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To cite this article: Shigeo Arai and Shuichi Abe 1978 *Jpn. J. Appl. Phys.* **17** 238

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Energy Losses of Electrons and X-Ray K-Absorption in KCl and KBr

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The energy losses of 20 keV electrons in KCl and KBr foils have been measured with the energy resolution of 0.4 eV. The energy loss spectrum of each material shows about 20 peaks in the energy range from 4 eV to 35 eV. These peaks correspond to the K-absorption maxima of potassium ions. The energy loss values for the peaks in KBr (excepting four peaks), if multiplied by $(6.59/6.28)^2$, are in good agreement with the energy loss values in KCl, where 6.59 and 6.28 are the lattice constants in Å of KCl and KBr crystals, respectively. From these facts, the quasi-stationary-state (qss) theory for K-absorption is likely to apply to the energy loss spectra. The energy loss values calculated by the qss theory are in good agreement with the observed values, and the existence of the four peaks in KBr is also explained reasonably.

§1. Introduction

The energy losses of electrons in alkali-halides have been studied by many authors, and the interpretation for the losses was tried by assuming the excitation of component atoms or ions, plasmon excitation and interband transition. Marton¹⁾ compared the loss peaks in KCl and KBr with K-absorption maxima, and expected dependency of the energy loss values upon the inverse square of the lattice constant by considering Hayasi's quasi-stationary-state theory²⁾ (qss theory) for K-absorption. But the dependency was confirmed only partly.

We have studied the energy losses in alkali-halides foils without substrates³⁾ in order to observe the energy loss spectra of the alkali-halides only. The energy losses of 20 keV electrons in KCl and KBr foils were measured by an energy analyser⁴⁾ with the energy resolution of 0.4 eV, and about 20 sharp peaks were recognized in each loss spectrum. The loss spectrum above 35 eV was too weak to observe.

The energy loss values for these peaks show good correspondence with K-absorption maxima of K atoms. The values in KBr, if multiplied by $(6.59/6.28)^2$, are in almost exact agreement with the values in KCl, excepting four peaks in KBr. Here 6.59 and 6.28 are the lattice constants in Å of KBr and KCl, respectively. So we applied the qss theory to the calculation of the energy loss values. The values calculated are in good agreement with the values measured,

and the four peaks in KBr, which were not observed in KCl, are also explained reasonably.

§2. Experiment and Results

KCl and KBr foils of thickness ca. 400 Å were prepared in the analyser, and the energy losses of 20 keV electrons passing through resolution of 0.4 eV. The photometer curves of the loss spectra are shown in Fig. 1. About 20 peaks superposed on a broad background band are recognized in each spectrum. The energy loss values for the these peaks are shown at the second and the fifth columns of Table I. E (KCl) means the energy loss values in KCl and E (KBr) those in KBr. Table I shows in its first and second columns the comparison between the energy loss values in KCl and those in KBr multiplied by $(6.59/6.28)^2$.

Excepting four peaks in KBr, almost exact

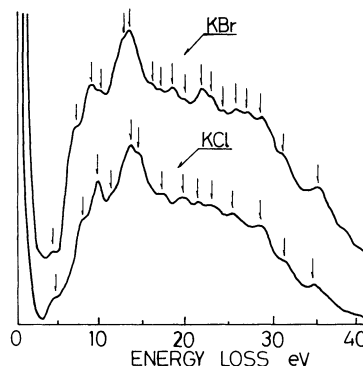


Fig. 1. The microphotometer curves of the loss spectra in KCl and KBr.

Table I. Comparison of the measured energy loss values $E(\text{KCl})$ and $E(\text{KBr})$ with the calculated values E_{calc} , and correspondence of $E(\text{KCl})$ to $E(\text{KBr}) \times S^2$, where $S = 6.59/6.28$.

$E(\text{KBr})$ $\times S^2$	KCl		$(h\ k\ l)$	KBr	
	$E(\text{KCl})$	E_{calc}		$E(\text{KBr})$	E_{calc}
5.0	4.9	4.5	(2 0 0)	4.5	3.9
8.3	8.2	8.2	(2 2 0)	7.5	7.4
10.0	10.0	10.2	(2 0 0)	9.1	9.0
11.3	11.5	12.0	(2 2 2)	10.3	10.8
14.1	13.9	13.9	(2 2 0)	12.7	12.5
14.5	14.6	15.8	(4 0 0)	13.2	14.2
17.4	17.5	17.7	(2 2 2)	15.8	15.9
18.5*			(3 3 1)	16.8	16.8
20.1	20.0	19.6	(4 2 0)	18.3	17.7
21.8	21.6	21.4	(4 0 0)	19.8	19.3
23.5	23.5	23.4	(4 2 2)	21.4	21.1
25.0	25.4	25.3	(4 2 0)	22.7	22.8
26.5*			(3 3 3)	24.1	23.7
28.1	28.6	29.1	(4 2 2)	25.5	26.2
29.3*				26.6 \equiv 13.2 \times 2	
31.4	31.5	31.1	(4 4 0)	28.5	28.0
34*			(5 3 1)	31	30.6
	34.5-M ₁ edge			35-M ₁ edge	

E_{calc} for underlined $(h\ k\ l)$ is given by ΔE_a and eq. (2), and the other E_{calc} by ΔE_c and eq. (2).

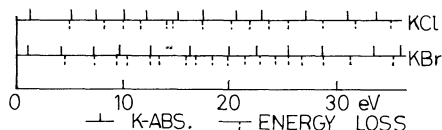


Fig. 2. Correspondence of the energy loss values to the K-absorption maxima.

agreement is seen. The four peaks will be explained later. The energy loss values correspond to K-absorption maxima⁵⁾ of K atoms as shown in Fig. 2.

§3. Discussion

The fact described in §2 may suggest that the energy loss values have a strong dependency on the crystal structure and that the qss theory may be valid there. The energy E_q of qss is given approximately by

$$E_q \approx (150/4A^2)(h^2 + k^2 + l^2) + E_p \quad \text{eV}, \quad (1)$$

where A denotes the lattice constant in Å, (hkl) the reflection indices and E_p the mean inner potential. (hkl) for forbidden reflection must be excluded.

Before the qss theory is applied, the states of electrons to be excited must be searched for.

The outermost electrons of ions K^+ , Cl^- and Br^- and those of neutral atoms K, Cl and Br will be considered as the electron to be excited. However, K^+ , Cl and Br are excepted from the consideration, because they need too much ionization energy. For instance, in order to ionize Cl at the lattice point, the sum of ionization energy 12.96 eV and the Madelung's energy 7.5 eV, namely, about 21 eV is necessary. It lies near the tail of the spectra. So the energy loss peaks for Cl will be weak, because the differential cross section for energy loss is proportional to the inverse square of the momentum transfer of incident electron. K^+ and Br are also the case.

Therefore, the valence electrons of K and Cl^- are predominant in the energy losses in KCl, and the valence electrons of K and Br^- are in KBr. To apply the qss theory, the energy gap between the mean inner potential and the state of these electrons must be known, since the energy E_q in eq. (1) includes the mean inner potential. Rough estimation for the gap will be made in the following.

First the states of the valence electrons of K and Cl^- are discussed. In KCl crystal adjoining atoms K and Cl will be assumed to exist in not negligible content, since K-Cl bond is not 100% but 82% ionic according to Pauling⁶⁾ and the charge-transfer⁷⁾ ($\text{K}^+\text{Cl}^- \rightarrow \text{KCl}$) by electron impact is considered. In order to calculate the energy gap between the mean inner potential and the state of the valence electrons of K, next processes are considered. (1) K atom is removed from the crystal into outer vacuo. (2) The K atom is ionized and K^+ and an electron are produced. (3) The K^+ returns to the former lattice point. (4) The electron enters into the crystal and has the mean inner potential energy.

The energy ΔE_c required to accomplish these processes is the energy gap. ΔE_c is given by $\Delta E_c = I - (\alpha - 1)e^2/r$,⁸⁾ where I means the ionization energy (4.3 eV) of K atom, α the Madelung constant (1.747) for KCl crystal and r (3.14 Å) the distance between the nearest neighbor ions. This calculation is made under the assumption that ions can be regarded as point charges and so the mean inner potential equals zero. Then we have $\Delta E_c = 0.9$ eV.

Under similar consideration, the energy gap between the mean inner potential and the state

of the valence electron of Cl^- is given by $\Delta E_a = E_f + \alpha e^2/r$, where ΔE_a denotes the energy gap and E_f (3.7 eV) electron affinity of Cl. Then we have $\Delta E_a = 11.2$ eV.

The same calculation can be made for K and Br^- in KBr, and the values of the same order are obtained. It will be difficult to calculate exactly the energy gap. Therefore, the optimum values for these gaps were obtained from the experimental results. Since the energy gaps are given and the energy of the qss is given by eq. (1), the energy differences between the qss and the states of the valence electrons of K, Cl^- and Br^- are given by the following equation;

$$E_{\text{calc}} = (150/4A^2)(h^2 + k^2 + l^2) + (\Delta E_c \text{ for K, } \Delta E_a \text{ for } \text{Cl}^- \text{ or } \text{Br}^-) \text{ eV, (2)}$$

where E_{calc} means the energy difference.

Here E_{calc} is the energy loss value itself. So the energy losses are considered to be superposition of the two sorts of the energy losses. The first one is owing to the transition of the valence electron of K atom to the qss, and the second one is owing to the transition of the valence electron of Cl^- or Br^- to the qss. The energy loss value E_{calc} for the former is calculated using ΔE_c and (hkl) , and the energy loss value E_{calc} for the latter is calculated using ΔE_a and (hkl) . Here (hkl) must be allowed indices.

Table I shows the comparison between the energy loss values measured and the energy loss values E_{calc} in KCl and KBr. Good agreement will be seen between them. In KCl, (hkl) must be all even, and $\Delta E_c = 0.6$ eV and $\Delta E_a = 6.3$ eV are assumed. In KBr, (hkl) must be all even or all odd, and $\Delta E_c = 0.5$ eV and $\Delta E_a = 5.6$ eV are assumed. Two energy loss

values 3.1 eV and 8.2 eV are considered for $(hkl) = (111)$. But the energy loss 3.1 eV can not be observed because of the masking due to the strong and broad zero loss line photographed. The energy loss 8.2 eV lies so near the strong peak (7.5 eV), and it may not be resolved from the peak.

Next the four peaks (16.8, 24.1, 26.6 and 31 eV) in KBr will be stated. It will be reasonable that the energy loss values (16.8, 24.1 and 31 eV) for all odd (hkl) in KBr have not corresponding partners in the energy loss values for all even (hkl) in KCl. Energy loss peak 26.6 eV in KBr will correspond to the duplication of the intense loss peak 13.2 eV.

§4. Conclusion

Either of the energy loss spectra in KCl and KBr shows about 20 sharp peaks, and the energy loss values for the peaks have a strong dependency upon the inverse square of the lattice constant. They show correspondence with K-absorption maxima. The energy loss values calculated by the qss theory are numerically in good agreement with the energy loss values measured.

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