Low Energy Electron Stimulated Emission of Neutral Particles from (100) Surfaces of KCl

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An investigation of emission of neutral particles, especially K and Cl_2 by irradiation of KCl (100) surfaces with low energy electrons. The dependence of emission rates on beam current, beam energy, and sample temperature is discussed on the basis of the Pooley model extended by Townsend et al. The rise of emission rates for electron energies above ≈ 190 eV indicates the opening of an additional emission channel, which may involve the 2p-level of Cl. Furthermore, the observed electron stimulated formation of COK shows the availability of elementary K on the electron irradiated KCl surface.

1. Introduction

Sputtering of atoms, ions, and molecules from surfaces of solids by electrons with energies of more than 300 eV is well known [1] – [8]. Optical, mechanical, and electrical properties of solids are also changed under electron bombardment [9]. Surface defects created in this way are of interest for epitaxial growth [10], [11] and for hetero nucleation on alkali halides [12] – [14]. Up till now little attention has been paid to the influence of low energy (< 300 eV) electrons, and surface investigation methods with low energy electrons (e.g. LEED, LEELS, ESCA) are often considered to be non-destructive. Observations of LEED patterns of alkali halides [15], [16] show signs of surface deterioration (e.g. LEED patterns of KCl with 100 eV electrons: measureable change of reflex-intensity relations after one minute, Kikuchi patterns disappear after two hours, and after twenty hours of irradiation the LEED spots are no longer detectable).

These extensive destruction processes in the solid may be accompanied by the ejection of particles of the solid and of surface adsorbates. Here we report the results of our measurements on electron stimulated emission of neutral particles from (100) surfaces of KCl with electron energies from 70 eV to 230 eV. Since the transfer of kinetic energy in elastic collisions between electrons and atoms is negligible (some meV for 100 eV electrons), the primary process of surface damage must be an excitation of the electronic system of the solid. Therefore some theoretical aspects of this excitation process are discribed in the next section.

2. The Pooley Model for Surface Dissociation

Production of colour centres is generally recognized as the pre-stage of electron stimulated dissociation of alkali halide surfaces. Formation of colour centres can be explained by ionization [1], [17] – [20] or, according to Pooley [21], by generation of excitons. According to Elliott et al. [4] the ionization models seem to be unsuitable for surface dissociation by electrons with very low energies and are not discussed here.

The model of Pooley [21] was extended by Townsend et al. [3], [4], [22] and refined by others [7], [23] – [26]. The principal idea is the excitation of a Cl^- ion to a bound state of Cl^- and an exciton (electron-hole pair). This state decays with a lifetime of approx. 10^{-12} s and finally forms a neutral Cl atom, which may have enough energy to combine with an adjacent Cl^- to an excited Cl_2^- molecule and a surplus electron [5] – [7]. The single steps are:

i) $Cl^- + e^-\,(\text{fast})$
$\Rightarrow\ (Cl^- + (e^- + h^+)) + e^-\,(\text{slow})\,,$

ii) $(CL^- + (e^- + h^+)) + Cl^-$
$\Rightarrow\ (Cl^- + Cl) + e^- \ \Rightarrow\ Cl_2^-{}^* + e^-\,.$

The last stage is an excited V_K centre coupled with an electron. After a lifetime of approx. 10^{-8} s the system decays by photon emission or by non-

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radiative separation in a vacancy (F-centre) and an interstitial (H-centre). In the last case the CL$_2^{-*}$ dissociates in Cl$^-$ and Cl with surplus kinetic energy. Collision of the Cl with neighbouring Cl$^-$ in ⟨110⟩ direction starts a sequence of focussing collisions with charge transfer. If such a collision is started just below the surface, the emission of a hyperthermic Cl atom or Cl$_2$ molecule is possible. This model has the following consequences, which can be detected by experiment:

1) Anticorrelation between the intensity of luminescence and the rate of defect formation under electron irradiation with changing temperature of the crystal [3], [4], [21].
2) Since the primary step is a one electron excitation, the rate of surface dissociation is proportional to the electron beam current.
3) As the emission of halogen is preferred, elementary alkali metal remains at the surface.
4) Emission of halogen should be enhanced in ⟨100⟩ direction [3].
5) The model is applicable only to materials which can form suitable X$_2^-$ molecules.
6) Focussing collisions in alkali halides of NaCl structure are possible only if $s/d \geqq 1/3$ (s = free distance between neighbouring halogen ions and d = diameter of the neutral halogen atom.) [5], [6]. This condition is satisfied by KCl.

3. Experimental Conditions

The experiments were performed in a standard stainless steel UHV system bakable up to 300 °C. The background pressure was always below 10^{-9} mbar. The KCl crystal was mounted in a sample holder, which could be heated up to 600 K. Clean (100) surfaces were prepared by cleaving in situ and then brought into the centre of a LEED system. The electron gun of this system was also used to stimulate the desorption processes. But in this case the crystal had a position 45 mm away from the centre and the electron beam hit the surface at an angle of incidence of 27°. The particles emitted from the surface were detected by a quadrupole mass spectrometer (QMS) An electric field between sample and ion formation space of the QMS prevented positive and negative charged particles from reaching the QMS. Thus all particles detected were neutral ones. The ion formation space of the QMS had a distance of about 40 mm from the sample and accepted particles emitted in a solid angle of 0.03 sterad. The mean emission direction of the particles detected by the QMS had an angle of inclination of 58° to the normal of the sample surface (Figure 1). The QMS was equipped with a channeltron as ion detector and a pulse counting system.

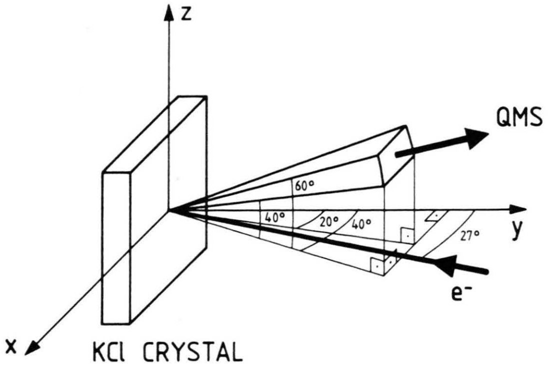

Fig. 1. Geometry of stimulation and particle detection (XZ-plane = (100) surface).

The counting rates of the different species of particles were investigated in dependence of electron beam current, electron energy, and crystal temperature as the most significant parameters of surface dissociation. The electron beam current was measured as the current drawn by the sample holder. With respect to the secondary electron emission of the KCl surface the sample holder was biased to +30 V with respect to ground (at this voltage saturation current was reached). Sample currents up to 10^{-5} A with a beam diameter of approx. 0.5 mm were applied. During the control measurements without electron stimulation the beam was cut off in the gun without interruption of the filament current. In this way change of background particle densities was avoided.

4. Experimental Results

4.1. *Neutral species emitted by electron stimulation*

All particles were detected by comparison of mass spectra measured with and without stimulating the KCl surface by the electron beam. As pointed out above these particles had left the sample surface as neutrals. The following description refers to a sample temperature of 600 K.

The background pressure ($< 10^{-9}$ mbar) was determined by H and H_2. Their signal was independent of electron stimulation. Other background species with a change of intensity lower than 10% at electron stimulation (electron beam current $2 \cdot 10^{-6}$ A/electron energy 230 eV) were ^{12}C, ^{14}N, $^{15}CH_3$, ^{16}O, ^{17}OH, $^{18}H_2O$, $^{26}C_2H_2$, $^{27}C_2H_3$, ^{28}CO/$^{28}N_2$, $^{30}C_2H_6$, and $^{32}O_2$, which are well known components of residual spectra. An electron beam of $8 \cdot 10^{-6}$ A caused an increased intensity of C, O, and CO only. These electron stimulated dissociation and desorption processes of residual gas molecules are not discussed here further. Detailed investigations of these problems were published by Higginbotham et al. [27].

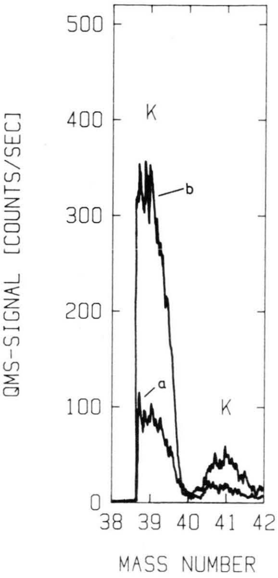

Fig. 2. Mass spectra ($M = 38 \ldots 42$) without (a) and with (b) electron stimulation. Crystal temperature: 600 K. a) Background signal; b) Signal with electron stimulation energy: 230 eV; current: $2 \cdot 10^{-6}$ A.

There were high peaks of ^{35}Cl and ^{37}Cl present, but it was not possible to separate the electron induced part from the statistical fluctuation of the background signal. Definitely electron stimulated was the emission of ^{39}K and ^{41}K (Fig. 2) with a much lower background of these species, which was, as in the case of Cl, also present, when the sample was retracted out of the range of acceptance of the QMS *.

In the range of mass numbers 56 to 76 no signal could be observed without electron stimulation. As shown in Fig. 3 electron stimulated emission of $^{70}Cl_2$, $^{72}Cl_2$, and $^{74}Cl_2$ was found with a ratio 9 : 6 : 1 corresponding to the natural ratio 3 : 1 of the isotopes ^{35}Cl and ^{37}Cl. The peaks at mass numbers 56 and 67 are attributed to ^{56}KOH and ^{67}COK. The corresponding species formed with ^{41}K have too low an intensity to be detected or are masked by the

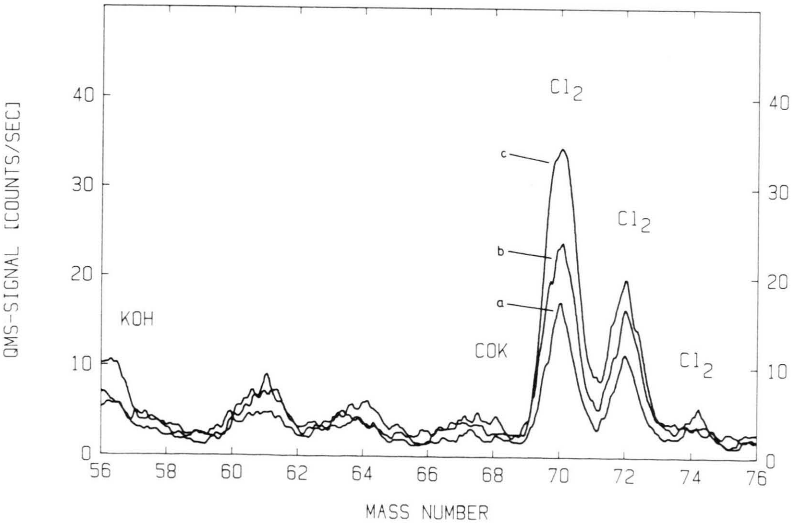

Fig. 3. Mass spectra ($M = 56 \ldots 76$) of KCl surface stimulated with different electron currents. Electron energy: 230 eV; crystal temperature: 600 K; electron current: a) $2 \cdot 10^{-6}$ A; b) $4 \cdot 10^{-6}$ A; c) $6 \cdot 10^{-6}$ A.

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* The background signal of Cl and K are probably caused by contamination of the LEED system in the course of previous investigations with KCl.

leading edge of the large $^{70}Cl_2$ peak. While the small peaks at mass numbers 61 and 64 are not identified, the peak at 68 may be attributed to $^{68}CFCl$ (a fragment of the $CFCl_2-CF_2Cl$ used for cleaning the vacuum system). It was not possible to decide whether these small peaks are dependent on electron current or not.

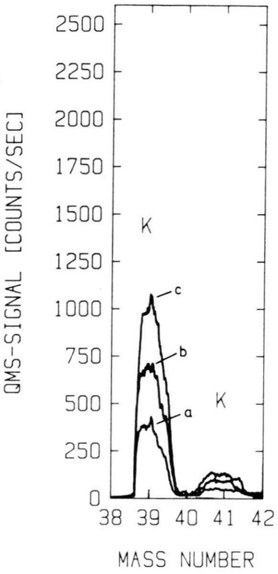

Fig. 4. Mass spectra ($M = 38 \ldots 42$) of KCl surface stimulated with different electron currents. Electron energy: 230 eV; crystal temperature: 600 K; electron current: a) $2 \cdot 10^{-6}$ A; b) $4 \cdot 10^{-6}$ A; c) $6 \cdot 10^{-6}$ A.

4.2. *Dependence of particle emission on current and temperature*

In Fig. 4 the QMS signal of potassium is shown for different electron currents up to $6 \cdot 10^{-6}$ A at an energy of 230 eV and a sample temperature of 600 K. A clear linear relation between electron current and particle emission rate was found for K atoms (Fig. 5) and Cl_2 molecules (Fig. 6) within an error ange of 5%. Also the emission of ^{67}COK had a considerable part, which is direct proportional to the stimulating electron current. The linear dependence of the particle emission rates on the electron current was also confirmed for lower electron energies as long as these rates were sufficient for reliable measurements.

A reduction of the sample temperature from 600 K to 300 K reduced the electron stimulated particle emission considerably. For a beam current of $8 \cdot 10^{-6}$ A at 230 eV the factor of reduction was (0.022 ± 0.005) for ^{39}K and (0.05 ± 0.03) for $^{70}Cl_2$. At 300 K only for ^{39}K the current dependence could be measured. But because of very low counting rates linearity could not be verified definitely.

4.3. *Energy dependence of particle emission*

The dependence of the emission of K atoms and Cl_2 molecules on the energy of the stimulating electrons was studied in the range up to 230 eV with a beam current of $4 \cdot 10^{-6}$ A and a sample tem-

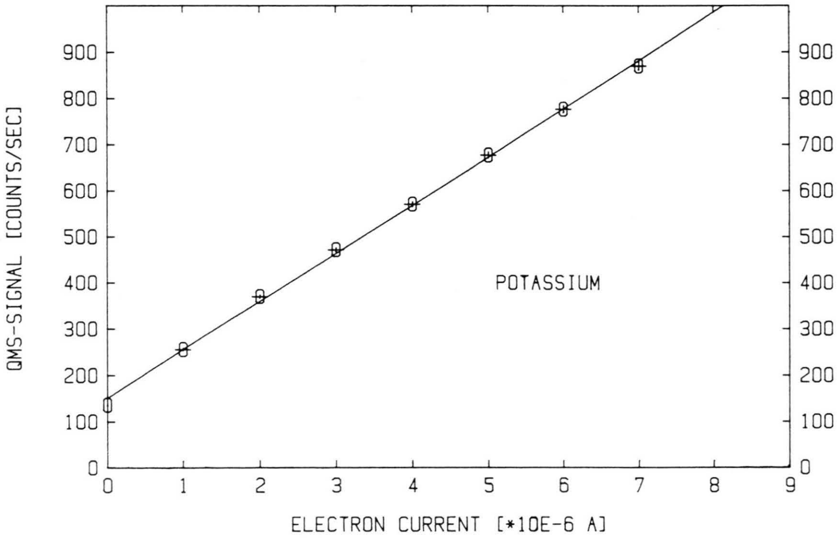

Fig. 5. QMS signal for ^{39}K vs. stimulating electron current. Electron energy: 230 eV; crystal temperature: 600 K.

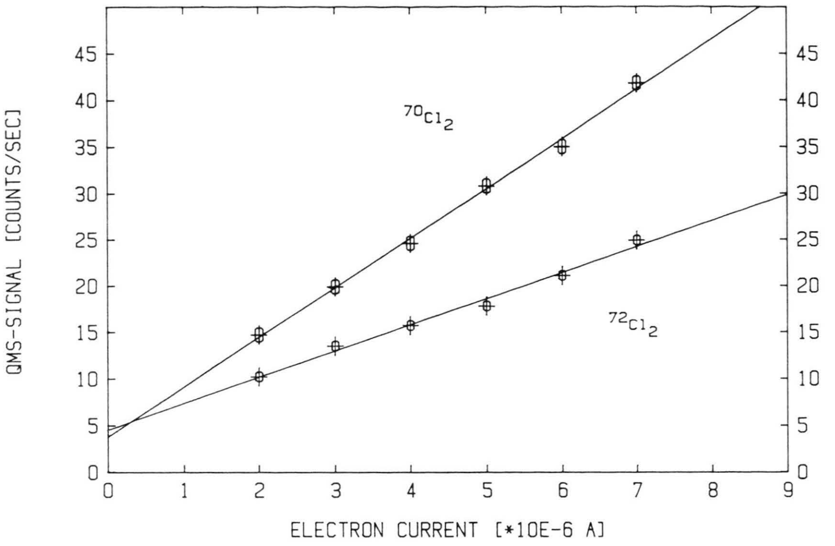

Fig. 6. QMS signals for $^{70}Cl_2$ and $^{72}Cl_2$ vs. stimulating electron current. Electron energy: 230 eV; crystal temperature: 600 K.

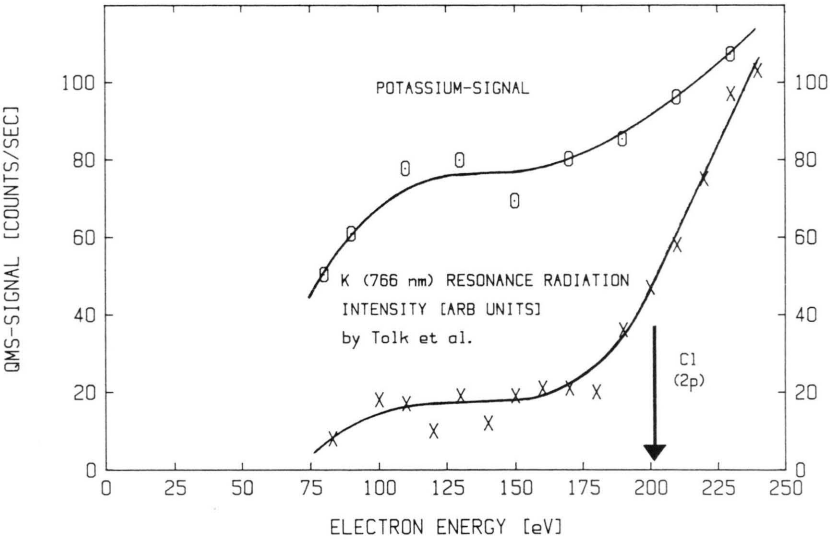

Fig. 7. QMS signal for ^{39}K vs. electron energy (background subtracted and reduced to $1 \cdot 10^{-6}$ A electron current). Intensity (arb. units) of K resonance radiation emitted at electron stimulation of KCl (after Tolk et al. [28]) and position of the 2p-level of Cl are shown for comparison. Crystal temperature: 600 K.

perature of 600 K. The results for K given in Fig. 7 show increasing emission rates with rising energy interrupted by a plateau from approx. 110 eV to 190 eV. For Cl_2 we found a similar result (Fig. 8) with a plateau of less extension (130 eV to 170 eV). Reduction of beam current to $2 \cdot 10^{-6}$ A did not change the shape of energy dependence of the emission rates.

5. Discussion

The preceding experiments have shown that irradiation of KCl-(100) surfaces with low energy electrons stimulates the emission of neutral particles especially at elevated temperature. For the investigated species K and Cl_2 the linear dependence of emission rates on electron current confirms that a one electron process initiates the emission. The large reduction (factor approx. 0.03) of the rates on lowering the sample temperature from 600 K to 300 K is in accordance with the observation of Townsend et al. [3] that with NaCl the electron stimulated desorption rate was diminished by a factor of 0.1 when the temperature was lowered from 500 K to 300 K, and confirms the Pooley model (cf. Section 2). In this model the emission of

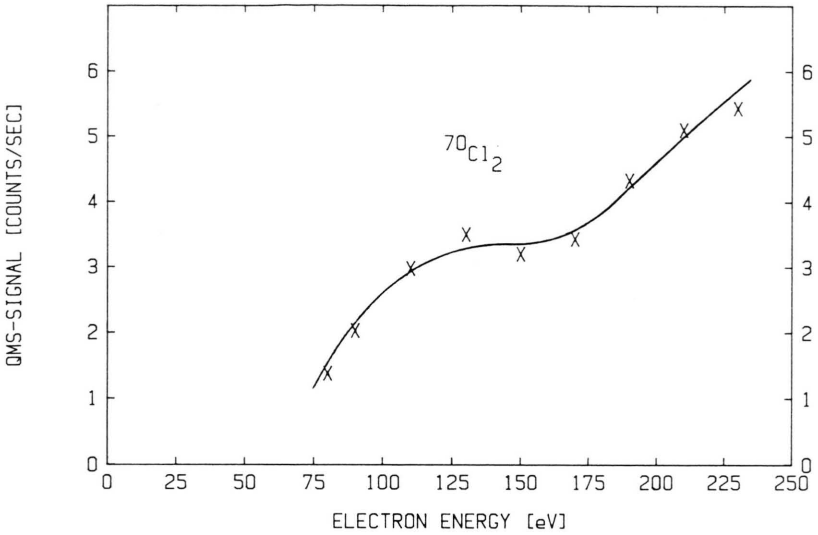

Fig. 8. QMS signal for $^{70}Cl_2$ vs. electron energy (background subtracted and reduced to $1 \cdot 10^{-6}$ A electron current). Crystal temperature: 600 K.

K is assumed to be a secondary process of thermal evaporation of the surplus potassium, which remains on the KCl surface after emission of the halogen.

The energy dependence of the emission rates of K and Cl_2 is nearly the same. The appearance potential is lower than 70 eV, and above 110 to 130 eV the emission rates are approximately constant up to 170 to 190 eV. The following further rise indicates the opening of a new channel for the emission process. This observation is in good agreement with measurements of Tolk et al. [28] (cf. Figure 7). They investigated the emission of excited K atoms stimulated by irradiation of KCl surfaces with low energy electrons and found an analog sharp rise of the rates at 180 eV. A relation to the excitation of the 2p-level of Cl at 201 eV was proposed. It should be remarked that the observation of excited K atoms in a one electron process is not compatible with a mere thermal evaporation of surplus potassium.

Although KCl evaporates as KCl molecules, in our measurements no significant electron stimulated emission of KCl could be found. According to Berkowitz et al. [29] the ionization of KCl molecules in the QMS ion source should yield 17% of the positive ions as KCl^+. The natural ratio of isotopes gives KCl molecules with mass numbers 74, 76, and 78 in the ratio 0.70:0.28:0.02. In our experiments the QMS signal at mass number 74 is completely explained as $^{74}Cl_2$ and no signals were found at mass numbers 76 and 78.

As last point of interest the detection of ^{67}COK in the electron stimulated desorption processes should be discussed. At 600 K we found a linear relation with the electron beam current. It is known that $(COK)_6$ is formed at temperatures above 350 K only in the presence of elementary potassium [30]. We assume adsorbed background CO to react with the surplus K on the sample surface to COK, which then desorbes before polymerisation to $(COK)_6$. The linear dependence of the emission rate indicates a surface concentration of the elementary potassium proportional to the electron beam current.

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