Vol. 32 (2001) *ACTA PHYSICA POLONICA B* No 2

EXPERIMENTAL DETECTION OF PHASE TRANSITIONS BY MEANS OF THE CHEMICAL POTENTIAL MEASUREMENT*

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(Received November 5, 2000)

We review some recently performed experiments concerning the detection of phase transitions in solids with the use of a single measurement of the chemical potential versus temperature. A new method of the indirect measurement of the chemical potential was demonstrated for Gd, Gd_5Si_4, Cr, TiNi (10% and 15% of deformation) and CuAlNiTiMn samples by means of a simple electrochemical experiment. For most cases the method allowed easily to detect all critical temperatures T_C (Gd, Gd_5Si_4), T_N (Cr) and the structural transition temperatures (TiNi, CuAlNiTiMn). The obtained results were in the exceptionally good agreement with other measurements and entirely supported the theoretical predictions concerning the applicability of the method. Presumably, it is also possible to detect phase transition anomalies, using the method of chemical potential measurement, either by thermoelectric or photoelectric effects.

PACS numbers: 75.30.Kz, 75.40.Cx

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[*] Presented at the XXIV International School of Theoretical Physics “Transport Phenomena from Quantum to Classical Regimes”, Ustroń, Poland, September 25–October 1, 2000.

1. Introduction

Phase transitions belong to the principal problems in the solid state physics. Many different methods have been elaborated to detect phase transitions, there is, however, a new possibility basing on the single measurement of the chemical potential. In a number of theoretical papers (see Refs. [1–10] and papers cited therein) a broad class of temperature or concentration driven different types of phase transitions has been investigated. Numerical calculations performed for many microscopic models exhibiting magnetic, superconducting, reentrant and structural phase transitions have revealed that all critical temperatures can be read off from the characteristic behaviour of the chemical potential. It turned out that the critical temperatures of the system are associated with the kinks (or jumps) in the temperature plot of the chemical potential. These kinks localize sufficiently well the critical temperatures connected with various types of phase transitions. Basing on this observation we came up with a supposition (see Refs. [2–10]) that the direct measurement of the chemical potential temperature dependence should also contain unambiguous information about critical temperatures of the real system under the condition that the measurement accuracy (as it was predicted theoretically) can reach 10^{-4}–10^{-3} eV. Besides, such a measurement should also bring into the open all, usually unnoticed, transitions between metastable states or “exotic” ones. These theoretical predictions were successfully verified in the recent experiments, Refs. [11,12] and we want to survey the main results presented therein. It is the aim of the present review to awake the interest of a broad audience of physicists to the problem of the chemical potential measurement as a new experimental tool to detect phase transitions and to popularize this idea.

2. Experiments review

In the experiments [11,12] a galvanic cell was used where one of the electrodes was an investigated metallic sample while the other one was the reference electrode. According to the Nernst’s formula (*cf. e.g.* Ref. [13]) the difference between the chemical potentials of electrodes is proportional to the measured voltage. Thus, changing the temperature of the electrolyte bath, one can measure the voltage as function of temperature, and accordingly the relative chemical potential temperature dependence. Such a measurement was performed for six different samples which were chosen to exhibit two types of magnetic (ferromagnetic and antiferromagnetic) and different sequences of structural transformations lying in the temperature range available for the experiment.

The single crystals of Gd (99.99 %), Gd_5Si_4 (the same sample as in Ref. [14]), Cr (spectral pure, Johnson Mattey) and the polycrystalline TiNi (deformation 10 %, 15 %) alloy with nominal composition of 49 at. % of Titanium and 51 at. % of Nickel (made by Advanced Material Technology, Belgium) and CuAlNiTiMn (Cu-80.1 wt. %, Al-11.9 wt. %, Ni-5.0 wt. %, Ti-1.0 wt. %, Mn-2.0 wt. %; the same sample as the alloy no. 2 in Ref. [15]) were studied. Both TiNi samples were treated, prior to the experiment, at 850° C for one hour with deformation 10 % (15 %) and treated again at 400° C also for one hour.

The electromotive force (EMF) was measured similar to Refs. [16,17], by measuring the voltage between the two electrodes dipped in one minor solution of hydroxide of potassium as function of temperature. The Autolab$^{\rm TM}$21 instrument was used where the first electrode was the investigated sample, the second one the reference electrode — a saturated calomel electrode. The voltage was measured directly with the accuracy of 0.1 mV.

In a complementary experiment the transformation temperatures were determined by the Differential Scanning Calorimetry (DSC) using a Perkin DSC 7 type equipment operating at a cooling/heating rate of 0.25° C/s for each sample separately.

The first measured Gd element undergoes the phase transition from ferromagnetic to paramagnetic state (*cf.* *e.g.* Ref. [18]) at the Curie temperature $T_{\rm C} \simeq 293$ K (20° C). In Fig. 1 this critical temperature can easily be identified by the pronounced discontinuous jump in EMF (jump in the relative chemical potential). This result is also supported by the auxiliary plot of the heat flow (see the inset in Fig. 1).

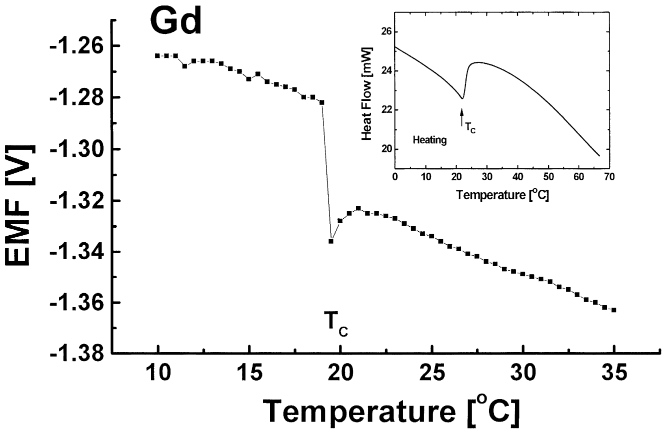

Fig. 1. Plot of experimentally measured EMF (multiplied by (−1)) *vs* temperature for Gd sample. The inset shows the heat flow (DSC) dependence on temperature.

The Gd_5Si_4 compound is also ferromagnetic (see Refs. [19–22,14]) with $T_C \simeq 336$ K (63° C). The measurement of the EMF in this case is plotted in Fig. 2, together with the auxiliary DSC measurement (see the inset). The Curie temperature manifests itself in the kink of the EMF at $T_C \simeq 62°$ C. At $T^* \simeq 55°$ C, however, we have another kink connected with the fact that we probably deal not with the strictly homogenous sample but rather with an inhomogeneous one. We should mention at this place that the resistivity measurement in Ref. [14] also reveals the existence of T^* characteristic temperature (a small kink in the resistivity) beneath T_C (see Fig. 2 in Ref. [14]). In other words, from the EMF measurement one can presumably conclude about the homogeneity of the sample as it can be done from the well-known thermomagnetic measurement (see *e.g.* Ref. [23] for details). By assuming the validity of this assumption one can even estimate the content of each constituent.

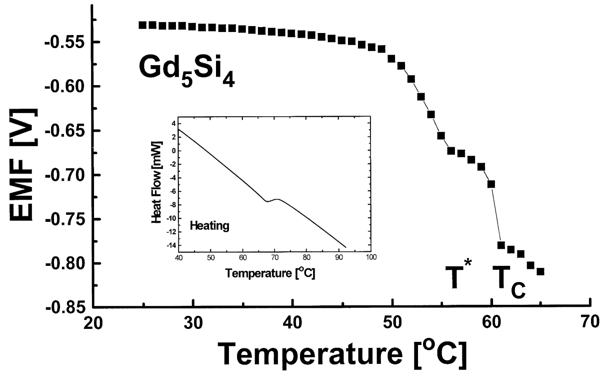

Fig. 2. The same as in Fig. 1 but for Gd_5Si_4.

In the case of the third measured sample (Cr) it is well known (*cf. e.g.* Ref. [24]) that at the Neel temperature $T_N \simeq 311$ K (38° C) (it depends on the quality and sample preparation) the phase transition from antiferromagnet to paramagnet takes place. Again, the transition point T_N can be read off from the EMF plot in Fig. 3. However, in the DSC plot this critical temperature is hardly noticeable. This is probably due to the fact that the critical temperature T_N is relatively high and in this particular case an additional purely paramagnetic reference sample should be measured and corresponding heat flows subtracted. In other words, the measurement of the relative chemical potential is much more reliable in this case. Moreover, the information about the value of the critical temperatures (T_C, T_N) in Figs. 1–3 we acquire without applying the external magnetic field which can influence the investigated system and thus change the values of critical temperatures.

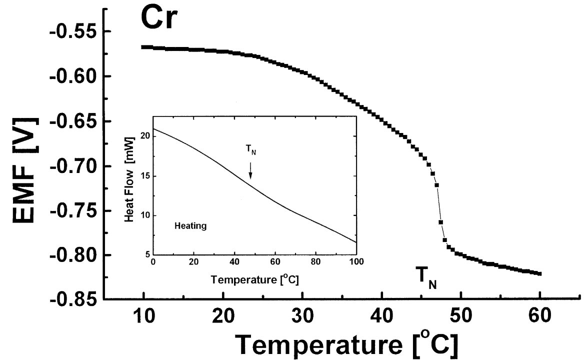

Fig. 3. The same as in Fig. 1 but for Cr.

In a similar way the measurement of EMF versus temperature for the next samples (TiNi 10 % and 15 % deformation shape memory alloys) was performed. Due to the applied preprocessing of these alloys a structural phase transformation in the measured temperature range should be expected. It is known from the literature (*cf. e.g.* Refs. [25–27] for details) that transitions B2–R and R–B19 take place and it is really the case while looking at Figs. 4 and 5. The insets display the plots of DSC. However, the curve of EMF carries apparently more information about these phase transformations than the heat flow measurement alone. It especially concerns the message about the well defined edges (martensitic: As, Af; R-type: RAs, RAf), where each type of the structural transformation begins or ends, as well as, about the characteristic temperatures where DSC peaks appear (here denoted by A* and RA*).

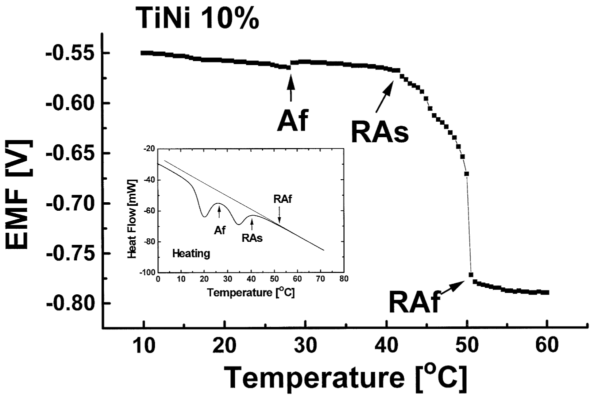

Fig. 4. The same as in Fig. 1 but for TiNi (deformation 10%).

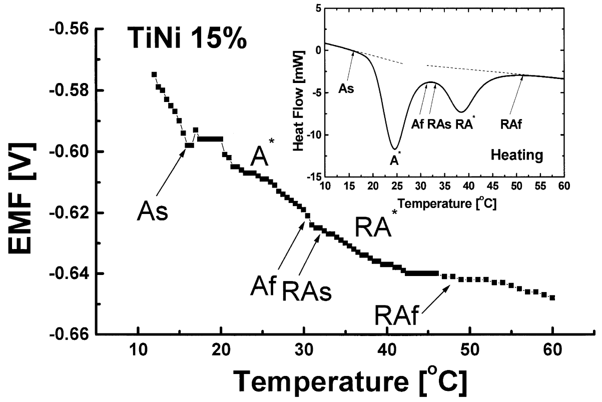

Fig. 5. The same as in Fig. 1 but for TiNi (deformation 15%).

The measurement for CuAlNiTiMn alloy is plotted in Fig. 6 and the exact transformation temperature reads $T_0 \simeq 41.6^\circ$ C (sigmoidal fit). Thus obtained critical temperature with the use of the indirect chemical potential measurement beautifully coincides with the transformation temperature obtained in Ref. [15] (see Fig. 5(d)). We have to stress at this point that the conventional DSC measurement completely fails (the kink at T_0 is hardly visible).

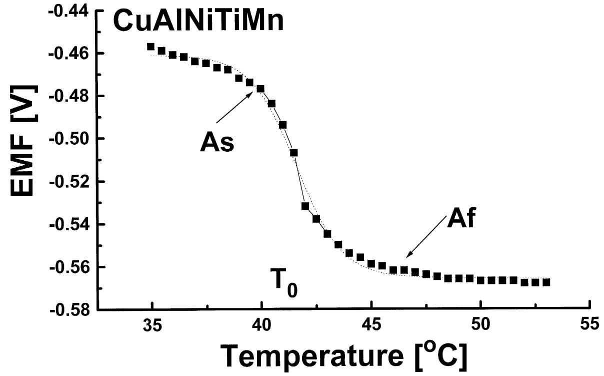

Fig. 6. The same as in Fig. 1 but for CuAlNiTiMn (dashed line — the sigmoidal fit).

3. Conclusions

From the results presented in this review we see that the idea of finding phase transitions in real substances by means of the chemical potential measurement as function of temperature, originally proposed in papers [2–10], is quite reasonable. The method has been demonstrated for different types of phase transitions (ferromagnet–paramagnet, antiferromagnet–paramagnet and structural phase transformations). This fact, and our earlier theoretical investigations, suggest that it can be extended over all phase transitions either first or second order. At a first glance the method possesses some noticeable advantages. It is sufficiently sensitive what can lead to the additional information gain with respect to other methods. Also the curves obtained in this way are very subtle and can better report on the local changes in a sample very often hidden for other methods. It is also important to stress that the cheap way we acquired information about critical temperatures can surely be supplemented by the existing or newly developed techniques based on the suggested here measurement of the chemical potential. Thus, one would expect to find out a method of a general applicability working in a broader temperature range and not restricted to metallic samples only. Hence, as a continuation of this idea one can imagine a method applying effects where the well-defined relation between the chemical potential and an actual measurable physical quantity is utilized (as in *e.g.* thermoelectric and photoelectric phenomena).

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