrosc. Relat. Phenom.* 79 (1996) 103.
- [4] A.N. Ogurtsov, E.V. Savchenko, J. Becker, M. Runne, G. Zimmerer, *Low Temp. Phys.* 23 (1997) 851.
- [5] R. Müller, M. Joppien, T. Möller, *Z. Phys. D.* 26 (1993) 370.
- [6] A. Salloum, H. Dubost, *Chem. Phys.* 189 (1994) 179.
- [7] J. Bahrtdt, N. Schwentner, *Chem. Phys.* 127 (1988) 263.
- [8] I.Ya. Fugol, L.I. Timchenko, Yu.B. Poltoratskii, A.G. Belov, *Bull. Acad. USSR, Phys. Ser.* 40 (1978) 471.
- [9] J. Fournier, H.H. Mohammed, J. Deson, C. Vermeil, *J. Chem. Phys.* 73 (1988) 6093.
- [10] G. Zimmerer, *Nucl. Instr. Meth. Phys. Res. A* 308 (1991) 178.
- [11] W. Laasch, H. Hagedorn, T. Kloiber, G. Zimmerer, *Phys. Stat. Sol. (b)* 158 (1990) 753.
- [12] E.V. Savchenko, A.N. Ogurtsov, S.A. Gubin, O.N. Grigorashchenko, *J. Luminesc.* 72–74 (1997) 711.
- [13] O.N. Grigorashchenko, S.A. Gubin, A.N. Ogurtsov, E.V. Savchenko, *J. Electron. Spectrosc. Relat. Phenom.* 79 (1996) 107.
- [14] G. Zimmerer, in: U.M. Grassano, N. Terzi (Eds.), *Excited-State Spectroscopy in Solids*, North-Holland, Amsterdam, 1987, p. 37.
- [15] E.E. Huber, J.D. Emmons, R.M. Lerner, *Opt. Commun.* 11 (1974) 155.
- [16] D.E. Grosjean, R.A. Vidal, R.A. Baragiola, W.L. Brown, *Phys. Rev. B* 56 (1997) 6975.
- [17] A.N. Ogurtsov, E.V. Savchenko, S.A. Gubin, O.N. Grigorashchenko, M. Runne, A. Karl, J. Becker, G. Zimmerer, in: M. Schreiber (Ed.), *Excitonic Processes in Condensed Matter*, Dresden University Press, 1996, p. 195.
- [18] Y. Baba, G. Dujardin, P. Feulner, D. Menzel, *Phys. Rev. Lett.* 66 (1991) 3269.
- [19] A. Ogurtsov, M. Runne, A. Karl, J. Becker, G. Zimmerer, *HASYLAB Annual Report 1995*, DESY, Hamburg, 1996, pp. II–77.
- [20] M. Kirm, E. Feldbach, R. Kink, A. Lushchik, Ch. Lushchik, A. Maaros, I. Martinson, *J. Electron. Spectrosc. Relat. Phenom.* 79 (1996) 91.
- [21] K.S. Song, R.T. Williams, *Self-Trapped Excitons*, Springer Series in Solid-State Sciences, vol. 105, Springer, Berlin, 1993.
- [22] J.T. Devreese, A.B. Kunz, T.C. Collins, *Solid State Commun.* 11 (1972) 673.