EFFECT OF CONCENTRATION GRADIENT ON THE INTERNAL ELECTROSTATIC POTENTIAL IN SILVER HALIDES

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By

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Abstract

The effect of inhomgeneous distribution of divalent ions on an internal electrostatic potential has been discussed on the basis of Kliewer's theory. The potential profile in case of linear concentration gradient shows several intresting features; a potential varies in accordance with the concentration gradient and, even changes its sign by choosing a proper distribution of impurity. Inhomogeneous surface charges due to the variation of internal potential may be useful for the study of an epitaxial growth on the substrates of ionic solids.

Presentation of the Problems

Since Lehovec[1] proposed the idea on the surface double layers (abbreviated as SDL in what follows) almost concurrently with Frenkel's works[2], detailed theoretical analyses have appeared in several pulibcations in recent years[3,4,5]; an electrostatic-potential difference exists between a surface and the interior of ionic crystal due to an easiness for lattice defects to form at the surface. The potential difference depends on temperatures and purities of a crystal. For example, an interior of a rock salt crystal of normal purity is high in an electrostatic potential relative to the surface at room temperature, an order of magnitude of the potential being a couple of tenths of a static volts. It changes its sign to negative values with increasing temperatures at an isoelectric temperature. Experimental investigations on SDL are relatively scarce. Sonoike and Wakabayashi[6] was the first to initiate the work of this field. Quite recently dielectric relaxation due to SDL has been measured by Fatuzzo and Coppo[7]. Meantime, the Kodak research group[8] have recognized an importance of the presence of SDL in the photographic processes in silver halides.

Experimental works on SDL are difficult to carry out because partly of sensitivity of the surface conditions, partly of an extreme thinness of a thickness of SDL. For example, SDL in NaCl with normal purity is roughly 10^{-5} to 10^{-6} cm thick at room temperature. Main theme of the present work is to discuss SDL in the presence of inhomogeneous distribution of impurity (exclusively a doubly ionized metallic ions) in ionic solids. Plus-minus sign and magnitude of an internal potential ϕ depend on the purity of a sample in a thermal equilibrium, so that ϕ may change its sign according as the concentration gradient varies within a crystal by choosing impurity concentrations properly. Of course the temperature must be such that diffusion of impurity ions is not appreciable.

General Considerations in a simple Case of Impurity Concentrations

An isoelectric temperature T_c at which ϕ vanishes is known to be approximated by the knee point of a conductivity vs. $1/T$ curve, where T stands for an absolute temperature. In other words, knowing the temperature of knee point, one can estimate T_c. Temperature dependence of ϕ as a function of impurity content has been worked out by Kliewer[3]. In silver halides, ϕ is positive in lower temperatures, negative in higher temperatures. The isoelectric temperature shifts towards low temperature region with increasing purity, as seen in Fig. 1 that was duplicated from Kliewer's paper. While at high temperatures potentials converge to the same values regardless of purity, divalent impurity concentration affects a profound influence on the behavior of ϕ.
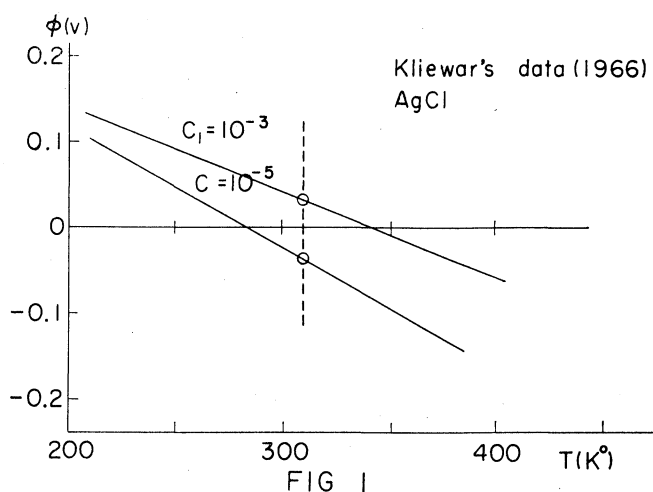
FIG 1

Suppose there exist two adjacent regions with different impurity concentrations, denoted as c_1 and c_2 in silver chloride crystal. Referring to Fig. 1, let c_1 and c_2 be taken 10^{-3} and 10^{-5}, respectively. Potentials for these concentratios are found to be $+0.03V$ and $-0.04V$, correspondingly. That is, an interior of impure region has a higher potential by $0.07V$ compared to that of purer region. Potential drop will take place in a more or less diffuse boundary between the two regions due to interdiffusion of impurity ions across the boundary; it is not possible that two regions exist in close contact as an infinite gradient of impurity is being kept in a considerable duration of time.

Consider a simple concentration gradient in a crystal shown in Fig. 2, in which divalent impurity ions distribute linearly with longitudinal distance in region III separating region I and region II. Region I contains more impurity of concentration c_1 than region II with concentration c_2. Assume that the ratio of c_1 to c_2 be 100 and a silver chloride crystal is kept at room temperature. In this case the potential in region I is positive, that in region II negative with the absolute value of the same order of magnitude as described in the previous paragraph. The validity of the assumption on a linear concentration gradient is understood by the fact that typical divalent impurity ions Cd^{++} diffuse with an activation energy of 10^{-13} cm^2/s through a silver chloride crystal lattice at room
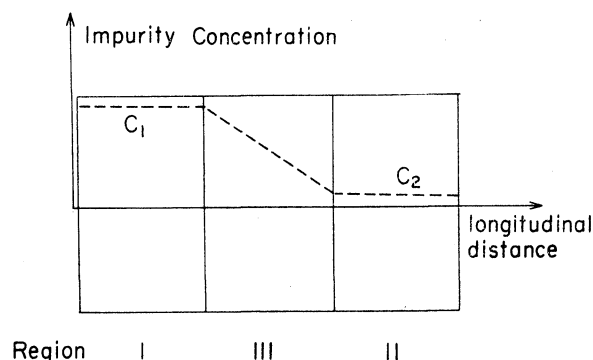
FIG 2

temperature[9]. Cadmium ions will displace by an order of micron in 100 hrs at an ambient temperature. It is not expected that this would affect the impurity concentration profile. Impurity distribution similar to that depicted in Fig. 2 could be obtained experimentally by means of zone refining technique[10], as far as a distribution coefficient of aliovalent impurity is smaller than 1. Ends of each pass would have to be gradually withdrawn. Silver chloride crystals with these distribution must be kept at room temperature long enough for SDL to establish at their surfaces. It is assumed that only one kind of impurity element is present in a crystal for the purpose of simplicity.

Internal Potential Profile for a simple inhomogeneous Distribution of Impurity Ions

Impurity distributions are assumed to be homogeneous throughout region I and II except thin layers just beneath the surfaces where SDL exists. A concentration c_1 in region decreases linearly down to c_2 in region II in crossing the center region III. Taking a AgCl single crystal as an example, c_1 and c_2 are assumed to be 10^{-3} and 10^{-5}, respectively. Notice that an ionic conductivity in region I is extrinsic, that in region II being instrinsic.

Requirements for ϕ to satisfy in region III are as follows: (1) ϕ, $d\phi/dx$, $d^2\phi/dx^2$ are all continuous with no singular points anywhere, here x being a longitudinal distance of a crystal, (2) a charge neutrality must be satified as a whole inside region III, (3) a net charge at any point is proportional to a magnitude of $d^2\phi/dx^2$, a sign of the net charge corresponding to that of $d^2\phi/dx^2$, and lastly (4) ϕ, $d\phi/dx$, $d^2\phi/dx^2$ must be continuous through the boundaries between both I and III, and III and II. The sign of the potential changes from plus to negative and its magnitude will become zero somewhere in region III. Let this point be taken at a midpoint of this region just for the concretion of analysis. The first derivative of ϕ with respect to x must stay negative in region III. It may be acceptable to infer that $-d^2\phi/dx^2$ is positive in the left side, negative in the right side and zero at the center of region III.

Determination of the distribution of lattice defects is possible by taking account of

the behaviors of ϕ, $d\phi/dx$, $d^2\phi/dx^2$. In silver halides, lattice defects now in question are interstitial silvers, silver vacancies and divalent impurity ions, densities of which will be denoted as n_i, n_v and $n.$, respectively. Interrelations among these densities in each region are following;

$$n_i^I + n_.^I = n_v^I , \qquad n_i^I , \quad n_v^I \gg n_.^I$$
$$n_i^I \cong n_v^I \qquad\qquad \text{in region I,}$$
$$n_i^{II} + n_.^{II} = n_v^{II} , \qquad n_.^{II} , \quad n_v^{II} \gg n_i^{II}$$
$$n_.^{II} \cong n_v^{II} \qquad\qquad \text{in region II,}$$
$$n_i^{III} + n_.^{III} = n_v^{III} , \qquad\qquad \text{in region III.}$$

Here a suffix at the upper right corner of each notation of density denotes the region to which the lattice defect belongs.

The potential profiles that meet these requirements are shown in Fig. 3 and Fig. 4. The thickness of SDL here drawn is in quite a exaggerated scale. Principal features of the results are as follows; (1) a potential changes its magnitude and its sign in a macroscopic scale in comparison with the case of surface double layer, (2) a net charge density is zero at a particular point in between region I and region II, (3) there exists an excess positive charge on the left half of region III, an excess negative charge on the right half, (4) the magnitude of $d\phi/dx$ could be changed as the width of region III varies, (5) the concentration of interstitial silver decreases rapidly at a boundary between region III and II, and (6) regardless of its extreme thinness the presence of SDL is essential in our discussion.
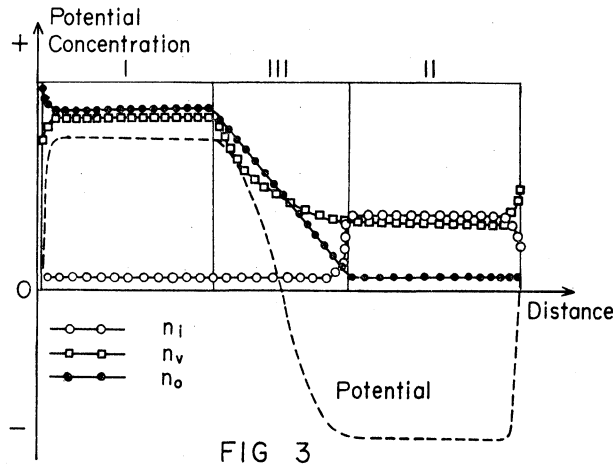

FIG 3

Short Remarks on the Results

The present discussion is of qualitative nature and a more quantitative analysis must be required to know an exact potential profile. Subjects that have been excluded so far are (1) the presence of dislocations, grain boundaries within the bulk of a crystal which might disturb a distribution of lattice defects, (2) a degree of association of divalent impurity ions with silver ion vacancies and (3) a discrepancy of the assumed concentration

transversal
direction
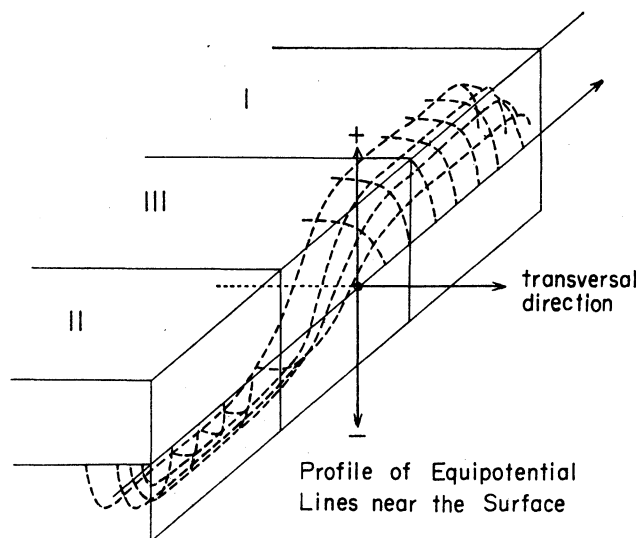
Profile of Equipotential
Lines near the Surface

FIG 4

gradient in a real crystal due to the diffusion and the diversity of the kinds of impurity ions. Nevertheless, general features of the results would not be corrected much.

The significance of the present research must be mentioned briefly. In recent years an epitaxial growth of thin film on a substrate of alkali halide has become an important theme. Sokol[11] studied the effect of external electric fields on the decoration of alkali halide and semiconducting crystals, confirming that surface electric charge have an important influence on the selective nucleation of the condensed phase particle. It is intresting to see if there is any difference in the degree of nucleation between surfaces of region I and region II. In this case, surface charges in either regions are opposite over the same mother-crystal surfaces.

Peferences

(1) K. LEHOVEC, J. Chem. Phys. **21**, 1123 (1953).
(2) J. FRENKEL, Kinetic Theory of Liquids (Oxford University Press, New York, 1946), p. 36.
(3) K. KLIEWER, J. Chem. Phys. Solids **27**, 705 (1966).
(4) R.B. POEPPEL and J.M. BLAKELY, Surface Science **15**, 507 (1969).
(5) I. LISFHITS and YA. E. GEGUZIN, Soviet Physics-Solid State **7**, 44 (1965).
(6) S. SONOIKE and H. WAKABAYASHI, J. Phys. Soc. Japan **14**, 1664 (1959).
(7) E. FATUZZO and S. COPPO, J. Appl. Phys. **43**, 1457 (1972).
(8) F. TRAUTWEILER, Photographic Science and Engineering **12**, 98 (1968).
(9) R.F. READE and D.S. MARTIN, Jr., J. Appl. Phys. **31**, 1965 (1960).
(10) F. MOSER, D.C. BURNHAM and H.H. TIPPINS, J. Appl. Phys. **32**, 48 (1961).
(11) A.A. SOKOL, Soviet Physics-Solid State **13**, 3118 (1972).