THE PHYSICAL ADSORPTION ON SURFACE DISTORTED ALKALI HALIDE CRYSTAL WITH A FREE (100) FACE

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The adsorption heat of the Ar atom adsorbed on the distorted (100) face of KCl is calculated. In numerical computations the summation was carried over 1183 crystal ions while hitherto only several hundred of ions were usually taken into account.

The obtained values for the adatom are in better agreement with experimental data than the previous ones. Thus, taking into account in the summation both the surface distortion and a greater number of crystal ions, are obtained results which approach better the experimental values.

1. Introduction

There are many papers devoted to calculations of the adsorption heat of rare gases adsorbed on the alkali halide crystals *cf.* Young and Crowell [1]. An important paper on this problem is that of Orr [2]. The author has calculated the dispersion energy by means of the Kirkwood-Müller formula (Müller [3]) using for ions the values of constants as given by Huggins and Mayer [4]. The summation was carried over 250 crystal ions. The electrostatical interaction was calculated on the basis of Lennard-Jones and Dent [5] results, and the repulsion energy using the exponential formula given by Huggins and Mayer [4] and by Herzfeld [6]. The results of Orr showed that the adsorption energy depends on the adsorption site. More detailed calculations were carried out by Hayakawa [7]. It was assumed in all papers devoted to the physical adsorption on alkali halide crystals, that the arrangement of the surface ions is the same as in layers situated inside the crystals. It has been recognized, however, for a long time *cf.* Madelung [8], Varvey [9] that the arrangement of ions in the surface layers of a crystal is different from that in the bulk. Calculations of a surface distortion in an alkali halide crystal bounded by a free (100) face were done by Benson, Freeman and Dempsey [10]. In the present paper we shall examine the influence of a surface distortion on the adsorption energy for KCl crystal bounded by a free (100) face. Following Orr and Hayakawa we shall calculate the adsorption energy of Ar on (100) face of KCl, taking also into account 1° the surface distortion, and 2° the interaction with many more crystal ions than in papers by Orr and Hayakawa.

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2. The adsorption energy

According to the papers by Orr [2], Young [11], Hayakawa [7] and Kiselev and Poshkus [12], the interaction energy between an atom and alkali halide crystal may be written as follows

$$W(r) = W_D(r) + W_R(r) + W_E(r) \tag{1}$$

were W_D is the dispersion energy, W_R the repulsive energy, W_E the electrostatic energy, and r is the distance between the atom and the crystal surface.

i) The dispersion energy is

$$W_D(r) = -C_1^{\pm} r^{-6} - C_2^{\pm} r^{-6} - C_3^{\pm} r^{-10} - \ldots, \tag{2}$$

with

$$C_1^{\pm} = -6m c^2 \frac{\alpha_0 \alpha_{\pm}}{\alpha_0/\chi_0 + \alpha_{\pm}/\chi_{\pm}} \tag{3}$$

$$C_2^{\pm} = \frac{45h^2}{32\pi^2 m} \alpha_0 \alpha_{\pm} \left[\frac{1}{2\left(\dfrac{\alpha_{\pm}}{\chi_{\pm}}\Big/\dfrac{\alpha_0}{\chi_0}\right)+1} + \frac{1}{2\left(\dfrac{\alpha_0}{\chi_0}\Big/\dfrac{\alpha_{\pm}}{\chi_{\pm}}\right)+1} \right] \tag{4}$$

$$C_3^{\pm} = -\frac{105\, h^4 \alpha_0 \alpha_{\pm}}{256\pi^4 m^3 c^2} \left[\frac{\alpha_0/\chi_0}{3\left(\dfrac{\alpha_{\pm}}{\chi_{\pm}}\Big/\dfrac{\alpha_0}{\chi_0}\right)+1} + \frac{3/4}{\dfrac{\chi_0}{\alpha_0}+\dfrac{\chi_{\pm}}{\alpha_{\pm}}} + \frac{\alpha_{\pm}/\chi_{\pm}}{3\left(\dfrac{\alpha_0}{\chi_0}\Big/\dfrac{\alpha_{\pm}}{\chi_{\pm}}\right)+1} \right] \tag{5}$$
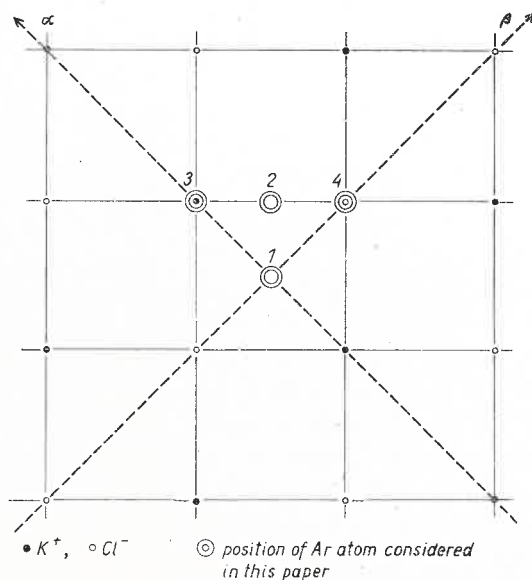

$\bullet\, K^+, \quad \circ\, Cl^- \qquad \circledcirc\ $ position of Ar atom considered in this paper

Fig. 1. (100) surface of KCl crystal

where α_0 is the polarizability of an adatom, χ_0 is the magnetic susceptibility and $\alpha_{\pm}$, $\chi_{\pm}$ are the polarizabilities and magnetic susceptibilities of crystal ions, respectively.

ii) The repulsion energy has the form

$$W_R(r) = C_4^{\pm} e^{-r/r_0} \tag{6}$$

where $C_4^{\pm}$ and r_0 are constants characterizing the adatom and crystal ions.

iii) The electrostatic energy can be written as

$$W_E(r) = -\tfrac{1}{2}\alpha F^2(r) \tag{7}$$

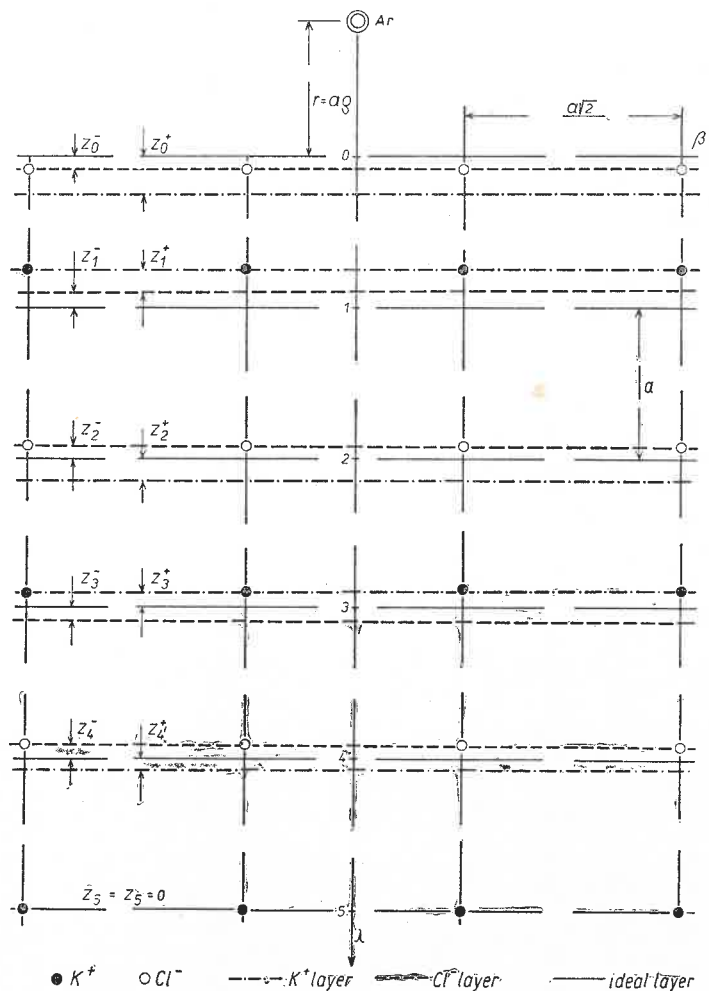where $F(r)$ is the electrostatic field caused by the crystal ions at the point where an adatom is situated.

Fig. 2. Section of a crystal by the plane perpendicular to the surface (100) and including the axis β (see Fig.1) Displacements of ions in the vicinity of a surface are marked

We shall calculate the interaction energy of an atom being present on four lines perpendicular to the (100) face of KCl. One of this line crosses the point 1 situated in the centre of a square formed by two K^+ ions and two Cl^- ions (Fig. 1). The third and fourth lines cross the point 2 situated between two neighbouring ions K^+ and Cl^-, the surface ion K^+ and the surface ion Cl^-, respectively. The surface distortion was introduced to the considered crystal (cf. Fig. 2) according to Benson *et al.* (1963). Denote the distance between nearest neighbours in the latice by "a"; the distortion in each layer is then, described by az_λ^+ and az_λ^-, where $\lambda = 0, 1, 2, ...,$ are numbers of the succesive layers formed by positive and negative ions, respectively. If in the orthogonal Cartesian system (α, β, λ) the position of an atom is given by $(a\sqrt{2}x, a\sqrt{2}y, -a\varrho)$, where $(\varrho = r/a)$ then distances from the Ar atom to crystal ions are the following:

K^+ in the layer with $\lambda = 0, 2, 4, ..., 2n;$

$$r_{\lambda=2n}^+ = a[2(\alpha+\tfrac{1}{2}-x)^2+2(\beta-y)^2+(\lambda+\varrho-Z_\lambda^+)^2]^{\frac{1}{2}}.$$

K^+ in the layer with $\lambda = 1, 3, 5, ..., 2n+1;$

$$r_{\lambda=2n+1}^+ = a[2(\alpha-x)^2+2(\beta+\tfrac{1}{2}-y)^2+(\lambda+\varrho-Z_\lambda^+)^2]^{\frac{1}{2}}.$$

Cl^- in the layer with $\lambda = 0, 2, 4, ..., 2n;$

$$r_{\lambda=2n}^- = a[2(\alpha-x)^2+2(\beta+\tfrac{1}{2}-'y)^2+(\lambda+\varrho-Z_\lambda^-)^2]^{\frac{1}{2}}. \tag{8}$$

Cl^- in the layer with $\lambda = 1, 3, 5, ..., 2n+1;$

$$r_{\lambda=2n+1}^- = a[2(\alpha+\tfrac{1}{2}-x)^2+2(\beta-y)^2+(\lambda+\varrho-Z^-)^2]^{\frac{1}{2}}.$$

Using relations (2–8) we may write $W_D(\varrho)$, $W_R(\varrho)$ and $W_E(\varrho)$ in the following form:

$$W_D(\varrho) = C_1^+ S_1^+ + C_1^- S_1^- + C_2^+ S_2^+ + C_2^- S_2^- + C_3^+ S_3^+ + C_3^- S_3^- \tag{9}$$

$$W_R(\varrho) = C_4^+ S_4^+ + C_4^- S_4^- \tag{10}$$

$$W_E(\varrho) = C_5(S_5^+ - S_5^-)^2 \tag{11}$$

where

$$S_1^+(x, y, \varrho) = \sum_{\alpha,\beta} \{\sum_{\lambda=2n} (r_{2n}^+)^{-6} + \sum_{\lambda=2n+1} (r_{2n+1}^+)^{-6}\},$$

$$S_1^-(x, y, \varrho) = \sum_{\alpha,\beta} \{\sum_{\lambda=2n} (r_{2n}^-)^{-6} + \sum_{\lambda=2n+1} (r_{2n+1}^-)^{-6}\},$$

$$S_2^+(x, y, \varrho) = \sum_{\alpha,\beta} \{\sum_{\lambda=2n} (r_{2n}^+)^{-8} + \sum_{\lambda=2n+1} (r_{2n+1}^+)^{-8}\},$$

$$S_2^-(x, y, \varrho), = \sum_{\alpha,\beta} \{\sum_{\lambda=2n} (r_{2n}^-)^{-8} + \sum_{\lambda=2n+1} (r_{2n+1}^-)^{-8}\},$$

$$S_3^+(x, y, \varrho) = \sum_{\alpha,\beta} \{\sum_{\lambda=2n} (r_{2n}^+)^{-10} + \sum_{\lambda=2n+1} (r_{2n-1}^+)^{-10}\},$$

$$S_3^-(x, y, \varrho) = \sum_{\alpha,\beta} \{\sum_{\lambda=2n} (r_{2n}^-)^{-10} + \sum_{\lambda=2n+1} (r_{2n+1}^-)^{-10}\},$$

$$S_4^+(x, y, \varrho) = \sum_{\alpha,\beta} \{ \sum_{\lambda=2n} \exp{(-r_{2n}^+/r_0)} + \sum_{\lambda=2n+1} \exp{(-r_{2n+1}^+/r_0)} \},$$

$$S_4^-(x, y, \varrho) = \sum_{\alpha,\beta} \{ \sum_{\lambda=2n} \exp{(-r_{2n}^+/r_0)} + \sum_{\lambda=2n+1} \exp{(-r_{2n+1}^-/r_0)} \}, \qquad (12)$$

$$S_5^+(x, y, \varrho) = \sum_{\alpha,\beta} \left\{ \sum_{\lambda=2n} \frac{\lambda+\varrho-z_n^+}{(r_{2n}^+)^3} + \sum_{\lambda=2n+1} \frac{\lambda+\varrho-z_\lambda^+}{(r_{2n+1}^+)^3} \right\},$$

$$S_5^-(x, y, \varrho) = \sum_{\alpha,\beta} \left\{ \sum_{\lambda=2n} \frac{\lambda+\varrho-z_\lambda^-}{(r_{2n}^-)^3} + \sum_{\lambda=2n+1} \frac{\lambda+\varrho-z_\lambda^-}{(r_{2n+1}^+)^3} \right\},$$

with $r_0^{-1} = 9{,}1$ Å^{-1}, α, $\beta = 0$, ± 1, ± 2, ..., $\lambda = 0, 1, 2, ...$ and $C_5 = -\frac{1}{2}\alpha_0 e^2$.

Using for the constans $C_j^i (i = \pm, j = 1, 2, ..., 5)$ the same values as those given by Orr and Hayakawa the interaction energy $W(\varrho, x, y)$ was computed numerically on the ODRA 1004 computer at the Institute of Numerical Methods of Wrocław University for each of four positions marked on Fig. 1. Summations were carried over 1183 crystal ions. Values of $Z_\lambda^+ = Z_\lambda^- = 0$ and Z_λ^+ and Z_λ^- were taken from the paper of Benson *et al.* 1963 (see Table I).

TABLE I

Displacements in "a" units

	Z_λ^+	Z_λ^-
0	-0.03347	-0.00469
1	0.01863	0.00071
2	-0.00586	0.00199
3	0.00319	-0.00026
4	-0.00076	0.00049

for $\lambda \geqslant 5$, $\quad Z_\lambda^+ = Z_\lambda^- = 0$

3. Results and discussion

The obtained results are given in Figs 3–7. Plots of the interaction energy *versus* a relative distance between Ar atom and the (100) face of KCl are shown in Figs 3–6. A comparison of the curves with those obtained by Orr, leads to the following conclusions; 1° the influence of the surface distortion on the adsorption energy is small, 2° the observed differences between our and Orr's results are, therefore, caused mainly by the fact that the summation in present paper was carried over a greater number of ions than that in Orr's paper. One should note also, that for every case considered in this paper, greater values of the adsorption heat and smaller values of the equilibrium distance r_0 were obtained in comparison to the corresponding results of Orr. This is a result of taking into account a greater number of ions and also the influence of the surface distortion.
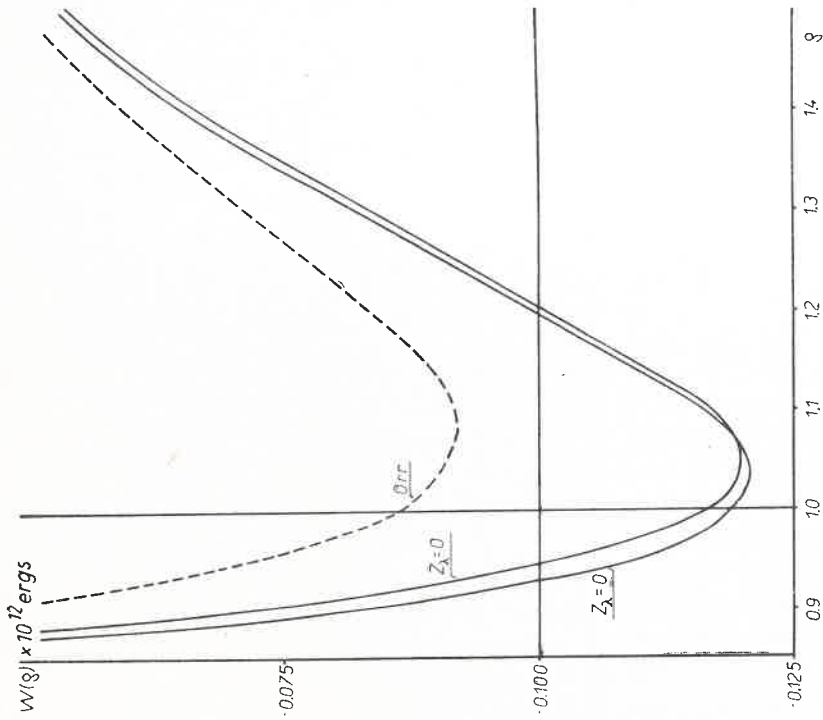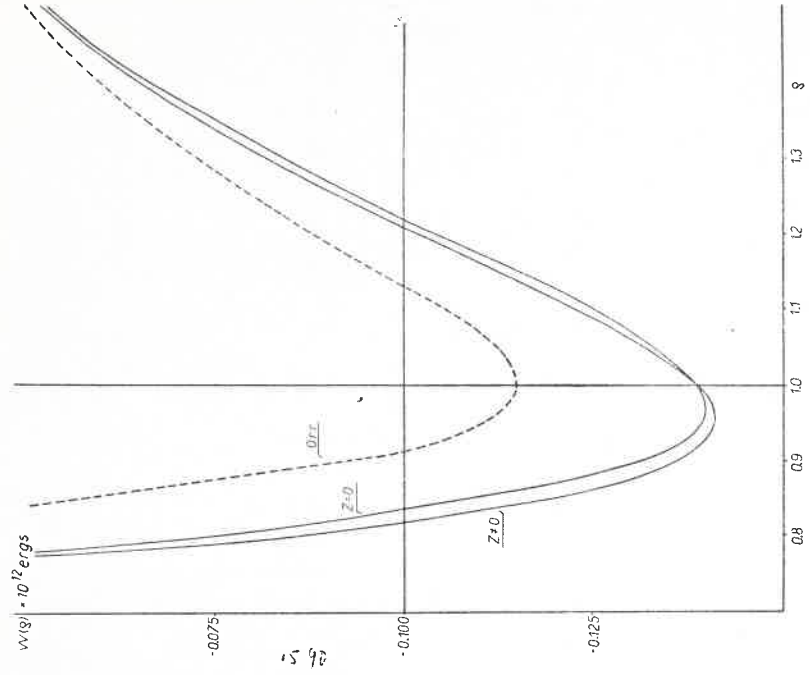
Fig. 3. Potential energy distance curves for an Argon atom situated over the centre of a KCl lattice cell. W_{min} $(z \neq 0) = 0.1413 \cdot 10^{-12}$ ergs
Fig. 4. Potential energy distance curves for an Argon atom situated over the mid-point of a lattice edge. W_{min} $(z \neq 0) = 0.1212 \cdot 10^{-12}$ ergs
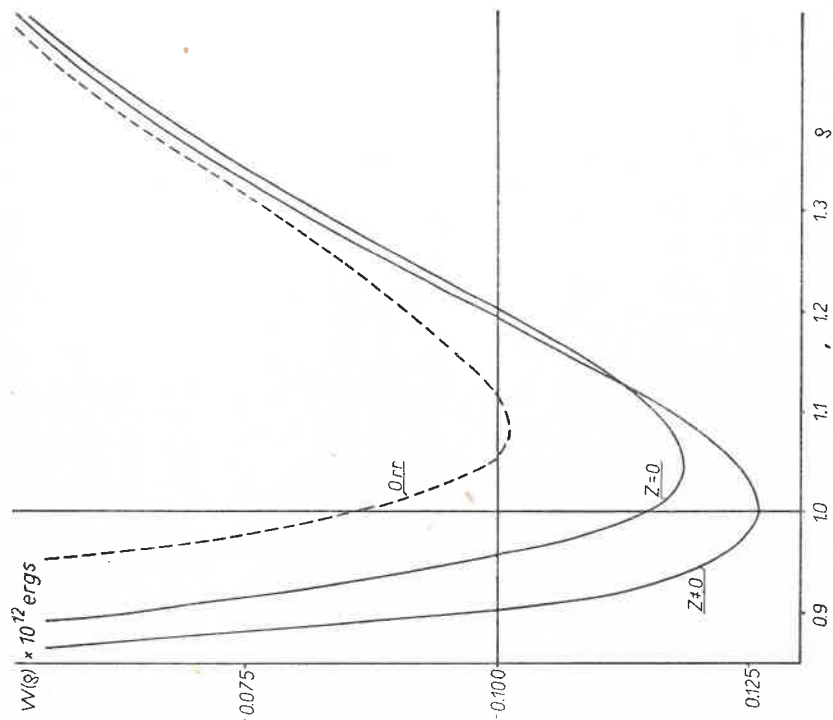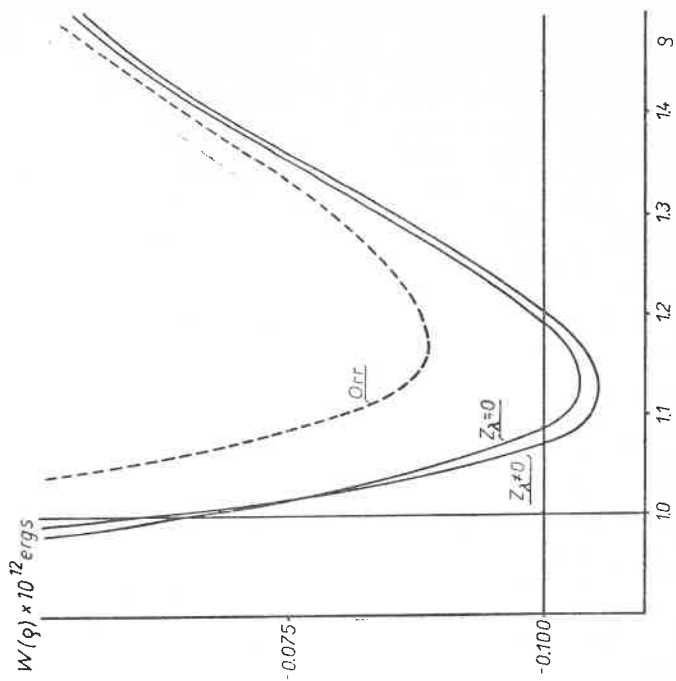
Fig. 5

Fig. 6

Fig. 5. Potential energy distance curves for an Argon atom situated over a K$^+$ ion. $W_{min}(z \neq 0) = 0.1258 \cdot 10^{-12}$ergs.
Fig. 6. Potential energy distance curves for an Argon atom situated over a Cl$^-$ ion. $W_{min}(z \neq 0) = 0.1190 \cdot 10^{-12}$ergs
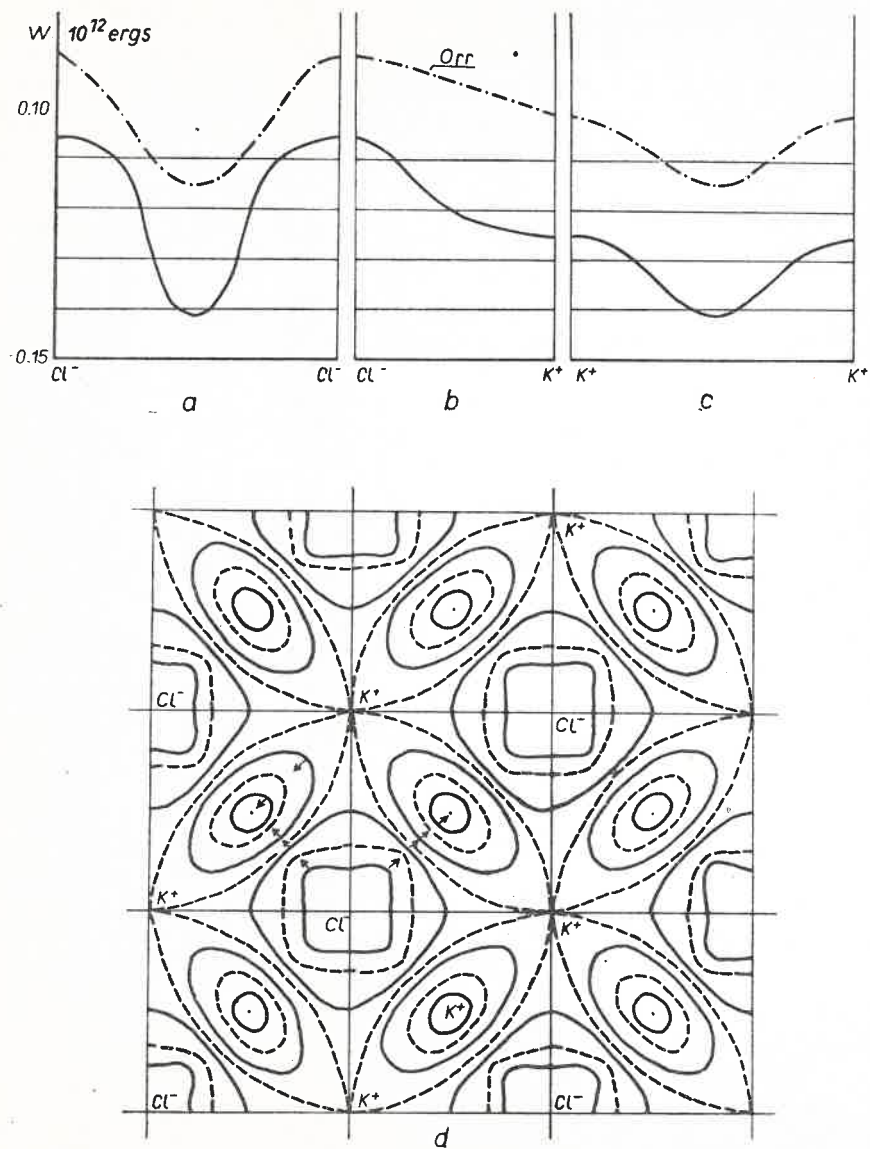
Fig. 7. The curves a, b, c are the cross-sections of the potential surface, involving the calculated points on the basis of these curves. Equipotential lines (d) were constructed giving a "map" of the potential surface for the (100) face of the crystal

TABLE II

Experimental and theoretical values of the adsorption heat (cal/mol) of Ar on (100) face of KCl

Experiment		Theory			
Young	Hayakawa	Orr	Young	Hayakawa	this work
2 100	2 080	1 593	1 800	1 900	1 988

Theoretical values of the adsorption heat calculated in this paper, are in better agreement with experimental data than the results previously obtained (see Table II).

In Fig. 7 a relationship between the adsorption heat and the position of the adatom over the surface of (100) face crystal is presented. Comparing curves in Fig. 7a, b, c one may see that the minima of the curves obtained in this paper are deeper and narrower than those in the paper of Orr, i. e. the adsorption centres are more pronounced.

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