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THE AUTHENTICATION OF PHASE TRANSITIONS *

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ABSTRACT

Phase transitions are sometimes introduced to explain observations of anomalous behaviour in solids without further evidence that a new phase is formed. We review the problems which can arise from this practice and possible means for avoiding them.

INTRODUCTION

The identification and characterization of phase transitions are important aspects of solid state science. The discovery of a phase transition in a particular crystal is always of interest, and occasionally lifts that substance from obscurity into the centre of a wide circle of scientific interest and activity, as has happened in the case of the high temperature superconductors. The theoretical basis for understanding phase transitions is fairly well developed and of continuing interest, but the experimental situation is less satisfactory.

At present there are no standards or guidelines for the use of the phrase "phase transition" which editors and referees might use to judge whether a report of a new phase transition has been adequately substantiated with experimental evidence. It is not uncommon for authors, when faced with otherwise unexplained anomalies in their data, to suggest a phase transition as the origin of the anomaly. An example originating from one of the present authors can be found in ref. 1; a recent example in the literature of high temperature superconductivity can be found in ref. 2. After publication of a paper claiming or suggesting a phase transition, it is to be expected that

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* Dedicated to Professor E.F. Westrum, Jr., on the occasion of his 70th birthday and in honour of his contribution to calorimetry and thermal analysis.

other workers will base their thinking, writing and experimental work on the assumption of the existence of the phase transition. In many cases the finding of an anomaly in one set of observations is followed by further supporting evidence, and the existence of a phase transition is confirmed.

However, a problem may arise if an investigator using an experimental method different from that of the original report fails to find evidence to support the existence of the phase transition. Publication of such results may be denied or delayed if a referee casts doubt on the accuracy of the new work, or on the effectiveness, for the purpose of detecting this particular phase transition, of the experimental method used. The result may be that an anomaly interpreted as a phase transition may remain in the literature without the nature of the alleged new phase being identified, and without further evidence for or against the transition being published. Papers giving proof of the non-existence of a phase transition are rare, although they do exist [3].

We suggest that it is desirable to consider setting standards of acceptable proof in the publication of claims for new phase transitions, similar to those which must be met when a new compound is reported.

PHASES AND PHASE TRANSITIONS

It is generally accepted within thermodynamics that a phase is that part of the system which is chemically and physically uniform throughout. Different solids, whether the chemical composition is the same or not, constitute different phases.

A phase transition is a process: one phase disappears and another phase takes its place. A phase transition can be characterized by means of the values of the relevant thermodynamic variables at the transition, which include chemical composition, temperature, pressure, latent heat and entropy of transition. A large body of calorimetric data on the thermodynamics of phase transitions is to be found, for example, in the work of Professor Edgar F. Westrum, Jr.

A classification of transitions was introduced by Ehrenfest in which the order of the transition is defined as the lowest order of differential coefficient of the Gibbs energy which shows a discontinuity on the transition line [4]. While this classification scheme has been useful in drawing attention to the different types of transition, it is of limited application since as the order increases it becomes less clear that the process represents a change from one phase to another, because the discontinuity becomes less significant. In practice, it is the first- and second-order transitions that fit experimental data best.

A more practical approach has been to classify phase transitions in terms of the mechanism responsible for the phenomenon, e.g. order–disorder transitions (which include positional, orientational and magnetic disorder), and soft mode transitions influenced by the lattice vibrations. Progress in these studies has occurred because of the development of sophisticated experimental techniques, not all of which are thermodynamic.

If the latent heat of a transition is not zero, it is possible to detect the transition by means of the transfer of heat into or out of the system. Many first-order transitions have been determined unambiguously by DTA or DSC methods based upon detection of the latent heat of transition. In adiabatic calorimetry the latent heat shows up as an enormous narrow peak in the apparent heat capacity. An example is to be found in ref. 5. It is not unusual for first-order transitions to be "non-isothermal" [6], and to have a correspondingly lower value of the peak heat capacity. When a heat capacity peak becomes extremely diffuse, the interpretation as a first-order phase transition becomes controversial; an example of such a feature can be found in ref. 6. Further complexity is encountered in cases of non-stoichiometric crystals, or where there is a disproportionation reaction in the solid [7].

If the latent heat is zero, the transition must be detected by measuring a change in some thermodynamic, spectroscopic or structural property when the system changes from one phase to the other. In such a case, proof of the existence of a phase transition requires proof that the system is in a different phase on either side of the alleged transition. The focus of attention must be shifted from the phase transition itself to differences between the properties of the two phases.

An analogy might be drawn between phase transitions and chemical reactions. A chemical reaction takes place when the reactant substances disappear and other substances are formed. The heat of reaction can be used as evidence of the existence of a chemical reaction, but the reaction can be properly described only by specifying the substances involved. Study of the reaction therefore requires identification of the reactants and products.

THE PROBLEM

The problem of identifying phase transitions on a firm experimental basis can be split into two parts. First-order transitions can be observed directly using relatively simple apparatus to record the latent heat. However, hysteresis in first-order transitions, and the existence of metastable phases [8], can lead to disagreements between different observers. In the case of higher-order transitions, the transition can only be detected by a change in properties, and it sometimes turns out that the changes are so small that it is difficult to measure them with sufficient precision to yield an unambiguous interpretation. In these cases controversy is likely to arise.

A SUGGESTED RESOLUTION

In order to avoid the introduction of phase transitions as "explanations" for observed anomalies, it might be reasonable to require that in the absence of clear evidence of a latent heat, a claim for a phase transition should be based on identification of each of the phases involved.

How much characterization is required for the phases involved in a higher order transition? The answer to this question will vary from case to case. A sharp discontinuity in the heat capacity, a sharply defined split in a line in a Raman or NQR spectrum or a discontinuity in one of the bulk properties such as density or electrical conductivity would be adequate evidence in most cases. In principle, a demonstration of a change in crystal structure by X-ray or neutron diffraction studies of both phases should be convincing, but even here there are difficulties. Ambiguities may arise in the interpretation of diffraction data, which lead to disagreements between different observers as to whether or not a new phase has been detected. An example is to be found in the literature of ammonium perchlorate [9,10]. Thus, although the International Union of Crystallography has set a standard for the publication of powder pattern data [11], which should in principle resolve the matter, ambiguities can still arise in some cases. The existence of polytypes [12] adds to the possibilities for controversy.

A set of criteria for the authentication of new chemical compounds is published annually in the Dalton Transactions of the Chemical Society [13]. A set of criteria for the authentication of new phases based upon these as a model might read as follows: "A phase is considered as new (a) if it has not been prepared before, (b) if it has been prepared before but not adequately purified, (c) if it has been purified but not adequately characterized, (d) if, earlier, it has been assigned an erroneous crystal structure, or (e) if it is a mineral isolated for the first time. In preliminary communications, phases are often recorded with limited characterizing data".

It is not clear whether application of such a set of criteria would serve to avoid controversy, but they would at least focus attention on the importance of characterizing the phases on either side of a higher-order phase transition rather than on observations of anomalous behaviour. It is clear that if a new phase transition is observed, there must be a new phase (unless the transition is to an already-known phase), and the criteria above can be applied. If it is not possible to authenticate the presence of a new phase, then the anomaly in the experimental results should remain as an anomaly requiring further investigation, and any mention of a phase transition is inappropriate.

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