DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

Line Shapes in Soft X-Ray Absorption Spectra of Solidified Rare Gases

R. Haensel, G. Keitel
II. Institut für Experimentalphysik der Universität Hamburg, Germany

C. Kunz, and P. Schreiber
Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany

LINE SHAPES IN SOFT X-RAY ABSORPTION SPECTRA

OF SOLIDIFIED RARE GASES

R. Haensel, G. Keitel

II. Institut für Experimentalphysik der Universität Hamburg

Hamburg, Germany

C. Kunz and P. Schreiber

Deutsches Elektronen-Synchrotron, Hamburg, Germany

We have performed measurements of the shape of the

absorption lines which are due to transitions from

the 2s-shell in solid Ne and the 3s-shell in solid

Ar. It was found, that the asymmetric and the "window"

line shapes seen in the absorption spectra of the

gases are preserved in the solids.

In the soft X-Ray region the absorption spectra are mainly due to elec-
tronic transitions from inner (core) shells. Those transitions to dis-
crete final states which normally show up in the absorption spectra as
lines of enhanced absorption, may however interfere with the underlying
continuum transitions from the outer shells to final states far above
threshold.

This configuration interaction between the discrete and continuum states is responsible for special asymmetric and "window" line shapes near the resonance frequency. In the rare gases those line profiles have been extensively investigated at the NBS[1] by means of synchrotron radiation.

Theoretically these line shapes are described by an expression for the absorption cross section by Fano[2]

$$\sigma = \sigma_a \frac{(q+\varepsilon)^2}{1+\varepsilon^2} + \sigma_b \tag{1}$$

σ_a is that part of the total continuum absorption which interferes with the discrete excitation, $\rho^2 = \sigma_a/(\sigma_a + \sigma_b)$ is the fraction of the interfering continuum in the total absorption continuum. q is a profile index. The photon energy $\varepsilon = 2(E - E_o)/\Gamma$ is measured in units of the broadening parameter $\Gamma/2$ with its zero at a nominal resonance energy E_o. The continuum absorption cross sections σ_a and σ_b are assumed to be constant over the energy region where the continuum-discrete interaction takes place.

Besides life time broadening due to the configuration interaction which is included in Fano's parametrization formula, the effect of another broadening mechanism such as phonons has been introduced into Eq. (1) by folding with a Gaussian profile of suitable width.[3]

Experimental evidence for asymmetric profiles in solids has been reviewed by Phillips,[4] Greenaway and Harbeke[5] and recently reported by Brown et al.[6] However the reported spectra do not allow a comparison of the spectra of one material in both the atomic and the solid state. Therefore we felt it would be interesting to investigate the correspond-

ing transitions in the rare gases in both states of aggregation. We have measured previously the absorption lines associated with 4d-transitions of solid Xe, 3d-transitions of solid Kr[7], and 2p-transitions of solid Ar[8]. As in the gas, lines of the enhanced absorption type have been found, which were attributed to exciton excitations in the solid. This paper presents an investigation of the 2s-transitions in solid Ne, for which Codling et al.[9] have found asymmetric lines in the corresponding gas spectra, and the 3s-transitions in solid Ar, for which Samson[10], and Madden et al.[11,12] have detected window lines in the gas spectra.

The 7.5 GeV electron synchrotron DESY was used as light source[13] for a 1m Rowland monochromator. The 2400 lines/mm grating was illuminated at a grazing angle of about 220 mrad. An open photomultiplier (Bendix M 306) served as the detector. Ne was evaporated onto a $\sim$2000 Å thick aluminum foil and Ar onto a $\sim$1000 Å thick antimony foil. The substrates were cooled in a He cryostat.

In the case of Ne the temperature was kept at 6° K and in the case of Ar it was kept at about 15° K. The substrates also served as filters to reduce higher order light. In addition to the spectra of the solids we have measured the line series of the 2s-transitions in Ne gas. The energy position of these lines as given by Codling et al.[9] served as calibration marks. The absorption coefficients were determined in arbitrary units with a relative accuracy of 3 %.

Figure 1 shows the absorption spectrum of solid and gaseous Ne in the energy range 44 eV to 50 eV. The spectral resolution of the monochromator, as derived from the width of the zero order reflection, is

0.04 eV for gaseous Ne and 0.025 eV for solid Ne. Therefore the structure of the solid Ne spectrum is not expected to be broadened by our monochromator. As in the case of gaseous Ne one recognizes asymmetric lines with similar line shape in solid Ne. The onset of the lines in solid Ne is shifted to higher energies, the lines are broadened and only two show up. Whereas the gas lines are sitting on a flat continuum background, the lines in solid Ne are superimposed onto a broad hump in the continuum absorption background, probably due to high lying valence band transitions.

Figure 2 shows the absorption spectrum of solid Ar in the energy range 26 to 29 eV. The spectral resolution is better than .015 eV. For comparison the absorption section of the gas spectrum as measured by Madden et al.[12] is included. The absorption spectrum of solid Ar shows two "window" lines which are less pronounced than those in the gas. The width compared to the gas lines has not increased as much as in the case of Ne. Again, there is a shift to higher energies and the relative distance of the lines has decreased appreciably. As in Ne the gas lines are superimposed onto a flat background whereas the lines in solid Ar are sitting on a hump which is obviously due to valence band transitions. It has also been seen in reflectance measurements of solid Ar at the high energy end of valence band transitions.[8]

In Table I the line shape parameters for the first lines of the Ne and Ar gas spectra are given after Madden et al.[12]. By simply folding the gas spectra with Gaussians of various width[3] we have tried to match the profiles of the first absorption lines of the solids. This procedure did not lead to a satisfactory result. We have also tried to fit the line

shapes with Eq. (1). It turns out, however, in solid Ne, that the para-
meters necessary to fit the lines shape at the low energy side (fit b)
are different from those necessary for an optimal fit (a) on the high
energy side. This discrepancy seems due to the fact that the background
continuum absorption is not constant as it is in the gas. For solid Ar
fit a and fit b give an equally good description of the profiles.

Although a quantitative description of the line profiles with Fano's
parametrization formula does not leed to a satisfying result, a compari-
son of the line shape parameters for the gas and the solid lines shows
that in going from gas to solid the fraction ρ^2 of the interfering back-
ground decreases the width Γ of the lines increases and the line shape
parameter q has the same sign and the same order of magnitude.

We have considered whether the large line widths especially in Ne,
could be due to impurities or imperfections in the samples. After having
reproduced these spectra several times with samples prepared under
different vacuum conditions and with different evaporation speeds we
do not believe that this is the case.

References

1. R.P. Madden and K. Codling, in Autoionization; Astrophysical,
    Theoretical and Laboratory Experimental Aspects, edited by
    A. Temkin (Mono Book Corporation, Baltimore, Md. 1966), p. 129

2. U. Fano, Phys.Rev. 124, 1966 (1961)

3. K.P. Jain, Phys.Rev. 139, A 544 (1965)

4. J.C. Phillips, in Solid State Physics, Vol. 18, edited by
    F. Seitz and D. Turnbull (Academic Press, New York and London, 1966)

5. D.L. Greenaway and G. Harbeke, Optical Properties and Band
    Structure of Semiconductors (Pergamon Press, 1968)

6. F.C. Brown, Ch. Gähwiller, H. Fujita, N. Carrera, and
    W. Scheifley, Proc. X. European Congress for Molecular
    Spectroscopy, Liège 1969 (to be published)

7. R. Haensel, G. Keitel, P. Schreiber, and C. Kunz
    Phys.Rev. 188, 1375 (1969)

8. R. Haensel, G. Keitel, E.E. Koch, M. Skibowski, and P. Schreiber,
    Phys.Rev. Letters 23, 1160 (1969)

9. K. Codling, R.P. Madden, and D.L. Ederer, Phys.Rev. 155, 26 (1967)

10. J.A.R. Samson, Phys.Rev. 132, 2122 (1963)

11. R.P. Madden and K. Codling, Phys.Rev. Letters 10, 516 (1963)

12. R.P. Madden, D.L. Ederer and K. Codling, Phys.Rev. 177, 136 (1969)

13. R. Haensel and C. Kunz, Z. Angew. Phys. 37, 276 (1966)

Table I: Line shape parameters according to Eq. (1) for Ne gas
(after Codling et al.[9]) and different fits to Ne solid
(see Fig. 1), for Ar gas (after Madden et al.[12]) and
different fits to Ar solid (see Fig. 2)

			E_o(eV)	Γ(eV)	ρ^2	q
Ne	gas		45.55	.013	.7	−1.6
	solid	fit a	46.90	.34	.125	− .76
		fit b	46.81	.36	.077	−1.31
Ar	gas		26.614	.08	.86	− .22
	solid	fit a	27.515	.12	.32	− .39
		fit b	27.525	.13	.30	− .20

Figure captions:

Fig. 1   Absorption spectrum of solid (solid curve) and gaseous

(dashed curve) Ne. Theoretical curves a and b are included,

according to Eq. (1) with two different sets of parameters

(see Table I).

Fig. 2   Absorption spectrum of solid Ar (solid curve). The absorption

spectrum of gaseous Ar as given by Madden et al.[12] is in-

cluded (dashed curve). Also theoretical curves a and b are

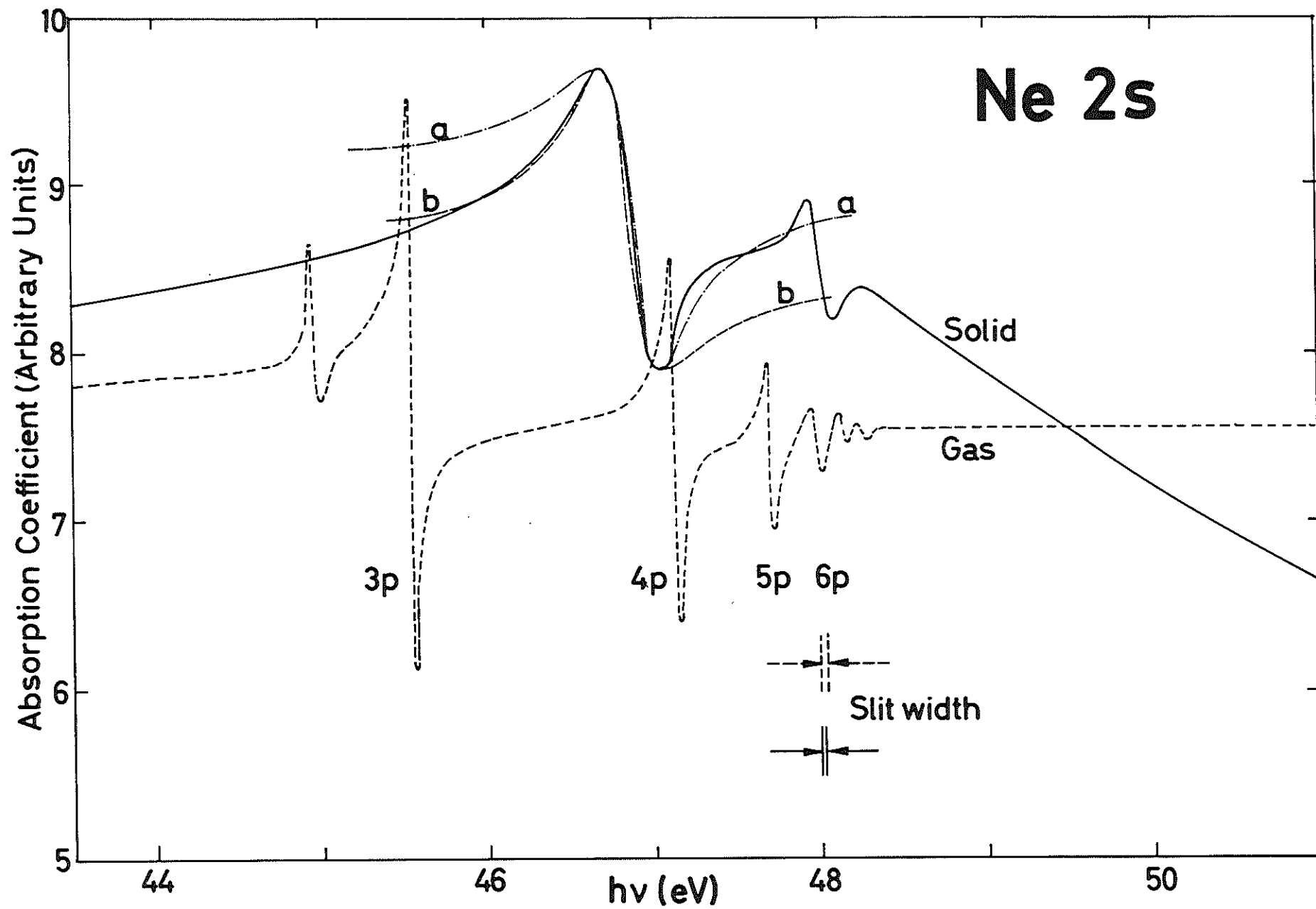included, according to Eq. (1) with two different sets of
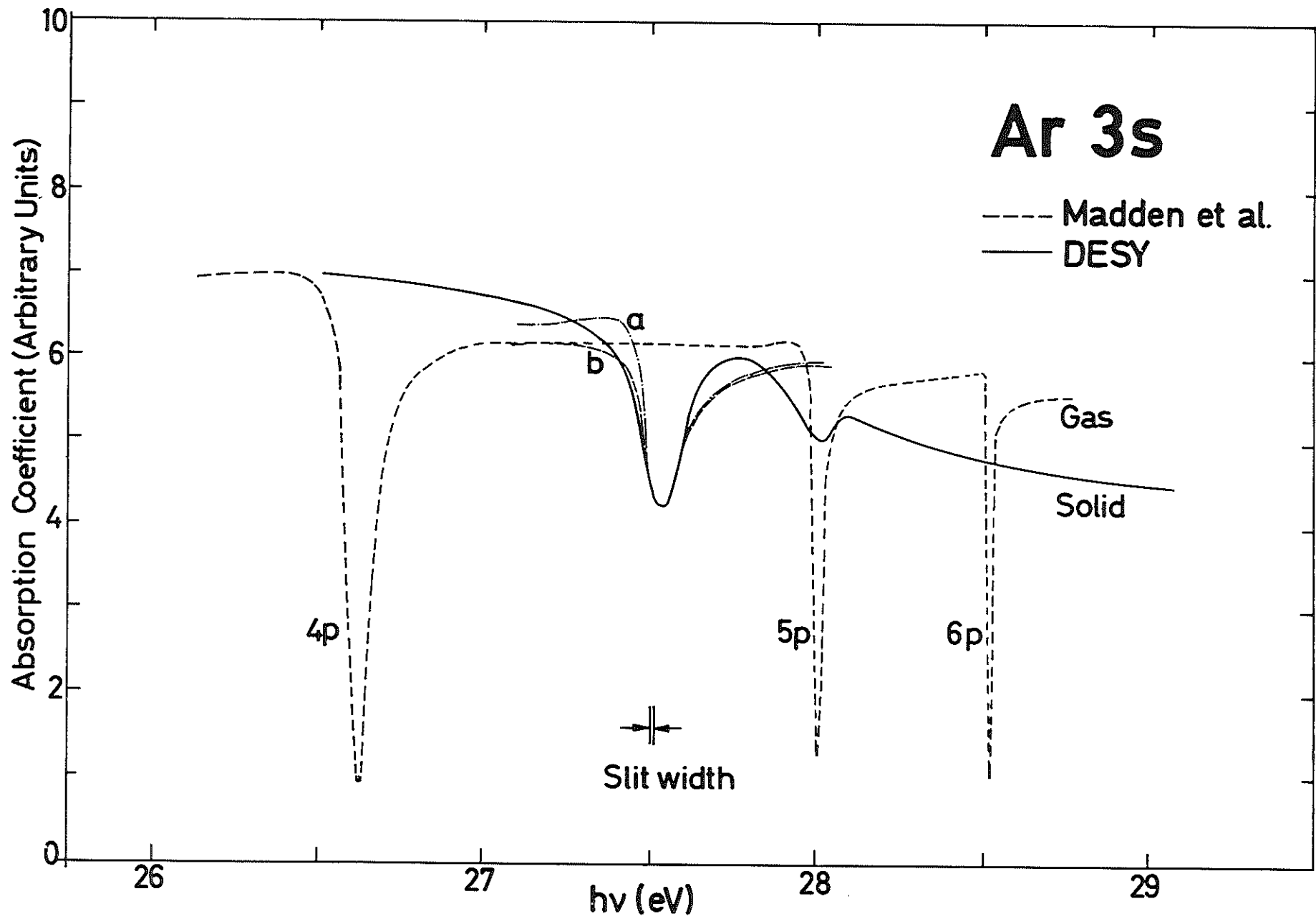
parameters (see Table I).

Fig.1

Fig. 2