Physica **44** (1969) 206–218 © *North-Holland Publishing Co., Amsterdam*

EXCITATION OF Cu ATOMS BY Ar IONS AND SUBSEQUENT RADIATIONLESS DEEXCITATION OF SCATTERED PARTICLES NEAR A Cu SURFACE

W. F. VAN DER WEG and D. J. BIERMAN
FOM-Instituut voor Atoom- en Molecuulfysica, Amsterdam, Nederland

Received 11 February 1969

Synopsis

The profile of a Cu I spectral line, excited by bombardment of a Cu crystal with 80 keV Ar ions is measured. The Doppler profile shows that the light-emitting particles have energies in the keV region. The wavelength shift of 0–0.5 Å depends on crystal and monochromator orientation.

Measurements of the line shape as a function of the angle of the target with respect to the primary beam and also as a function of azimuthal rotation of the target, indicate that the emitting particles originate predominantly from collisions of Ar ions with surface Cu atoms. The fact that the emission is found in front of the target points in the same direction.

Evidence is presented for the occurrence of a radiationless deexcitation process, which is supposed to be tunnelling of an electron from the excited atom into the metal. The probability for escape from the surface in an excited state depends therefore on the particle velocity. A calculation of the line profile based on this assumption is made. Comparison with the experiments yields a value $10^{14}\,s^{-1}$ for the transition rate for the tunnelling process, when the distance of excited atom to the metal surface is a few Å.

1. *Introduction*. When an ion with an energy in the keV range collides with an atom located in the surface of a metal target, excitation of the collision partners can take place.

This excitation can result in the emission of electrons[1]); also ions are believed to originate from highly excited scattering products[2]). In the third place, photon emission from ionically bombarded metal targets has been observed by many authors, as well in the visible and UV-range[3–8]) as in the soft X-ray region[9,10]).

In this paper we confine ourselves to the study of spectral lines in the near UV region. In earlier work lines of the atomic and ionic spectra of projectile and target particles have been found[4,5]).

An estimation of the velocity of light-emitting particles was found by a qualitative study of the shape of Cu I spectral lines observed during bombardment of a Cu surface by 60 keV Ar^+ ions[6]). The Doppler profile and also the thickness of the luminous region in front of the target showed that the light was emitted by Cu atoms having keV energies. These high-energy particles can be created in collisions of beam ions with surface atoms[11,12]).

Experiments on light emission from Cu and Ta targets bombarded with H^+ and H_2^+ showed that the observed H_α, H_β and H_γ lines also originated from surface collisions[8]). Particles leaving the surface with low velocity, which are abundant in these experiments do not contribute to the light emission.

An explanation for this phenomenon is the presence of radiationless de-excitation processes, which reduce the number of slow excited particles. Near a metal surface radiationless deexcitation is a process, competing with deexcitation by photon emission. Atomic levels can extremely fast be depopulated by tunnelling of the excited electron into a vacant metallic state[13–16]). It has been shown that for atom-metal distances of a few Å, the tunnelling process is much more probable than emission of a photon[13,14]).

In this paper the shift and shape of spectral lines of the Cu I spectrum excited by 80 keV Ar^+ ions is studied experimentally. It is shown that the observed line profiles can be explained in terms of radiationless deexcitation of scattered particles during their way near the metal. In a part of the experiments, the conditions are such that the excited particles are created by binary collisions between projectile ions and surface target atoms. The differential scattering cross section is known well for these collisions. Furthermore, the excitation probability as a function of impact parameter must be used in order to calculate the number of emitting particles with a certain velocity. No data exist in literature for this function, therefore we have used some simple trial functions.

The line profile can be obtained from these data in combination with the probability for radiationless deexcitation. Comparison of profiles calculated in this way with the measured ones yields the value of the integrated probability for electron transitions during the outward journey of the scattering products.

Also, the experiments show in an unambiguous way, that the radiation takes place in front of the target, with no detectable contribution from inside the material.

2. *Apparatus.* The ion accelerator and scattering chamber are already described elsewhere in detail[11,12]).

The experimental setup is schematically shown in fig. 1. A Cu crystal is placed in the centre of a scattering chamber in a targetholder which permits rotation around three perpendicular axes. The pressure in the scattering chamber is maintained at 1×10^{-6} torr during experiments by

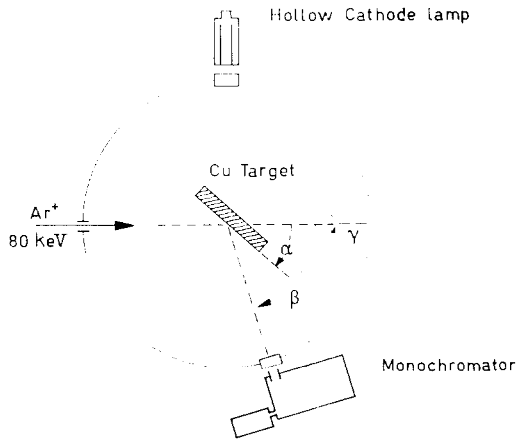

Fig. 1. Schematic diagram of the experimental setup.

means of a mercury diffusion pump. Cleaning of the target takes place by sputtering; the surface condition with the actual experimental conditions is extensively dealt with in a previous paper[2]).

The monochromator is separated from the scattering chamber by a quartz window. Photons emitted under an angle β with the direction of the primary beam are observed (β can be continuously changed over 100°).

At one of the ports of the scattering chamber a hollow cathode lamp is mounted for absolute wavelength calibration. It consists of a hollow cylindrical Al anode and a Cu cathode, which is water cooled. The lamp operates by introducing Ar gas to a pressure of about 0.2 Torr with 500 V between the electrodes. Sharp spectral lines (Doppler width < 0.05 Å) of the atomic spectrum of Cu are emitted.

When the monochromator is set at $\beta = 90°$, wavelength calibration can be performed by simply removing the target (which is possible without breaking the vacuum). We used a grating monochromator of the Czerny-Turner type (fig. 2) with a bandwidth of 0.4 Å.

Wavelength scanning is usually performed by rotation of the grating. However, it was found that this method was not suitable to reproduce a certain wavelength setting within 1 Å. A common alternative for high precision wavelength scanning is parallel displacement of the exit slit, which is technically hard to achieve. Therefore we used the following fine-scanning method. In the path of the light beam between the second mirror and the exit slit a small plane parallel quartz plate was mounted, which could be rotated around an axis parallel to the exit slit (see fig. 2). The spectral line shifts over the slit on rotation of the plate due to the displacement in the quartz.

This displacement d varies in first order approximation linearly with the

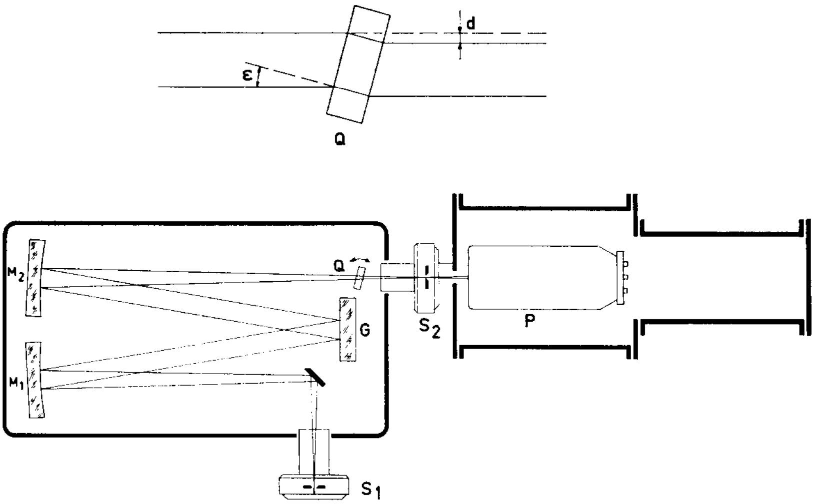

Fig. 2. Diagram of the monochromator with photomultiplier.
The entrance slit S_1 is placed at one of the ports of the scattering chamber. M_1 and M_2 are spherical mirrors, G is the grating. The light enters the photomultiplier P through the quartz plate Q and the exit slit S_2.
The displacement of the light beam, by rotation of the quartz plate over ε is shown separately.

angle of rotation ε

$$d = t[\sin \varepsilon - \cos \varepsilon \sin \varepsilon \, (n^2 - \sin^2 \varepsilon)^{-\frac{1}{2}}],$$

which for small ε reduces to

$$d \approx t\varepsilon \left(1 - \frac{1}{n} + \frac{\varepsilon^2}{2n} - \frac{\varepsilon^2}{2n^3}\right).$$

In this expression, n is the index of refraction of the quartz and t is the plate thickness. The deviation from linear behaviour is smaller than 2% for $0° < \varepsilon < 20°$. We made use of this fact by connecting a potentiometer to the axis of the plate, which drove the X axis of an XY recorder, the Y signal of which was the photomultiplier output.

Thus a line profile can be fast and accurately recorded by setting the monochromator at the desired wavelength and subsequent fine scanning by the quartz plate.

3. *Experimental results.* In order to determine the influence of the presence of the metal on the excitation state of scattered particles two types of experiments were performed:

a) With a fixed orientation of the monochromator ($\beta = 60°$) the line profile of the Cu I 3247 Å resonance line was studied as a function of target orientation (or angle of beam incidence).

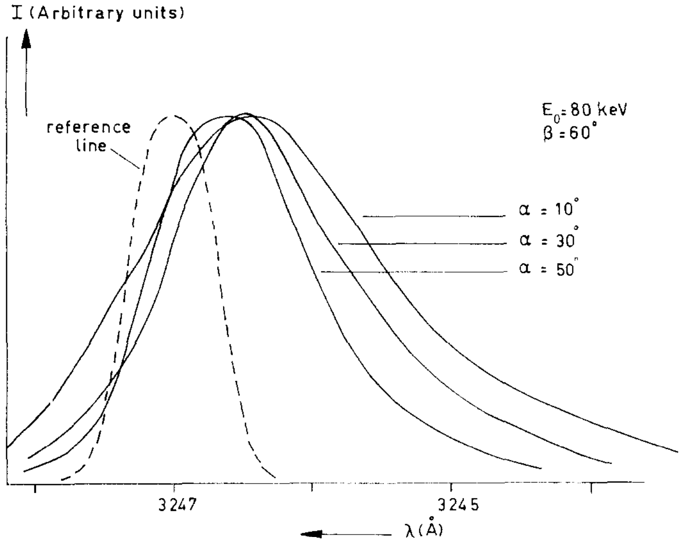

Fig. 3. Line shapes of the 3247 Å Cu I resonance line for different target orientations α. The intensities are normalized.

b) For fixed monochromator position ($\beta = 90°$) the line profile of the same line was studied for one angle of beam incidence as a function of azimuthal rotation γ of the target. This azimuthal rotation is performed around the primary beam direction. Rotation of the target in this plane keeps the angle of the primary ion beam with the surface constant but the orientation of the surface with respect to the monochromator changes.

Typical results of measurements a) are shown in fig. 3. Measured line profiles are given and the reference line $\lambda = 3247$ Å, as determined with the hollow cathode lamp is also included. The shift and asymmetrical shape of the lines from the solid target is obvious. This can more clearly be seen in fig. 4, where the deviation from the reference wavelength of the maximum of the profile is given. Besides, the full width at half maximum of the lines is also indicated.

Both the wavelength shift of the top of the line and the half-width increase for small α.

The observed wavelength shifts correspond with an appreciable energy of the emitting particles. For instance 0.4 Å wavelength shift corresponds with 450 eV Cu particles. The fact that by far the greatest part of the lines correspond with energies higher than 100 eV confirms the conclusion of a preliminary paper[6]), in which it was stated that the emitting particles are scattering products arising from violent collisions of beam ions with surface Cu atoms. Sputtered particles, resulting from collision cascades in the material are abundant in these experiments, but they clearly do not contribute

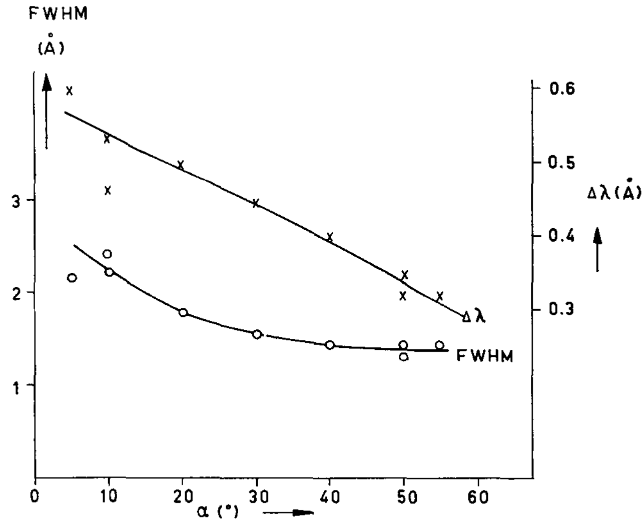

Fig. 4. Wavelength shift of the top ($\Delta\lambda$) and full width at half maximum (FWHM) of the line profiles *vs* target orientation α ($\beta = 60°$, $E_0 = 80$ keV).

to optical radiation. This may become clear by comparing the following numbers.

The number of low energy Cu particles coming from the target per incoming ion (the sputtering ratio) is of the order 2–5 [17]), while the contribution of particles scattered off after one surface collision is about 0.001 [12,18]).

The concept of singly scattered particles being the origin of the light is consistent with the behaviour of the line width *vs* target orientation α (fig. 4). For small α more Cu particles scattered under a small angle and thus having high energies are able to leave the target. These particles contribute to the low wavelength part of the line, making the centre of gravity shift to low λ. Also the increase in width with decreasing α is explained naturally in the same way.

A second conclusion can also already be drawn. The cross section for scattering of target particles under 10° is 2–3 orders of magnitude smaller than for scattering under 80° [12,18]). Yet, the effect of small numbers of high energy particles appearing when decreasing α influences the line shape considerably. This fact indicates that the excitation state of faster particles ($E > 1$ keV) is much less influenced by the presence of a surface than the slower ones ($E < 100$ eV), of which we have seen that they do not radiate. It suggests that the probability of escape in an excited state from a surface increases rapidly with velocity. However, the experiment described is not suitable for extraction of numerical results for the tunnelling probability, because collisions of beam ions with the second and third layer of the crystal are also possible for most values of α.

In order to avoid this difficulty experiment b) was performed. The conditions are chosen in such a way now, that only collisions of beam ions with surface Cu atoms are possible, *e.g.* the ions are directed in a channel direction of a single crystalline target. This direction is found by rotating a (110) surface of a Cu single crystal around a [111] axis in the surface. For $\alpha = 30°$ an open [011] direction coincides with the beam direction. A precise determination of this channel is performed by measuring the total light intensity of a spectral line as a function of α. The resulting curve[4,5]), which is strikingly similar to curves of yield of sputtering[19]) or secondary electrons[20]), exhibits minima corresponding with low index crystal directions. For the case of $\beta = 90°$ and $\alpha = 30°$ the line shape of the 3247 Å resonance line was measured as a function of γ. The azimuthal angle γ is defined as zero, when the target is perpendicular to the plane of incoming beam and direction of observation. Results are given in fig. 5. The line shape and the relative intensities of the lines are presented for $0 \leq \gamma \leq 90°$.

Again, the line is appreciably shifted for $\gamma = 0°$ (corresponding to the target position as used in fig. 3). However, $\gamma = 90°$ leads to a completely symmetrical line and the wavelength of the top coincides with the 3247 Å position as given by the calibration line. This result is obvious when considering the fact that for $\gamma = 90°$ as many scattered particles are moving away from the detector as are moving towards it. The change in line shape with γ is due to the changing of the *projection* of the velocity distribution of the light emitting particles on the direction of observation. A remarkable feature is that the total intensity of the lines hardly changes on variation of γ.

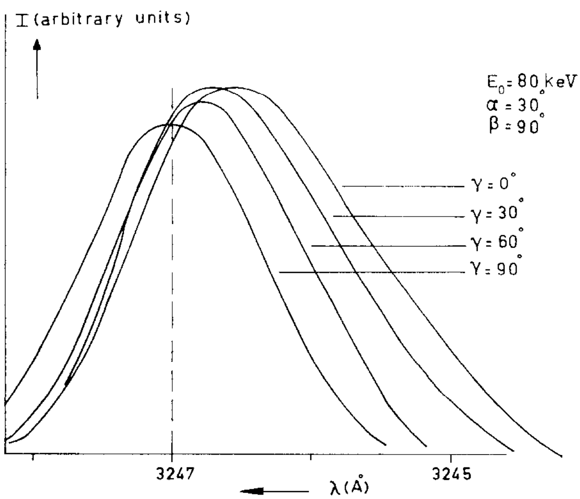

Fig. 5. Profiles of the 3247 Å Cu I line for different azimuthal angles γ. The intensities are not normalized.

This observation proves two important points. In the first place it follows that the surface roughness of the target is insignificant. Secondly, the emission must originate from a region *in front* of the target. Particles which are excited inside the target are either fastly deexcited still in the crystal, or their radiation is absorbed in the material. Simple geometrical arguments show that the *integrated* light intensity from a region outside the target cannot be dependent on γ, for fixed α.

4. *Calculations.* The line profile as arising from the velocity distribution of the light emitting scattered particles can be obtained in the following way.

Let $P_{\text{exc}}(\varphi)$ be the probability for excitation to the level under consideration of particles which are scattered under an angle φ; the differential scattering cross sections is $\sigma(\varphi)$ and the chance for an excited particle to escape from the surface without radiationless deexcitation $R(\varphi, \alpha)$. In this case the number of particles contributing to radiation with wavelength $\lambda + \Delta\lambda$ is given by:

$$N(\lambda + \Delta\lambda)\,\mathrm{d}\lambda = \int\!\!\int [P_{\text{exc}}(\varphi)]\,[\sigma(\varphi)]\,[R(\varphi, \alpha)]\left[\delta\left(\frac{v_\beta}{c} - \frac{\Delta\lambda}{\lambda}\right)\right] \times \tag{1}$$

$$\times\; 2\pi \sin\varphi\,\mathrm{d}\varphi\,\mathrm{d}\gamma\,\mathrm{d}\lambda.$$

The original wavelength of the line is λ, v_β is the component of the particle velocity in the direction of observation β, thus the δ-function denotes the condition for Doppler shift over $\Delta\lambda$, when c is the velocity of light. Scattering angles are measured by φ, the azimuthal angle by γ. The limits of integration over φ are determined by the condition that the particles are scattered out of the target, thus $\varphi > \alpha$. The integration limits for γ are fixed by the intersection of the cone around the primary beam direction having semiapex angle φ, with the crystal surface.

We will briefly describe the used functions:

1) The estimation of the excitation probability during a collision resulting in a scattering angle φ is a serious problem. For the case of collisions in a gas, this probability is known for some combinations of beam and target material. However, the perturbation caused by the presence of the metal surface on the excitation process has never been determined. Therefore we made some simple assumptions about the behaviour of P_{exc} with scattering angle. We started with P_{exc} independent of φ. Secondly a behaviour taking into account the violence of the collision was used, *e.g.* $P_{\text{exc}}(\varphi) = c_1 \cos\varphi$, c_1 being a constant only depending on the considered level of excitation. So for φ near $= 90°$ which corresponds with the weakest interactions the probability is supposed to be small. Also a stronger dependence on scattering angle, *viz.* $P_{\text{exc}}(\varphi) = c_1 \cos^2\varphi$ was tried.

Summarizing,

$$P_{\rm exc}(\varphi) = c_1 \cos^n \varphi, \qquad n = 0, 1, 2. \tag{2}$$

2) The cross section $\sigma(\varphi)$ is well known for these collisions. It can be derived from a potential appropriate for the considered interaction, which in our case is a screened Coulomb or a Firsov potential. An approximation to the latter potential is an inverse power potential with exponent -2. The cross section as derived in the impulse approximation is easily calculated to be[21]:

$$\sigma(\varphi) = c_2 \cos^{-2} \varphi. \tag{3}$$

With reference to the gross simplification as used in 1) it was found irrelevant to use the exact expression for $\sigma(\varphi)$.

3) The probability for escape in an excited state $R(\varphi, \alpha)$ can be derived from the probability for electron tunnelling from the excited atom to the metal.

This probability P has been estimated by many authors mainly for application in experiments on potential electron ejection. It depends on the distance s of the atom to the metal

$$P(s) = A\, \mathrm{e}^{-as}. \tag{4}$$

We now determine the chance $R(s)$, that a particle leaving the surface has not experienced a radiationless deexcitation at a distance s;

$$\mathrm{d}R(s) = -R(s)\, P(s)\, \mathrm{d}s/v_\perp. \tag{5}$$

$\mathrm{d}s/v_\perp$ is the time which the particle spends at a distance s in the interval $\mathrm{d}s$, when $v_\perp$ is the velocity component perpendicular to the surface. The solution for $s = \infty$ follows from (5) taking into account that $R(s) = 1$ for $s = 0$.

$$R(\infty) = \mathrm{e}^{-(A/av_\perp)}. \tag{6}$$

This is the function $R(\varphi, \alpha)$, used in (1). (R depends on φ and α through $v_\perp$.)

The profile of the $\lambda = 3247$ Å line, emitted by Cu atoms scattered from a Cu surface ($\alpha = 30°$) by 80 keV Ar^+ ions has been calculated by formula (1), substituting (2), (3) and (6) (omitting the constants c_1 and c_2). Values of $n = 0$, 1 and 2 in (2) were used and several values of the integrated transition probability A/a in (6). Results could in no way describe the experimental line shape when taking $n = 0$ and 2, but $n = 1$ fits rather well.

Results obtained with $n = 1$ for the case of $\alpha = 30°$, $\beta = 90°$ and $\gamma = 0°$ are presented in fig. 6. Because the bandwidth of the analyzing instrument cannot be neglected in comparison with the half-width of the measured lines, we have convoluted the results obtained by expression (1) with the instrument function, which is a Gaussian.

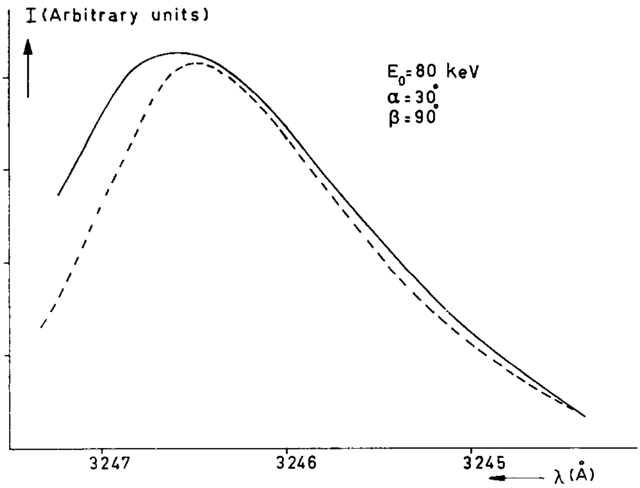

Fig. 6. Experimental (solid) and calculated (dashed) line shapes for $\alpha = 30°$, $\beta = 90°$ and $\gamma = 0°$.

The value of $A/a = 2 \times 10^4$ (m/s) yielded a line shape, which fitted best. The sensitivity of the calculation for A/a is expressed by the fact that the calculated position of the top of the line shifts 0.2 Å on increasing A/a by a factor two.

The value of the parameter a in (4) follows directly from the radial part of the atomic wave function, which essentially determines the magnitude of the overlap of atomic and metallic electron wave functions, leading to the tunnelling probability $P(s)$. It has been shown that $a = 2 \times 10^{10}\ \mathrm{m}^{-1}$ is a resonable value for many combinations of excited atoms and metals[13, 22]. This number, combined with the value of the integrated transition probability as determined by the line shape yields the absolute value of $A = 4 \times 10^{14}\ \mathrm{s}^{-1}$.

The result for the radiationless deexcitation probability of the $4p^2P_{3/2}$ level of Cu near a Cu surface is:

$$P(s) = 4 \times 10^{14}\ \mathrm{e}^{-2s} \qquad (s \text{ in Å}). \tag{7}$$

The probability for electron capture by scattered ions near a Cu surface has been derived in a previous paper[2]. Comparison shows that the probability for electron capture by ions is of the same order of magnitude as the probability of tunnelling of an electron from an excited atom into the metal.

Values of $P(s)$ determined for the case of electron transitions between alkali ions and metals are an order of magnitude larger than values derived from (7). The reason for this divergence may lie in the fact that the radius of the Cu 4s shell is of the order of 1 Å, the alkali atoms being twice as large[23]. Thus the overlap integral will be considerably larger for alkali

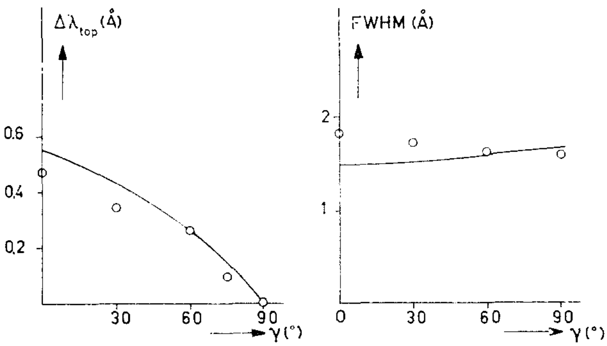

Fig. 7. Wavelength shift of the top ($\Delta\lambda$) and full width at half maximum (FWHM) of the line profiles *vs* azimuthal angle γ ($\alpha = 30°$, $\beta = 90°$, $E_0 = 80$ keV). Circles indicate experimental values, the solid lines are calculated.

atoms near a metal, as compared with Cu atoms, for a fixed distance metal-atom.

A final check for the validity of our model consists in the calculation of the line profile as a function of azimuthal rotation of the target. We adopt the value of A/a, determined for $\gamma = 0°$ and calculate the integral (1) for several values of γ, ranging from 0° to 90°. Results are shown in fig. 7. We can make two remarks about the calculated profiles. Firstly, the integrated intensity proves to be independent of γ as should be the case. In the second place the overall shape and the magnitude of the wavelength shift of the top agrees fairly well with the experimental results. This means that the velocity distribution of excited atoms is reasonably well described by the used formalism.

A slight variation in the value of A/a can match the experimental and theoretical profile exactly, but this is felt to be meaningless in view of the approximations used in eqs. (2)–(4).

5. *Discussion.* The Doppler profile of Cu I lines excited by fast ion bombardment indicates that the light emitting particles have an energy which is characteristic for scattering products of binary collisions between beam ions and surface target atoms. This type of interaction also produces ions of beam and target material in many charge states. The ionization probability can be related to corresponding probabilities for the case of collisions in a gas. This is understandable in view of the large amount of energy transfer involved in such processes, justifying the neglecting of effects of other lattice atoms on the collision process.

However, it may well be that the process of excitation of neutral atoms of a metal, involving energies of a few eV proceeds in quite a different way than in the gas phase. In the first place, the presence of the conduction band in the metal will influence the excitation process itself. Secondly, near a metal neutralization processes of ions occur. Neutralized excited ions can thus contribute to the number of excited neutral atoms. It might be instructive to measure the line shape of atomic spectral lines excited in a collision of projectiles with a Cu vapour to determine the number of excited particles. It must, however, be kept in mind that the deexcitation processes near a metal make comparison of results obtained respectively with a vapour and a solid target very hard.

It has been observed that the intensity of the 3247 Å Cu I line resulting from bombardment of a Cu_2O target is an order of magnitude higher than the intensity obtained from a pure Cu target, while the linewidth with a Cu_2O target is greatly reduced. These observations indicate that for the case of an oxyde surface, low velocity Cu particles too, are able to radiate.

The reason for this phenomenon is supposed to be the presence of a large forbidden energy gap in the semiconductor formed by the oxyde (2 eV for Cu_2O), prohibiting tunnelling transitions of electrons to this region. The possibility for radiationless deexcitation of atoms near a semiconductor surface is thus greatly reduced, resulting in an increase of light intensity.

Finally one can estimate the chance of escape from a Cu surface for a low energy excited sputtered Cu particle. As a representative energy we take 10 eV[24]). We use the value $A/a = 2 \times 10^4$ m/s for the integrated transition probability as determined before.

The probability of survival for an excited state is given by (6):

$$R(\infty) = e^{-(A/av_{\perp})} = e^{-(2\times 10^4)/(5.5\times 10^3)} = e^{-3.6} = 2.8 \times 10^{-2}.$$

Hence, approximately 3% of the sputtered neutral particles, if they are ejected in an excited state, will emit a photon. This figure does not indicate anything, however, about the line intensity due to sputtered Cu atoms, as we have no data about the cross section for excitation of Cu atoms at kinetic collision energies of about 10 eV. Such cross sections should be determined in Cu–Cu and Cu–Ar atomic beam experiments.

Acknowledgements. We are indebted to Professor J. Kistemaker, Dr. C. Snoek and Dr. D. Onderdelinden for their comments and discussions. We thank S. Doorn and H. H. Roukens for their assistance during the measurements.

The computer calculations have been carried out with the X8 computer of the "Mathematisch Centrum", Amsterdam.

This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental Research on Matter) and was made possible by financial support from the Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Pure Research).

REFERENCES

1) Parilis, E. S. and Kishinevskii, Soviet Physics – Solid State, English Transl. **3** (1960) 885.
2) Van der Weg, W. F. and Bierman, D. J., preceding paper, Physica **44** (1969) 177.
3) Sporn, H., Z. Phys. **112** (1939) 278.
4) Fluit, J. M., Friedman, L., van Eck, J., Snoek, C. and Kistemaker, J., Proc. Vth Int. Conf. on Ionization Phenomena in Gases, Munich, 1961.
5) Kistemaker, J. and Snoek, C., Le Bombardement Ionique, Centre National de la Recherche Scientifique (Paris, 1962) p. 51.
6) Snoek, C., van der Weg, W. F. and Rol, P. K., Physica **30** (1964) 341.
7) Sterk, A. A., Marks, C. L. and Saylor, W. P., Phys. Rev. Letters **17** (1966) 1037.
8) Gritsyna, V. V., Kijan, T. S., Koval', A. G. and Fogel', Ja. M., Phys. Letters, **27A** (1968) 292.
9) Khan, J. M., Potter, D. L., Worley, R. D. and Smith Jr., H. P., Phys. Rev. **163** (1967) 81.
10) Saris, F. W., van der Weg, W. F. and Kistemaker, J., Phys. Letters **26A** (1968) 592.
11) Datz, S. and Snoek, C., Phys. Rev. **134** (1964) A347.
12) Snoek, C., thesis, Amsterdam, 1966.
13) Hagstrum, H. D., Phys. Rev. **96** (1954) 336.
14) Sternberg, D., thesis, Columbia University, 1957.
15) Van der Weg, W. F. and Rol, P. K., Nuclear Instr. and Meth. **38** (1966) 274.
16) Propst, F. M., Phys. Rev. **129** (1963) 7.
17) Behrisch, R., Ergeb. exakt. Naturwiss. **35**, Springer (Berlin, 1964) p. 325.
18) Fuls, E. N., Jones, P. R., Ziemba, F. P. and Everhart, E., Phys. Rev. **107** (1957) 704.
19) Onderdelinden, D., thesis, Leiden, 1968, p. 32.
20) Fagot, B., Colombie, N. and Fert, Ch., Proc. Conf. Application of Ion Beams to Semiconductor Technology, Grenoble, 1967, editions Ophrys, p. 401.
21) Lindhard, J., Nielsen, V. and Scharff, M., Mat. Fys. Medd. Dan. Vid. Selsk. **36** (1968) 1.
22) Gadzuk, J. W., Surface Science **6** (1967) 133; 159.
23) Slater, J. C., Quantum Theory of Atomic Structure, Vol. I, McGraw-Hill, 1960.
24) Kaminski, M., Struktur und Eigenschaften der Materie **25**, Springer (Berlin, 1965).