Influence of surface charge field on the electron impact fragmentation pattern of KCl molecules in the free surface vaporization of single crystals

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Abstract

A mass-spectrometric method was used to investigate the temperature dependence of the electron impact fragmentation pattern of KCl molecules [ion current ratio $I(K^+)/I(KCl^+)$] vaporizing from a free surface of a potassium chloride single crystal. In the temperature range 766–945 K a very good correlation is observed between the variation in fragmentation pattern with temperature and the pattern of the curve E versus T, where E is the strength of surface charge field. It is concluded that molecules desorbing from an open crystal surface may possess excessive vibrational and rotational energy compared to that characteristic of thermal excitation. (Int J Mass Spectrom 194 (2000) 69–73) © 2000 Elsevier Science B.V.

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1. Introduction

Free surfaces of ionic crystals generate electric fields originating from the surface nonstoichiometry (unbalanced number of positively and negatively charged ions) that is related to energetics of the defect formation processes. These fields cause long-range interaction energy between the crystal and the polar molecules adsorbing on or desorbing from its surface. Such interactions are believed to play an important role in, for example, processes of crystal growth, sublimation and dissolution, film growth, heterogeneous catalysis, etc. [1–3]. On the other hand, the energy shift experienced by the admolecules in the field of surface charge may affect their excitation states, and thus the vigor of surface reactions.

In our recent mass spectrometric studies [4,5] of sublimation kinetics of alkali halides it has been demonstrated that the field of surface charge exerts influence on the vaporization rate of both monomeric and polymeric molecules. We have also found out that the electron impact fragmentation pattern of monomeric molecules, i.e. the ion current ratio $I(M^+)/I(MX^+)$ (M^+ and MX^+ are the fragment and molecular ions, respectively, formed from alkali halide molecules via electron impact) is temperature dependent. However, this effect has not received ample attention. The aim of the present work was to examine it more thoroughly in an attempt to establish a

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correlation, if any, between the electrical surface properties and the salient features of the ionization and fragmentation processes. For this purpose potassium chloride has been chosen. The only criterion for this choice was the fact that reliable values of the Gibbs free energies for the formation of individual cation and anion vacancies, necessary for the calculation of the strength of surface charge field, are well known namely for this compound [6].

2. Experimental

The measurements were carried out with a single focusing magnetic-sector mass spectrometer MI 1201 (200 mm radius of curvature, 90), modified for high temperature studies. A more complete description of the apparatus is given elsewhere [4]. The furnace assembly consisted of a ceramic crystal holder, molybdenum resistance heater, tantalum radiation shielding, calibrated tungsten/tungsten-rhenium thermocouple held tightly between the crystal and the holder, and a movable stainless steel shutter plate. Heating was controlled to provide temperatures that could be maintained at a constant value to within ± 0.5 K. The shuttering of the vaporizing fluxes was used to distinguish ions formed by electron bombardment of neutral species vaporized from the crystal surface from those formed by electron bombardment of residual background gas. The ions produced via electron impact were accelerated in an electrostatic field to an energy of 3 keV, mass analyzed in a variable magnetic field, and collected on the first plate of an electron multiplier. The output from the multiplier was amplified by an electrometer utilizing 100-MΩ resistor and then recorded. The sensitivity of the registration system was as high as 10^{-17} A.

In this work the samples to be vaporized were cleaved from commercial high-purity KCl single crystals (optical lens material; mole fraction of divalent metal impurities is ~1 ppm) into $3 \times 3 \times 8$ mm pieces that were inserted into a ceramic holder. Only (100) cleavage planes were exposed for vaporization. The samples were maintained for several hours at about 450 K under low vacuum (10^{-1} Pa) prior to being heated up to the test temperatures.

3. Results and discussion

The shutterable ion peaks detected in the electron impact ionization mass spectrum of potassium chloride in the temperature range 766–945 K are the isotopes of K^+, KCl^+, and K_2Cl^+ ions. Based on the analysis of the ion appearance energies [7], the apparent sublimation enthalpies [8–10], and the results obtained by the angular distribution technique [11–14], it has been established in previous studies of KCl equilibrium vaporization that the individual mass spectra of the monomers KCl and the dimers K_2Cl_2 do not overlap. In other words, the ions K^+ and KCl^+ originate from monomers, whereas the ions K_2Cl^+ are formed from dimers. In the case of free-surface vaporization, the fraction of dimers in the vaporizing fluxes does not exceed that obtained under equilibrium conditions [4]. Therefore, the current intensities of $^{39}K^+$ and $^{39}K^{35}Cl^+$ ions of the most abundant isotopes were taken readily to calculate the electron impact fragmentation pattern of KCl molecules. The temperature dependence of this pattern, obtained in three successive experimental runs of two cooling and one heating, with an ionizing energy of electrons of 30 V is shown in Fig. 1. Note that prior to measurements the sample was heated up to about 950 K and kept at this temperature for about 20 min. Such a thermal treatment enhanced the evolution of surface morphology and facilitated the outgassing of other parts of furnace assembly. This made it possible to maintain the same level of vacuum during measurements over the entire temperature interval. The time intervals between the two successive readings of $I(K^+)/I(KCl^+)$ in each run were about 10 min. Such fairly prolonged intervals in going from one sample temperature to another were believed to be enough for the equilibration of defect concentrations in the near-surface region.

It is seen in Fig. 1 that in all the runs the current ratio has a similar dependence on temperature, passing reproducibly through a minimum at about 788 K,
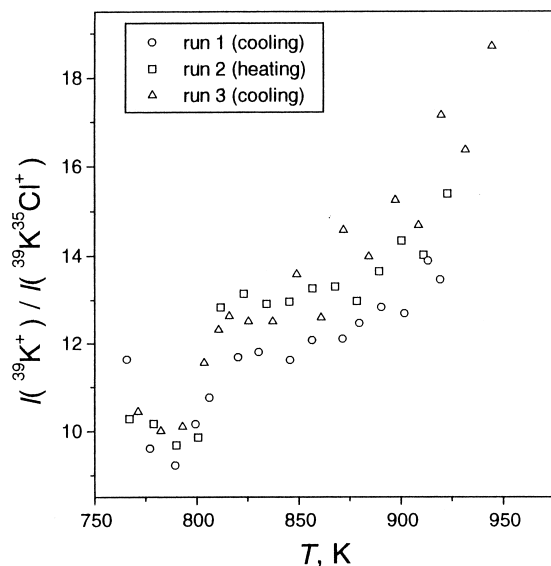
Fig. 1. Temperature dependence of the electron impact fragment-ation pattern of KCl molecules.

although with some hysteresis. We can offer the following explanation of this observation. It is known that the temperature dependence of the electron impact fragmentation pattern is connected with a change in the Franck–Condon factors for ionization. These in turn depend both on the vibrational and rotational excitation states of a molecule to be ionized and the internuclear distances in this molecule and its ion. The interplay of these parameters may yield both increasing and decreasing fraction of the fragment ions in a fragmentation pattern with a change in the temperature. It has been demonstrated theoretically by Dronin and Gorokhov [15] for the case of cesium chloride that with increasing temperature the increase in ion current ratio $I(Cs^+)/I(CsCl^+)$ may result from rotational excitation that is almost completely transferred from a molecule to an ion upon ionization. The decrease in $I(Cs^+)/I(CsCl^+)$ may stem from the anharmonicity factor characteristic of a molecule to be ionized. However, in a narrow temperature interval these opposing tendencies can hardly become evident to yield a sharp minimum exhibited by the fragmentation pattern, even if it is assumed a nearly equal effect of both types of excitation on the fragmentation exists. Therefore, the temperature of the vaporizing

solid alone cannot cause such a specific temperature dependence of the fragmentation pattern, as is observed. In our opinion, the most likely speculation is that the passing of fragmentation pattern through a minimum is indicative of the action of a surface-charge-related factor. The hysteresis mentioned above for the three runs in Fig. 1 corresponds probably to the changes in surface electrical properties due to the continuous surface roughening in the course of prolonged vaporization.

To provide support for the above assumption, the temperature dependence of the fragmentation pattern is to be compared with that of the magnitude of the strength of the surface charge field. To calculate the latter, account should be taken of the following. Application of the surface charge model to alkali halides shows a material-specific dependence on temperature. Because the Gibbs free energy of formation of cation vacancies is less than that of anion vacancies (at least in the KCl case this fact is firmly established [6]), the surface has an intrinsic positive charge owing to the preferential formation of cation vacancies there. However, the presence of divalent cationic impurities in alkali halide crystals of nominal purity leads to the occurrence of a negative extrinsic surface charge at sufficiently low temperatures when the concentration of extrinsic cation vacancies exceeds that of the intrinsic ones. The surface potential, ϕ_s, in the extrinsic range is given by [16]

$$\phi_s = -(g^- + kT \ln \alpha)/e \qquad (1)$$

where g^- is the Gibbs energy of formation of the cation vacancies, e is the elementary charge; k is Boltzmann's constant, and α is the concentration of unassociated extrinsic vacancies. The latter parameter is defined by [6]

$$\alpha = \chi/\{1 + 12 \exp[-(g^- + \xi)/kT]\} \qquad (2)$$

where χ represents the total mole fraction of divalent impurities and ξ stands for the Gibbs free energy for the association of divalent impurity with a cation vacancy. The crossover point at which the charge vanishes is the extrinsic isoelectric temperature, T_i, which is defined by [16]

$$T_i = g^-/k \ln(1/\alpha) \tag{3}$$

The defects of thermal origin become predominant above the so-called knee temperature, T_k, which is somewhat higher than T_i and is given by [16]

$$T_k = -(g^+ + g^-)/2k \ln \alpha = -gS/2k \ln \alpha \tag{4}$$

where g^+ and gS are the Gibbs free energies for the formation of anion vacancies and Schottky pairs, respectively. In the intrinsic range the surface potential is [16]

$$\phi_s = (g^+ - g^-)/2e \tag{5}$$

The magnitude of the field strength of surface charge was computed in the planar model approximation by the formula [4]

$$E = (2\varepsilon nkT)^{1/2}\varepsilon_0^{-1/2} \sinh(e\phi_s/2kT) \tag{6}$$

where ε_0 is the permittivity of free space, ε is the dielectric coefficient, and n is the concentration of cation vacancies in the bulk. The value of n was calculated by the following equations for the intrinsic and extrinsic temperature intervals, respectively [16]:

$$n = N \exp(-gS/2kT)/\gamma \tag{7}$$

and

$$n = \alpha N/\gamma \tag{8}$$

Here N is the number of lattice sites (cation and anion) per unit volume and γ is the activity coefficient that can be determined from the Debye–Hückel–Lidiard theory [17].

The following parameters and approximating equations were used in calculation of the temperature dependence of the magnitude of E: $\chi = 1 \times 10^{-6}$; $g^-(\text{eV}) = 1.256 - 4.53\, kT$ [6]; $gS(\text{eV}) = 2.52 - 8.35\, kT$ [18,19]; $\gamma = 1.18 - 3.77 \times 10^{-7}\, T^2$ [18]; $\varepsilon = (2.14 + 4.21 \times 10^{-7}\, T^2)^2$ [20]; $\xi(\text{eV}) = -0.6 + 1.8\, kT$ [20]; $N = 1.61 \times 10^{28}$ m^{-3} [21]. The results of this calculation are shown in Fig. 2.

A remarkably good correlation between the variation in fragmentation pattern with temperature (Fig. 1) and the pattern of the curve E versus T in Fig. 2 is observed. It should be noted that the excellent con-
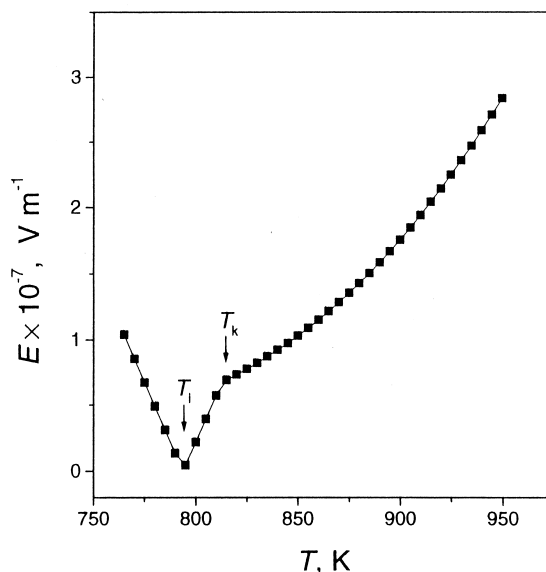

Fig. 2. Temperature dependence of the strength of surface charge field calculated for KCl crystal in the planar model approximation.

sistency of the values T_i and T_k in Fig. 2 with the temperatures associated with the minimum and apparent knee points of the experimental curves of Fig. 1 is fortuitous. The error in the calculated values of T_i and T_k is estimated to be 20–25 K. This error does not diminish the significance of the correlation itself, which is taken as support for the assumption about the influence of surface charge field on the fragmentation pattern, i.e. about the change in the excited state of molecules vaporizing in the field of surface charge. We now propose an explanation for the excessive excitation.

The molecular energy shift, ΔW, due to an external field of the strength E is given by

$$\Delta W = -\beta E^2/2 \tag{9}$$

where β is the electric dipole polarizability of a molecule. As can be seen in Fig. 2, in the vicinity of T_i the field strength varies from zero to values of the order of magnitude of 10^6 V · m^{-1}. Because of unknown energies for kink formation, in our calculations of E no account has been taken of possible reduction in surface charge density due to limitations of surface sites available for extra charge [22]. More-

over, because of the nonuniformity in surface charge density, local field strengths at the terraces from where molecules desorb are expected to be less than those at the ledges [23]. Thus the real electric field experienced by vaporizing molecules may be substantially weaker than is calculated. But it is reasonable to suggest that the energy shift of a KCl molecule, which possesses appreciable polarizability of 4.6×10^{-24} cm^3 [24], may exceed significantly the value of kT, or at least be comparable to this value. Therefore, the conversion of the energy ΔW to the energy of vibrational and/or rotational excitation when the subliming molecule leaves the surface would lead to a change in the fragmentation pattern. The ratio $I(\text{K}^+)/I(\text{KCl}^+)$ would approach an extreme value, as the surface temperature approaches the value of T_i (i.e. when the magnitude of E approaches zero).

4. Conclusions

It is found that the electron impact fragmentation pattern of KCl molecules vaporizing from an open surface of potassium chloride single crystal is temperature dependent. In the temperature range 766–945 K it passes reproducibly through a minimum at about 788 K.

It is concluded that molecules desorbing from an open crystal surface may possess excessive vibrational and rotational energy compared to that characteristic of thermal excitation. A very good correlation is observed between the temperature dependence of the fragmentation pattern and the temperature dependence of the strength of the surface charge field. This observation provides support for the proposal that the gain of excessive energy by vaporizing molecules occurs as a result of conversion of the energy of molecular shift in the field of surface charge to the energy of vibrational and/or rotational excitation.

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