EXOELECTRON EMISSION DURING POLYMORPHIC PHASE TRANSITIONS OF SOME AMMONIUM SALTS

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(Received October 5, 1987)

Results of experimental investigations of the photostimulated exoelectron emission (EEE) accompanying polymorphic phase changes in ammonium chloride, ammonium bromide and ammonium iodate are reported for the first time. The temperature-dependences of the intensity of photostimulated EEE from reagent grade powder materials were measured in air at atmospheric pressure, the exoelectrons being detected with an open air point counter with saturated ethanol quenching vapour. The DTA control measurements were performed at the same heating rate, with reagent grade Al₂O₃ as a reference. A comparison of the results of the EEE and DTA measurements shows clearly that the polymorphic phase transitions of the investigated materials are accompanied by peaks of the EEE intensity, thereby allowing the detection of solid-solid phase transitions in inorganic compounds with the EEE technique.

Exoelectron emission (EEE) is an unstationary emission of low-energy particles (mainly electrons, but in some cases positively charged and even neutral particles have also been observed) from thermodynamically unstable systems returning to the equilibrium state. The process of removal of the emitter from equilibrium by an external perturbation (e.g. irradiation, quenching or mechanical deformation) is commonly called excitation. An additional energy supply, necessary for observing the EEE from an excited sample, is called stimulation. The factors most commonly used to stimulate EEE are illumination (photostimulation) with light of appropriate wavelength (larger than the long-wavelength limit for an external photoeffect) and/or heating (thermostimulation) according to a known programme, usually in the form of a linear temperature ramp.

EEE has been known for a long time [1]. Many famous nuclear physicists have measured EEE without realizing it. The first to investigate the phenomenon systematically was Kramer [2, 3]. The results of his comprehensive studies in the
early forties stimulated further activities. Currently, after almost fifty years of investigations, the phenomenon of EEE is still poorly understood. Nevertheless, the phenomenon is often used, or is seriously considered, as a research tool in radiation dosimetry studies of the surface and defect structure of solids, as well as in investigations of the structural transformations in metallic materials [4].

Through several experimental investigations [4–7], it has been shown that the phenomenon of EEE is very sensitive to the phase transformations in metallic materials. Some data in the literature [8, 9] confirm the possibility of following the thermal decompositions of inorganic salts via EEE. We recently started systematical experimental investigations of the EEE accompanying the first-order phase transitions of inorganic compounds. The results we have obtained for alkali metal nitrites and nitrates have been already presented [10]. In the present communication, the results of parallel DTA and EEE investigations of polymorphic phase transitions in some ammonium salts will be reported.

Experimental conditions

The temperature-dependences of the intensity of photostimulated EEE were measured with the apparatus described in detail in [11]. The detector of (exo) electrons was an open air point counter with saturated ethanol vapour above the free surface of the liquid as a quenching gas [12]. Throughout the measurements, the samples were illuminated with the unfiltered radiation of a quartz lamp with a Q-400 burner. Prior to measurement, the samples were not subjected to any form of excitation (irradiation or deformation). The temperature of the sample was changed by means of a resistance heater at a constant rate of 10 deg/min. An iron-constantan thermocouple permitted temperature measurements with an accuracy of about 5 deg.

DTA control measurements were made with a Linseis L62/30/80 thermoanalyser with the use of standard nickel crucibles, the heating or cooling rate being the same as in EEE experiments. Reagent grade Al₂O₃ powder was used as a reference.

All the EEE and DTA measurements were carried out in air under atmospheric pressure. All the materials investigated, produced by POCh Gliwice, were labelled as pure for analyses.

Results and discussion

The results of measurements for ammonium chloride are shown in Fig. 1. In both the heating and cooling runs, the DTA curves always displayed thermal effects with