DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

DESY 70/38
August 1970

Optical Excitation of Solid Neon in the Vacuum Ultraviolet

by

R. Haensel, G. Keitel, E. E. Koch, N. Kosuch, and M. Skibowski

2 HAMBURG 52 · NOTKESTIEG 1

Optical Excitation of Solid Neon in the Vacuum Ultraviolet[≠]

R. Haensel[+], G. Keitel[+], E.E. Koch[‡], N. Kosuch[+], and M. Skibowski[‡]

Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany

The reflection and transmission spectra of solid Ne films have been measured at 6° K for photon energies between 10 and 35 eV where transitions from the valence band occur. The use of the continuous spectrum of synchrotron radiation of DESY enabled us to resolve an exciton series with sharp maxima beginning at 17.8 eV and converging to 21.4 eV. At higher energies solid Ne exhibits additional weak structures in the conduction band continuum.

≠ Work supported by the Deutsche Forschungsgemeinschaft

+ II. Institut für Experimentalphysik der Universität Hamburg, Germany

‡ Sektion Physik der Universität München, München, Germany

In the past years excitations from the valence bands of solid Argon, Krypton and Xenon have been studied optically[1-4] and by electron energy loss experiments[5,6], but no optical experiments have yet been performed on solid Neon. By use of the continuum of synchrotron radiation the valence band excitations of Ar, Kr and Xe were studied recently up to 30 eV with high resolution.[2,3] In these experiments an efficient reflection technique was used. The improvement of our knowledge of the spectra of the heavier rare gases obtained by these investigations encouraged us to study also solid Ne with the same technique. According to the absorption of gaseous Ne[7,8] and a theoretical work on the solid[9], Ne was expected to show its first electronic resonances around 20 eV, a region difficult to investigate with high resolution using conventional light sources.

We measured the reflectance of solid Ne at 6° K for an angle of incidence of 15° in the energy range from 10 to 30 eV. The synchrotron radiation of the 7.5 GeV DESY[10] electron synchrotron was monochromatized by a normal incidence monochromator in a modified Wadsworth mounting.[11] The resolution was about 2 Å in wavelength over the whole energy range. The wavelength calibration was accurate to ±2 Å. Gaseous Ne (purity 99.99 %, purchased from L'Air Liquide) was evaporated either onto a cleaved KCl single crystal or a polished LiF plate, or a 500 Å thick Mg foil, respectively, which were cooled in a He cryostat. The light reflected from the Ne surface was detected with an open magnetic photomultiplier Bendix M 306. When a Mg foil was used as a substrate the transmission could be measured simultaneously with the reflection by means of a second magnetic multiplier behind the sample. Cryostat

and multipliers were placed in a modified commercial ultrahigh vacuum system.[12] After baking the whole system for 8 hours the basic chamber pressure was of the order of 10^{-9} Torr. During evaporation oscillatory changes of the intensity of the reflected light due to interference effects with increasing thickness were observed for photon energies below the onset of absorption (16 eV). The evaporation was stopped when these oscillations in intensity disappeared thereby indicating that the films were sufficiently thick to exclude interference. Because of the good vacuum conditions the reflectance remained constant within 10 % over one hour.

Figure 1 shows the reflectance of solid Ne evaporated onto a LiF-plate or a KCl single crystal measured between 16 and 30 eV. Below 16 eV no structure was observed. Above 16 eV the spectrum is dominated by an intense reflectance peak at 17.8 eV followed by a series of weaker maxima at 20.3 eV, 20.9 eV and 21.3 eV, respectively. Between 22 eV and 30 eV no prominent structures were observed.

The reflectance value for the dominant peak at 17.8 eV was estimated to be 60 % with an error of ±20 % by comparison with the known reflectivity of the KCl substrate. This first line is about forty times more intense than the second one. The positions of the first three lines agree within 0.1 eV with those found in electron energy loss experiments.[13,14] The fourth line is only resolved in the optical experiment.

In contrast to the other rare gas solids no spin-orbit splitting is observed. The splitting is expected to be close to the value of 0.14 eV found for gaseous Ne.[7] It should be detectable with the experimental resolution of about 0.05 eV at 18 eV. However, Webber et al.[9] predicted a broadening of the lines in the solid and a halfwidth of the order of 0.4 eV. Therefore we believe that the first line in solid Ne, for which we found a halfwidth of 0.5 eV consists of the spin-orbit partners broadened so much that the spectrum exhibits only one broad peak.

As for the other rare gas solids one can tentatively ascribe the lines to a Rydberg series, the energies of which are determined by $E_n=E_o-Bn^{-2}$.[15] Using the n=2 and n=3 lines one obtains for the series limit $E_o=21.4$ eV and the binding energy B=4.3 eV. This value fits quite well into the series of binding energies derived from measurements on the other rare gas solids[1-3]: $B_{Ar}=2.3$ eV, $B_{Kr}=1.4$ eV and $B_{Xe}=0.8$ eV. However, a binding energy of 4.3 eV is unusually large for Wannier excitons. Furthermore in the case of Wannier excitons the line intensities[16] should vary as n^{-3} whereas we find a much stronger decrease.

On the other hand one might discuss this part of the solid Ne spectrum in terms of localized Frenkel-excitations. In Fig. 1 the vertical lines indicate the positions of the gas absorption lines for the spin-orbit split series $2p\rightarrow\nu s$ and $2p\rightarrow\nu s'$ ($\nu>3$) with series limits 21.56 eV and 21.7 eV respectively.[8,9] This figure shows a close relationship between

the line positions in gaseous and solid Ne. For example one can find a correspondence between all pairs of spin-orbit split lines of the gas and the lines of the solid. However, the lines in the solid are shifted to higher energy as compared to the corresponding lines in the gas. This blue shift decreases with increasing quantum number so that the series limit of the gas and that of the solid calculated above with the Rydberg formula (21.4 eV) lie close together. It is interesting to note, that the shift ΔE of the first line in Ne is 1 eV which is much larger than the corresponding shifts in the other rare gas solids (ΔE_{Ar}=0.48 eV, ΔE_{Kr}=0.22 eV, ΔE_{Xe}=0.02 eV).

We have applied both the Wannier and Frenkel picture in discussing the observed excitations. Neither of the pictures seems to be sufficient, so that we suggest the excitons in solid Ne to be of an intermediate type.

Figure 2 shows the transmission I/I_o of solid Ne between 15 and 35 eV as taken from films evaporated on thin Mg foils. The arrows indicate the positions of the first two sharp maxima of the corresponding reflection spectrum.[a)] As in the spectrum of Fig. 1 a series of well resolved sharp minima converging to about 22 eV can be seen. The first minimum at 17.4 eV is very broad and asymmetric. Above the series limit additional structures were observed. Since no corresponding atomic resonances are known in this region[8] we ascribe these structures to interband transitions from the 2p valence band to the conduction band. An exact interpretation of these structures will be possible, when detailed energy band and density of states calculations are available.

We thank P. Schreiber for participation in the early stages of the experiment. We are grateful to H. Boersch, O. Bostanjoglo, L. Schmidt and P. Krüger for making available to us electron energy loss data on solid Ne prior to publication and U. Rössler for providing us an unpublished KKR-band-calculation on solid Ne.

References

1. G. Baldini, Phys.Rev. 128, 1562 (1962)
2. R. Haensel, G. Keitel, E.E. Koch, M. Skibowski and P. Schreiber, Phys.Rev. Letters 23, 1160 (1969)
3. R. Haensel, G. Keitel, E.E. Koch, M. Skibowski and P. Schreiber, to be published in Optics Comm.
4. I.T. Steinberger, C. Atluri and O. Schnepp, J.Chem.Phys. 52, 2723 (1969)
5. P. Keil, Z. Physik 214, 251 (1968)
6. O. Bostanjoglo and L. Schmidt, Phys.Letters 22, 130 (1966)
7. C.E. Moore, Atomic Energy Levels, Vol. I, Circular of the NBS 467 (1958)
8. K. Codling, R.P. Madden, and D.L. Ederer, Phys.Rev. 155, 26 (1967)
9. S. Webber, S.A. Rice, and J. Jortner, J.Chem.Phys. 41, 2911 (1964)
10. R. Haensel and C. Kunz, Z.Angew. Physik 23, 276 (1967)
11. M. Skibowski and W. Steinmann, J.Opt.Soc.Am. 57, 112 (1967)
12. B. Feuerbacher, R.P. Godwin and M. Skibowski, Rev.Sci.Instr. 40, 305 (1969)
13. H. Boersch, O. Bostanjoglo and L. Schmidt, Tagung für Elektronenmikroskopie, Aachen 1965 (unpublished)
14. P. Krüger, Diplomarbeit, Universität Hamburg, 1970
15. R.S. Knox, The Theory of Excitons, Academic Press, Inc., New York (1963)
16. R.J. Elliott, Phys.Rev. 108, 1384 (1957)

Footnotes:

a) An additional broad maximum has been found between the first two resonances in the corresponding reflection spectrum. This effect is not yet understood, but could be due to a possible hexagonal phase of Ne instead of the commonly adopted fcc-structure.

Figure captions

Fig. 1 Reflectance of solid Ne evaporated on a LiF plate or a KCl single crystal at 6° K (solid line). The vertical lines indicate the spin orbit split series $2p \rightarrow \nu s$, $2p \rightarrow \nu s'$ ($\nu \geq 3$) with their limits L_{III} and L_{II} for gaseous Ne.[8]

Fig. 2 Transmission of solid Ne films evaporated on Mg-films.

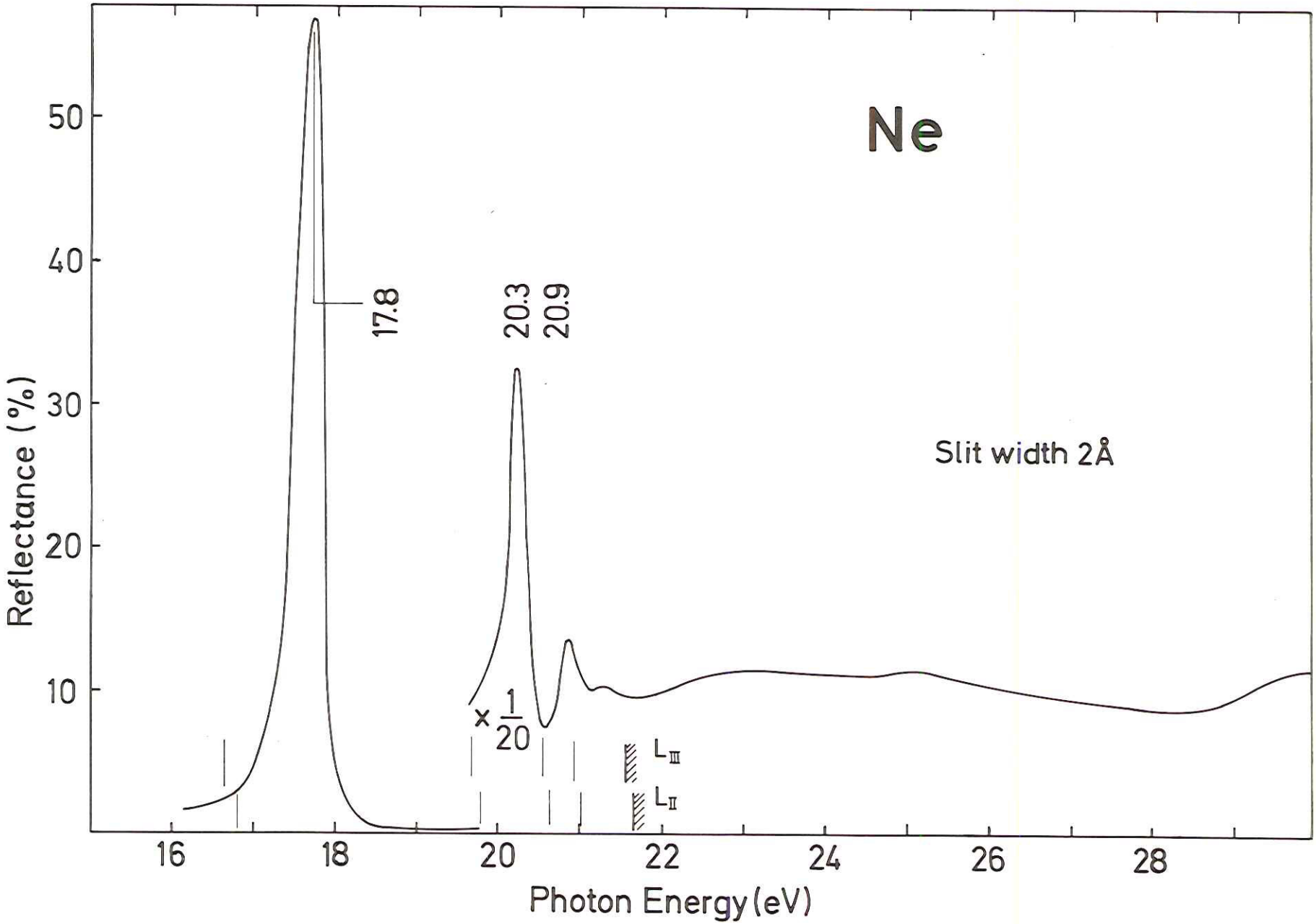
Ne
Slit width 2Å
Reflectance (%)
50
40
30
20
10
17.8
20.3
20.9
× 1/20
L_III
L_II
16
18
20
22
24
26
28
Photon Energy (eV)

Fig. 1

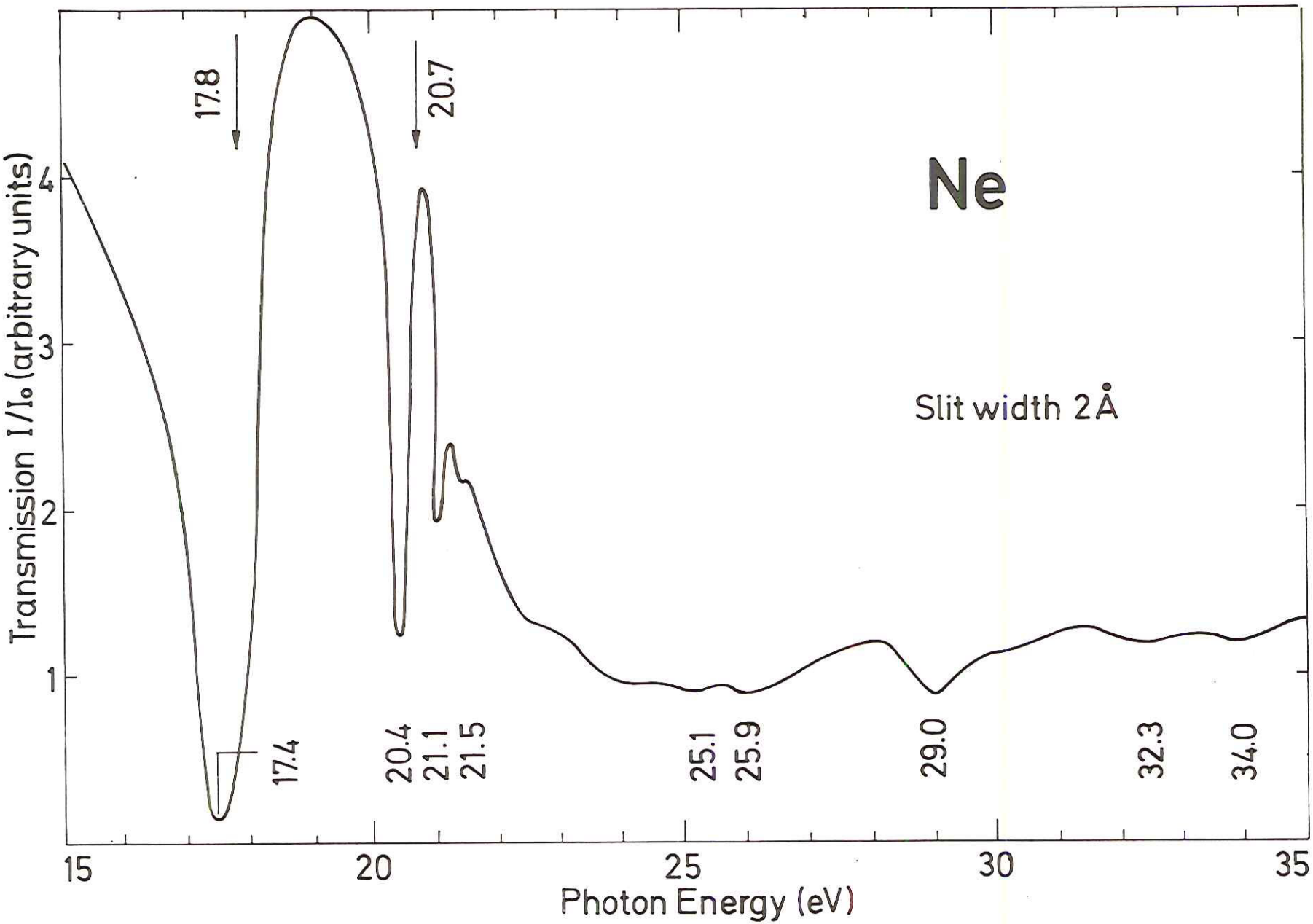
Ne
Slit width 2Å
Transmission I/I₀ (arbitrary units)
Photon Energy (eV)
17.8
20.7
17.4
20.4
21.1
21.5
25.1
25.9
29.0
32.3
34.0
1
2
3
4
15
20
25
30
35

Fig. 2