

EXOELECTRON EMISSION ACCOMPANYING THE PHASE TRANSFORMATIONS IN SOME SILVER SALTS

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ABSTRACT

Results of experimental investigations of the photostimulated exoelectron emission (EEE) accompanying polymorphic phase changes in silver iodide, silver nitrate and silver sulphate are reported. The measurements of the temperature dependence of the intensity of photostimulated EEE from reagent grade powder materials were performed in air at atmospheric pressure, the exoelectrons being detected with an open air point counter with saturated ethanol quenching vapour. The differential thermal analysis (DTA) control measurements were performed at the same heating rate. A comparison of the results of the EEE and DTA measurements shows clearly that the polymorphic phase transitions in the investigated materials are accompanied by enhancement (peaks) of the EEE intensity. This enables the detection of the solid–solid phase transitions in inorganic compounds to be made by the EEE technique.

INTRODUCTION

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

Exoelectron emission 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 Johannes Kramer. His comprehensive studies started in the early forties and the results were first

published in the late forties [2,3]. These studies have 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 structures of solids and in investigations of the structural transformations in metallic materials [4].

In several experimental investigations [4–7] it has been shown that the phenomenon of exoelectron emission is very sensitive to the phase transformations in metallic materials. There are also data in the literature [8,9] which confirm the possibility of following the thermal decomposition of inorganic salts by the exoelectron emission technique. Recently, we have started systematic experimental investigations of the EEE accompanying the first-order phase transitions of inorganic compounds. The results we obtained for alkali nitrites and nitrates have already been presented [10]. In this work the results of parallel differential thermal analysis (DTA) and EEE investigations of polymorphic phase transitions in some silver salts are presented.

EXPERIMENTAL CONDITIONS

Measurements of the temperature dependence of the intensity of photo-stimulated exoelectron emission were accomplished with the apparatus described in detail in our previous work [11]. The detector of (exo)electrons was an open air point counter. Saturated ethanol vapour above the free surface of the liquid was used as a quenching gas [12]. Throughout the measurements the samples were illuminated with unfiltered radiation from a quartz lamp with a Q-400 burner. Prior to measurement the samples were not subjected to any form of excitation (irradiation, deformation). The temperature of the sample was changed by means of a resistance heater at a constant rate of 10 K min^{-1} . An iron–constantan thermocouple enabled the temperature measurements to be made with an accuracy of about 5 K.

The control DTA measurements were performed using a Linseis L62/30/80 thermoanalyser and standard nickel crucibles, the heating or cooling rate being the same as in the EEE experiments. An empty nickel crucible was used as a reference.

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

RESULTS AND DISCUSSION

The results of measurements on silver iodide are shown in Fig. 1. In both the heating and cooling runs the DTA curves display thermal effects (peaks),

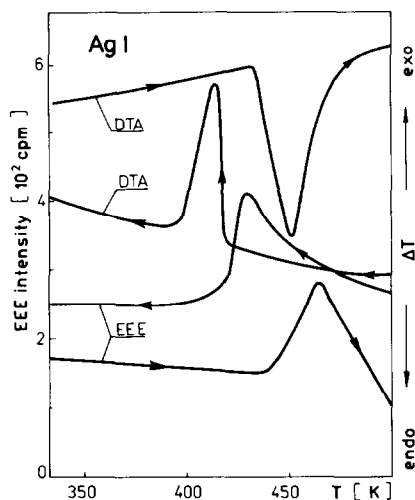


Fig. 1. DTA curves and temperature dependence of the intensity of photostimulated EEE from silver iodide. The arrows indicate the heating and cooling runs.

with onset at ~ 430 K (heating) and ~ 420 K (cooling), corresponding to the well-known polymorphic phase transition between the low temperature phase (with normal ionic conductivity) and the high temperature phase (with superionic conductivity) [13,14]. The temperature dependences of the intensity of photostimulated exoelectron emission (EEE) also display maxima, the positions of which coincide with those on the DTA curves. Thermal hysteresis of the phase transition in the AgI sample is also clearly seen on both the DTA and EEE curves.

Figure 2 represents the DTA and EEE curves registered for silver nitrate. The DTA curves measured in both the heating and cooling runs display two endothermic events corresponding to the polymorphic phase transition and the solid-liquid phase transition [15,16]. The temperature dependences of the exoelectron emission intensity also display two peaks both in the heating and in the cooling runs. The positions of the EEE peaks coincide well with those on the corresponding DTA curves.

The low temperature solid-solid phase transformation in AgNO_3 (manifesting itself by the occurrence of the low temperature peaks on both the DTA and EEE curves) is the polymorphic phase transition between the ferroelectric (low temperature) and the paraelectric (high temperature) state. Therefore one can assume that the exoelectron emission effect accompanying this phase transformation is the so-called apparent emission, resulting from the generation of electrical microdischarges at the surfaces of the grains of the sample owing to the changes in the domain structure over the temperature interval close to the phase transition temperature (Curie point) [17]. The solid-solid phase transition in AgNO_3 exhibits a remarkable hysteresis which is clearly visible on both the DTA and EEE curves.

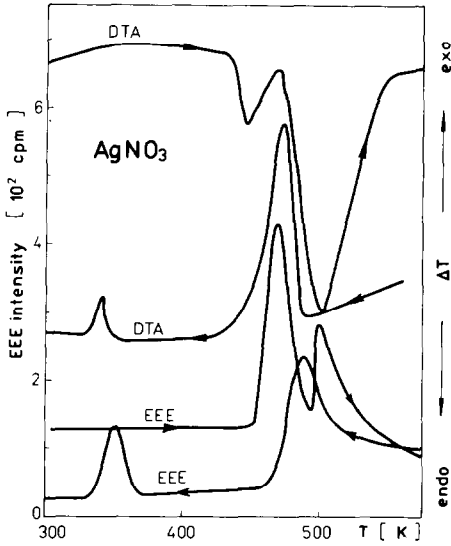


Fig. 2. DTA curves and temperature dependence of the intensity of photostimulated EEE from silver nitrate. The arrows indicate the heating and cooling runs.

The results obtained in experiments with silver sulphate are represented in Fig. 3. The DTA curve registered in the heating run displays an endotherm associated with the polymorphic phase transformation [18,19]. The EEE curve displays three peaks. The two low temperature peaks on the temperature vs. EEE intensity curve (having no counterpart on the DTA curve) are most probably connected with the liberation of the physically and chemically adsorbed water. The high temperature peak of the exoelectron emission intensity precedes markedly the bulk thermal effect connected with the polymorphic phase transformation. It is probable that the phase transitions on the surfaces of the grains of the sample occur more rapidly than those in

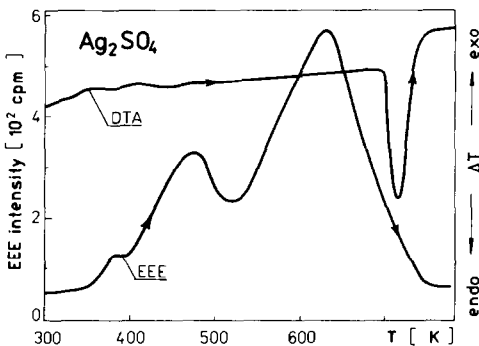


Fig. 3. DTA curve and temperature dependence of the intensity of photostimulated EEE from silver sulphate as measured in the heating run.

the deeper layers. Exoelectron emission is a surface effect (escape depth of exoelectrons is of the order of several nanometres) and therefore the peak of the EEE intensity precedes that on the DTA curve (which represents the heat effect of the phase transition occurring in the bulk of the sample).

The results we obtained show clearly that the polymorphic phase transitions in the silver salts investigated are accompanied by peaks on the temperature vs. photostimulated exoelectron emission intensity curves. This opens up the possibility of detecting the phase transformations in inorganic compounds by the EEE technique.

The main drawback of the EEE method, as compared with DTA, is that there is no possibility of distinguishing between the endothermic and exothermic phase transformations. However, our experience with metallic materials [4–7] shows that the EEE technique may have many advantages. The most important of them lies in the fact that the exoelectrons are emitted from a thin surface layer of the sample with a thickness of the order of 10 nm. Therefore it could be hoped that the EEE technique may be applied to detect the phase changes in thin films of chemical compounds (e.g. protective coatings on various substrates).

However, there remain many problems to be solved and the technique must be improved before the method can be widely used in practice. First of all the possible mechanisms of the emission processes accompanying the phase transformations must be recognized. Further studies are in progress.

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