

Experimental method to detect phase transitions via the chemical potential

M. Matlak*

Institute of Physics, University of Silesia, Uniwersytecka 4, PL-40007 Katowice, Poland

M. Pietruszka†

Faculty of Biology, University of Silesia, Jagiellońska 28, PL-40032 Katowice, Poland

E. Rówiński‡

Institute of Physics and Chemistry of Metals, University of Silesia, Bankowa 12, PL-40007 Katowice, Poland

(Received 17 July 2000; published 10 January 2001)

We propose an experimental method to confirm theoretical predictions concerning the detection of phase transitions in solids via the measurement of the chemical potential as a function of temperature. Here, as experimental evidence of the validity of these predictions, we perform indirect measurements of the chemical potential vs temperature for Gd, Cr, and TiNi samples by means of an electrochemical experiment. This made it possible to easily localize all critical temperatures connected either with magnetic phase transitions [T_C (Gd), T_N (Cr)] or structural phase transformations in the shape-memory alloy NiTi. The values of the critical temperatures, obtained in this way remain in exceptionally good agreement with the results of the auxiliary heat flow measurements and the existing literature data concerning critical temperatures. We hope that further development of the experimental techniques, based on chemical potential measurements, can provide a new experimental tool in the search for phase transitions (induced by temperature, pressure, concentration, etc.) in real materials, regardless of the type of phase transitions and irrespective of the underlying mechanism.

DOI: 10.1103/PhysRevB.63.052101

PACS number(s): 64.60.-i, 75.30.Kz, 75.40.Cx

During the past decades many different methods have been proposed to detect phase transitions in solids. However, there exists a new possibility based on a single measurement of the chemical potential predicted recently in a number of theoretical papers (see Refs. 1–9, and references cited therein), where a broad class of temperature or concentration driven 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 behavior of the chemical potential at the critical point. 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 tiny kinks localize the critical temperatures connected with various types of phase transitions sufficiently well. Based on this observation we put forward a hypothesis (see Refs. 2–9) that the measurement of the chemical potential temperature dependence should also contain unambiguous information about critical temperatures of the real system. It can be accomplished under the assumption that the measurement accuracy (as was predicted in Refs. 2–9) can reach 10^{-4} – 10^{-3} eV. Moreover, we suggested (see, e.g., Ref. 6) that such a measurement should also bring into the open all the normally unnoticed transitions between the metastable and “exotic” states.

Taking these observations into account we could not resist the temptation to check the effect experimentally. For this purpose we have adopted a simple experimental method and we utilized a galvanic cell where one of the electrodes is the investigated metallic sample while the other one is the reference electrode. According to the Nernst’s formula (see, e.g.,

Ref. 10) the difference between the chemical potentials of electrodes is proportional to the measured voltage

$$\mu^{(\text{sample})} - \mu^{(\text{ref})} = l(\phi^{(\text{ref})} - \phi^{(\text{sample})}), \quad (1)$$

where l is a constant. Thus, by changing the temperature of the electrolyte bath, one can measure the voltage as function of temperature and, accordingly, the relative chemical potential temperature dependence. To demonstrate the effect such a measurement has been performed for three different

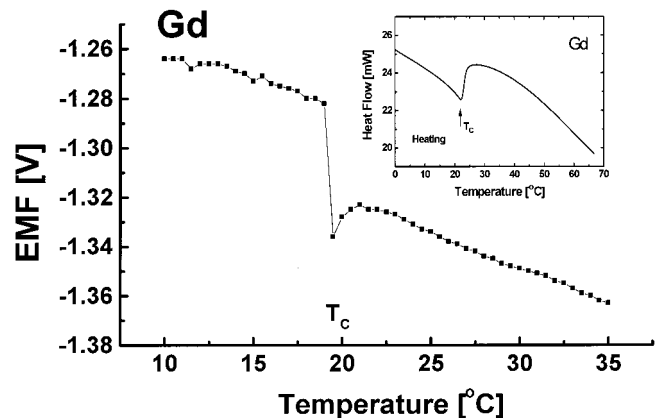


FIG. 1. Plot of experimentally measured EMF [multiplied by (-1)] vs temperature for Gd sample. The inset shows the heat flow dependence on temperature (DSC).

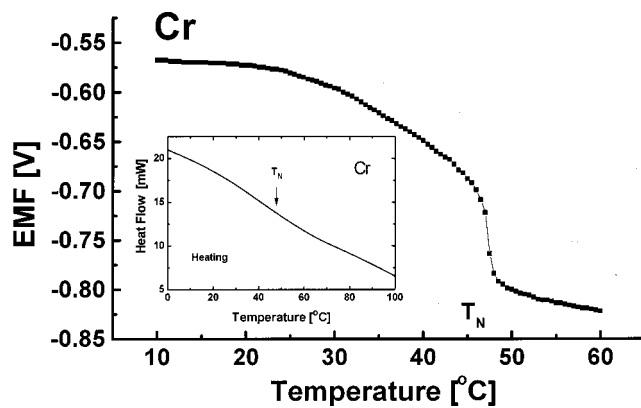


FIG. 2. The same as in Fig. 1 but for Cr sample.

samples which were chosen intentionally to exhibit two types of magnetic phase transitions (Gd,Cr) and structural transformations (TiNi).

The single crystals of Gd (99.99%), Cr (spectral pure, Johnson Matthey), and the polycrystalline TiNi alloy with nominal composition of 51 at. % of nickel and 49 at. % of titanium (made by Advanced Material Technology, Belgium) were studied. TiNi sample was treated, prior to our experiment, at 850 °C for one hour with deformation 10% and treated again at 400 °C also for 1 h. The electromotive force (EMF) measurement has been performed similar to Refs. 11,12. Two electrodes were dipped in one minor solution of hydroxide of potassium. The AutolabTM21 instrument has been used where the first electrode was the investigated sample, the second one was the reference electrode—a saturated calomel electrode. The EMF has been measured directly with the accuracy of 0.1 mV as a function of temperature.

In a complementary heat flow 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. The first measured Gd sample undergoes the phase transition from ferromagnetic to paramagnetic state (see, e.g., Ref. 13) at the Curie temperature T_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).

In the case of the second measured sample (Cr) it is well known that at the Neel temperature T_N (see, e.g., Ref. 14) the phase transition from antiferromagnet to paramagnet takes place. Again, the transition point T_N can be read off from the plot of the EMF in Fig. 2. However, in the plot of the heat flow 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 sensitive in this case.

In exactly the same way the measurement of the EMF vs

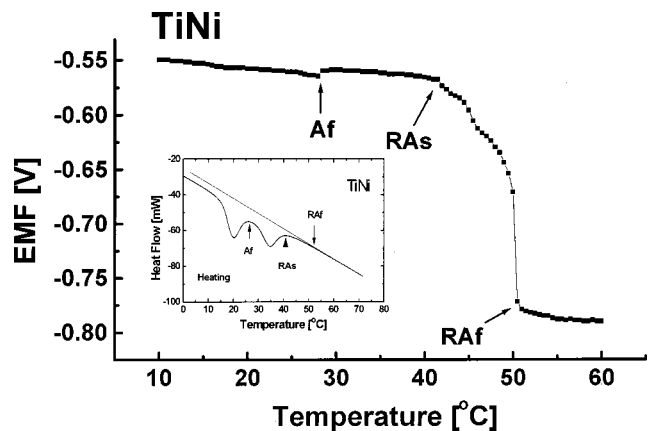


FIG. 3. The same as in Fig. 1 but for TiNi alloy sample (DSC, here endothermic process).

temperature for the third sample (TiNi alloy) was performed. Due to the relatively narrow temperature range available in our experiment only the end of the Martensitic transformation (Af), as well as the beginning (RAS) and the end (RAF) of the R transformation (see Refs. 15–17 for details) could be detected (see Fig. 3). The values of the critical temperatures corresponding to transitions As, RAS, RAf coincide pretty well with the values measured in Ref. 17 and displayed in the inset to Fig. 3 (heat flow measurement).

From the results of the present paper we have seen that the idea, initially proposed in Refs. 2–9, of finding phase transitions in real substances by means of a chemical potential measurement as a function of temperature is not only realistic but also successful. The method has been demonstrated for different types of phase transitions (ferromagnet-paramagnet, antiferromagnet-paramagnet, and structural phase transitions). This fact, and our earlier theoretical investigations, suggest that it can be extended over all phase transitions either of the first or the second order. At a first glance the method possesses some noticeable advantages. It is sufficiently sensitive which can lead to the additional information gain in comparison to other methods. Also the curves obtained in this way are very subtle (compared to the smeared out curves of the DSC experiment) and may report the local changes in a sample very often hidden for other methods. Moreover, the information about the values of critical temperatures for magnetic systems can be obtained without applying the magnetic field which may in turn influence the investigated system and hence—the measured value of the critical temperature. The obvious drawbacks of the experiment we used to demonstrate the applicability of the chemical potential measurement (here the galvanic cell) are the relatively narrow temperature range available for the experiment and the restriction to the metallic samples only. These disadvantages hinder as yet the broader popularization of the chemical potential measurement as a method to detect all kinds of phase transitions which may appear in real solids by performing a single measurement. We expect, however, that these difficulties can be overcome in the nearest future by adopting a suitable experimental technique.

- *Electronic address: matlak@server.phys.us.edu.pl
†Electronic address: pietruma@uranos.cto.us.edu.pl
‡Electronic address: rowinski@us.edu.pl
- ¹M. Matlak and M. Pietruszka, *Physica C* **311**, 151 (1999).
²M. Matlak and M. Pietruszka, *J. Alloy Compd.* **291**, 21 (1999).
³M. Pietruszka and M. Matlak, *Acta Phys. Pol. A* **96**, 725 (1999).
⁴E. Gosławska and M. Matlak, *Phys. Status Solidi B* **217**, 939 (2000).
⁵M. Matlak and M. Pietruszka, *Acta Phys. Pol. A* **97**, 253 (2000).
⁶M. Matlak, M. Pietruszka, E. Gosławska, B. Grabiec, and Kh. Eid, *Phase Transit.* **71**, 73 (2000).
⁷M. Matlak and M. Pietruszka, *Physica B* **291**, 12 (2000).
⁸M. Matlak, E. Gosławska, B. Grabiec, and Kh. Eid, *Acta Phys. Pol. A* **97**, 365 (2000).
⁹E. Gosławska, M. Matlak, and Kh. Eid, *Acta Phys. Pol. A* **97**, 713 (2000).
- ¹⁰G. Kluge, G. Neugebauer, *Grundlagen der Thermodynamik* (VEB Deutscher Verlag der Wissenschaften, Berlin, 1976), p. 191.
¹¹G.E. Rindune, E. Day, and R. Caporelli, *J. Am. Ceram. Soc.* **43**, 571 (1960).
¹²U.G.A. Taubor and E.R. Schmidt, *Nature (London)* **218**, 105 (1968).
¹³R.J. Elliot, *Magnetic Properties of Rare Earth Metals* (Plenum, London, 1972).
¹⁴F. Keffer, in *Handbuch der Physik* (Springer, New York, 1966), Bd. 18.
¹⁵T. Tadaki, Y. Nakata, and K. Shimizu, *Trans. Jpn. Inst. Met.* **28**, 883 (1987).
¹⁶A.I. Lotkov, S.F. Dubinin, S.G. Teplouchov, V.N. Grishkov, and V.P. Scorobogatsov, *J. Phys. IV* **5**, C8-551 (1995).
¹⁷K. Tanaka, K. Kitamura, and S. Miyazaki, *Arch. Mech.* **51**, 785 (1999).