Journal of Thermal Analysis, Vol. 34 (1988) 1295–1300

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 Al_2O_3 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

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[+] Work sponsored by the Polish Ministry of Science and Education within the Central Project of Fundamental Research CPBP 01.08.A4.

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 themocouple 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 Al_2O_3 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

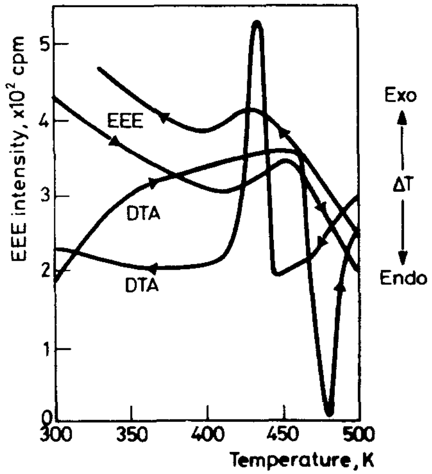

Fig. 1 DTA curves and temperature dependences of the intensity of photostimulated EEE from ammonium chloride. The arrows indicate the heating and cooling runs

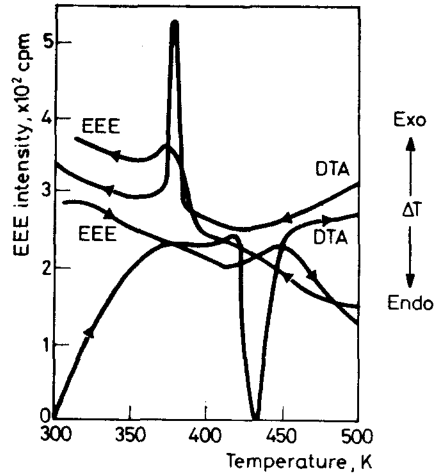

Fig. 2 DTA curves and temperature dependences of the intensity of photostimulated EEE from ammonium bromide. The arrows indicate the heating and cooling runs

onset at 460 K (heating) and 445 K (cooling), corresponding to the polymorphic phase transition in the investigated material [13, 14]. The temperature-dependences of the EEE intensity also displayed maxima, the positions of which coincided with those of the DTA peaks.

Figure 2 presents the DTA and EEE curves registered for ammonium bromide. The DTA curve observed upon heating revealed an endothermal event at 425 K, corresponding to the polymorphic phase change [13, 14]. The reverse transition was also clearly detectable as an exothermal effect in the DTA curve recorded in the cooling run. The temperature-dependences of the EEE intensity displayed a maximum in both the heating and cooling runs, the position of the maximum coinciding with the corresponding DTA peak.

The results obtained in experiments with ammonium iodate are presented in Fig. 3.

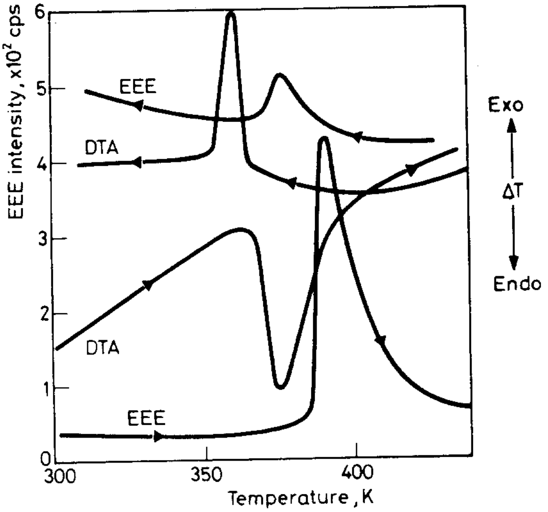

Fig. 3 DTA curves and temperature dependences of the intensity of photostimulated EEE from ammonium iodate. For the sake of clarity the EEE curve registered in the cooling run is shifted by 400 cpm towards larger values

In both heating and cooling runs, the DTA curves showed the thermal effect associated with the reversible polymorphic phase transformation [15]. The EEE curves exhibited a peak which always preceded the onset of the polymorphic phase change determined from the deflection point in the DTA curve, the shift between the DTA and EEE peaks being comparable with the sum of the possible inaccuracies in the temperature determination in both the DTA and EEE experiments. Both the DTA and the EEE effects accompanying the polymorphic phase transition in ammonium iodate showed marked hysteresis.

The results clearly reveal that the polymorphic phase transitions in the investigated ammonium salts are accompanied by peaks in the curves of the temperature-dependences of the intensity of photostimulated EEE. This leads to a possibility to detect the phase transformations in inorganic compounds with the EEE technique.

The main drawback of the EEE method, as compared with DTA, is that there is no possibility to distinguish between the endo- and exothermal phase transformations. Our experience with metallic materials [4–7], however, shows that the EEE technique may also have many advantages. The most important of these lies in the fact that the exoelectrons are emitted fom 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, many problems remain to be solved and the techniques must be improved before the method could be widely used in practice. First of all, the mechanism of the emission processes accompanying the phase transformations must be elucidated.

Further studies are in progress.

References

1 A. Scharmann, PTB-Mitteilungen, 80 (1970) 319.
2 J. Kramer, Z. Physik, 125 (1949) 739.
3 J. Kramer, Der metallische Zustand, Vandenhoeck-Ruprecht, Goettingen, 1950.
4 T. Górecki, Latin Am. J. Met. Mater., in press.
5 B. Sujak and T. Górecki, Wiadomości Chemiczne, 27 (1973) 361 (in Polish).
6 T. Górecki, Acta Univ. Vratislaviensis, 272 (1976) 119 (in Polish).
7 T. Górecki, Proc. VIth Int. Symp. Exoelectron Emission and Applications, Ahrenshoop, October 1979, p. 114.
8 J. Kramer, Z. Phys. Chem. N.F., 289 (1960) 300.
9 T. Górecki, Acta Phys. Polon., A41 (1972) 707.
10 Cz. Górecki and T. Górecki, Jap. J. Appl. Phys. 24, Suppl. 24–4 (1985) 106.
11 T. Górecki and B. Sujak, Acta Phys. Polon., A42 (1972) 487.
12 I. Stępniowski, Acta Phys. Polon., 30 (1966) 163.
13 L. Erdey, S. Gál and G. Liptay, Talanta, 11 (1964) 913.
14 I. V. Kudryashov, N. I. Gusev and S. D. Kamyschenko, Zh. Fiz. Khim., 41 (1967) 967 (in Russian).
15 D. F. Vaisa, A. I. Barabash, I. G. Vertegel and V. I. Pakhomov, Ukr. Fiz. Zh., 27 (1982) 1850 (in Russian).

Zusammenfassung — In dieser Arbeit wird zum ersten Mal über die Untersuchung der photostimulierten Exoelektronenemission (EEE) berichtet, die die polymorphen Phasenübergänge von Ammoniumchlorid, -bromid und -jodat begleitet. Die Temperaturabhängigkeit der Intensität der photostimulierten EEE wurde an analysenreinen pulverisierten Proben bei Normaldruck in Luft untersucht, wobei die Detektion der Exoelektronen mit einem offenen Spitzenzähler und Äthanol als Löschdampf diente. Als Bezug dienten DTA-Messungen mit analysenreinem Al_2O_3 als Referenz und mit der gleichen Aufheizgeschwindigkeit. Der Vergleich von EEE- und DTA-Ergebnissen zeigt, dass die polymorphen Phasenübergange der untersuchten Substanzen von einer verstärkten Exoelektronenemission begleitet sind. Dies ermöglicht die Anwendung der Exoemissionstechnik zur Detektion von Fest-Fest-Phasenumwandlungen anorganischer Verbindungen.

Резюме — Исследована температурная зависимость интенсивности фотостимулированной экзоэлектронной эмиссии (ЭЭЭ) в окрестности полиморфных фазовых переходов хлорида, бромида и йодата аммония. Измерения экзоэлектронной эмиссии проводились в атмосфере воздуха с помощью открытого остриевого счетчика с насыщенным паром этанола. Сравнение кривых температурной зависимости интенсивности ЭЭЭ и ДТА, полученных при одинаковых скоростях изменения температуры показало, что полиморфные фазовые переходы исследуемых материалов сопровождаются пиками интенсивности ЭЭЭ. Это открывает перспективы разработки экзоэмиссионного метода детектирования фазовых переходов в неограничеcких соединениях.