THE POSSIBILITY OF USING REFERENCE POINTS
IN THE PRESSURE SCALE

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The differences between the polymorphic transition temperatures in the "reference" metals Tl, Cs, and Ba found by different authors for different samples may be accounted for by hysteresis being present in these transitions of the first kind, the amount being essentially dependent on the experimental conditions (nature of the stresses produced in the sample). In view of this, it seems better to calibrate high pressure apparatus from measurements on a number of independent physical phenomena under pressure, such as the pressure dependence of electrical resistance, melting points, compressibility, etc.

High pressure studies above 50,000 kg/cm² are as a rule made on equipment that requires a pressure calibration. The calibration consists of finding the relation between the pressure in the operating volume of the apparatus and the applied load. To this end, a pressure scale is used based on fixed pressure points—known values of phase transformation pressures at known temperatures.

The present paper discusses possible discrepancies in the experimentally determined phase transition parameters which can occur as a result of using some particular kind of apparatus, and along with this, ways of using known transition pressures as reference points in the pressure scale.

At the present time, the most widely used pressure scale is the one for which the reference points are the transition pressures observed from a jump in the electrical resistance of bismuth, thallium, cesium, and barium at room temperature. These transitions were first studied by Bridgman, [1], and his data have so far been used for calibration. However, there are appreciable discrepancies between the values of the transition pressures

in the above elements as found by Bridgman from measuring the electrical resistance and the bulk compressibility, and this has led to a need to recheck the transition parameters.*

The paper by Kennedy and La Mori [2] gives new data on the phase transformations in Bi, Tl, and Cs at 25°C, obtained from volume measurements.

The table gives values of the transition pressures in Bi, Tl, and Cs, found by various authors using different methods.

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* It should be noted that the discrepancies between the values for the transition pressures in Tl, Cs, and Ba found from the jump in volume and from the jump in electrical resistivity at the transition are hard to account for as a systematic error in the way the pressure was measured in [1]. While Tl, Cs, and Ba gave values for the transition pressures greater than the parameters found previously from the volume jump, Sr gave a value for the transition pressure of 46,000 kg/cm² instead of the value 65,000 kg/cm² found previously from the volume jump.

Phase Transition Pressures of Bi, Tl, and Cs (kg/cm²) at Room Temperature

Transition	Bridgman		Kennedy and La Mori*	Boyd and England
	volume measurement	electrical resistance	volume measurement	electrical resistance
BiI — BiII	25.420 [4]	24.700 [6]	25.911±97 †	—
BiII — BiIII	26.960 [4]	26.600 [6]	27.507±194	—
CsI — CsII	23.000 [5]	22.070 [6]	23.046±612	—
CsII — CsIII	45.000 [8]	54.950 [1]	42.624±1020	—
TlII — TlIII	40.000 [7]	45.000 [1]	37.414±112	37.730

* Kennedy and La Mori give their data in bars. The table gives the transition pressures in kg/cm², from the relation 1 bar = 1.01972 kg/cm².
† The uncertainties given show the hysteresis observed in the transition.

It may be seen from the table that at pressures above 25,000 kg/cm^2, the discrepancies in the data get as high as 30%. On this basis, Kennedy and La Mori made the assumption that the values for the transition pressures in barium, found by Bridgman from the jump in electrical resistance at 80,000 kg/cm^2, and in bismuth, found by Bandy at 125,000 kg/cm^2, are too high by ~30%.

An additional comparison of the results of studies on a number of substances made on Kennedy and La Mori's equipment with similar work done on the same substances under purely hydrostatic pressure shows the following. The transition point in thallium found by Kennedy and La Mori to be 37,414 kg/cm^2 lies near the TlIII—TlII transition branch of the p, T diagram for Tl found for pure hydrostatic pressure [9], i.e., along a line corresponding with "superheating" (transition from the more dense to the less dense modification).

The limit of coexistence between the high and low pressure phases InSbI—InSbII, found using equipment similar to that described by Kennedy and La Mori [10], coincides almost exactly with the "hot" boundary of the InSbI—InSbII transition on the p, T diagram of InSb taken for purely hydrostatic pressures [11], with, as in the case of thallium, the InSb I—InSb II transition occurring with considerable hysteresis under hydrostatic pressure.

Thus, a comparison of these data with the values for the transformation hysteresis observed by Kennedy and La Mori (see table) shows that in addition to the large discrepancies mentioned above in the values of the transition pressures, especially for thallium and cesium, there is also a large discrepancy in the values for the hysteresis of the transitions studied.†

Having hysteresis in these transformations is, generally speaking, not very surprising, since hysteresis is the usual phenomenon in phase transitions of the first kind such as these transformations are. The hysteresis may be accounted for by the fact that it is usually rather difficult to satisfy the conditions for establishing true equilibrium in the system. If however it is in some way possible to make the system approach the equilibrium state, it is obvious that there will be less hysteresis. Theoretical considerations and the experimental facts also show that the hysteresis in a transformation as a rule increases as the temperature of the transformation is reduced, and that the hysteresis may be reduced to where it disappears completely by increasing the temperature of the transformation [9, 12]. A large effect is exerted on the pressure and temperature of the transformation, as well as on the hysteresis associated with it, if there are impurities in the substance undergoing the phase transformation.

The experimentally determined values of the transition pressure given in the table are the mean of the transition pressures when raising and lowering the pressure in the experiment. It may be shown that these values are not the equilibrium parameters of the transition, i.e., they do not define the pressure at which the thermodynamic potentials of the two phases are equal. The probability of a transition between two phases will be greater, the greater the energy of the atoms and the lower the activation energy of the transition. At low temperatures (small kT) the activation energy is considerably greater than the energy of the atoms, and hence the transition probability is relatively small, i.e., the transition accompanies superheating and supercooling (for practically realizable rates of change in the temperature and pressure of the system). However, true equilibrium is not reached exactly at the temperature found by averaging the transition temperatures found in heating and cooling. The transition probability increases as the temperature is raised, while it drops as the temperature is lowered. Thus, the superheating is, as a rule, small in comparison with the supercooling. We have a similar picture in isothermal phase transformations, i.e., where the transition is brought about by raising and lowering the pressure. In this case, the transition probability and the associated transition rate decrease as the pressure is increased, and, conversely, increase as the pressure is dropped. In this sense, increasing the pressure is equivalent to lowering the temperature. Accordingly, it may be concluded a priori that the mean values of the transition temperature and pressure from the "direct" and "reverse" processes (raising and lowering the temperature or pressure in the isobaric or isothermal process respectively) are not the equilibrium phase transformation parameters, when appreciable hysteresis is present. Obviously, the true equilibrium curve in the p, T plane must pass closer to the superheating line and not through the averaged points between the superheating and the supercooling lines. This is made clear by the figure, where a possible position of the equilibrium line between the two phases is shown dotted.
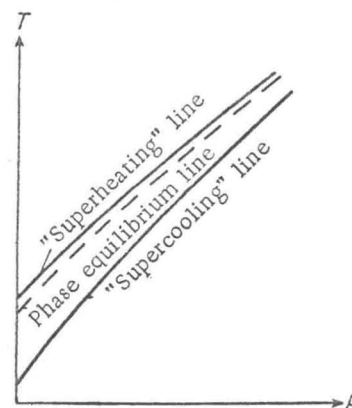
In [2, 10], the measurements were made under quasi-hydrostatic conditions, where the conditions of the experiment, the lack of packing rings, and the rotation of the piston leave reason to suppose that displacement forces were acting [14].

† For bismuth under hydrostatic conditions, a hysteresis of 1000 kg/cm^2 was found for the Bi I—Bi II transition, and 900 kg/cm^2 for Bi II—Bi III [13].

It might be expected that these conditions would bring the substance close to an equilibrium state, thus greatly reducing the hysteresis (see table). In the case of bismuth, where the hysteresis in the transitions is in general small, there is no reason to expect any large discrepancies in the mean values found for the transition pressures.‡ Unfortunately, there are no data on the transition hysteresis in cesium and barium taken under purely hydrostatic conditions, and so it is impossible to say anything very definite about the transitions in these elements. It must however be kept in mind that since the viscosity and internal friction in the material increase at high pressures, it is to be expected that the transitions in cesium, barium, bismuth and other solids at very high pressures will occur with a large amount of hysteresis. Bridgman, who repeatedly made studies on different materials under high pressure with displacement stresses applied at the same time, came to the conclusion that such stresses can have a substantial effect on the sharpness and rate of occurrence of the transition, and in some cases could apparently even shift the phase equilibrium line. Bridgman has written in [15] that under high displacement stresses the transition in Tl was found to occur at room temperature at 25,000 kg/cm². The principal effect of the displacement forces, in Bridgman's opinion, is to reduce the viscous forces which prevent the transition from developing or possibly even from occurring at all.

In any actual case of working with apparatus of a definite type, some account must be taken of what kinds of stresses can be produced in the sample, and with this in mind one must be more careful about using a pressure scale based on the "new" (Kennedy and La Mori) or "old" (Bridgman) pressure reference points. Depending on the conditions under which the apparatus is operating and on the calibrating samples themselves (for example, degree of contamination, cold working, the medium transmitting the pressure, etc.), the mean transition pressures found from increasing and then decreasing the pressure may be appreciably different from either set of reference values.**

Note also that it is apparently best to calibrate on the way down (corresponding to "superheating" a material), since in this case "supercooling" is eliminated. The transition will be sharper and more rapid when the pressure is being lowered, because the transition probability is higher than when the pressure is being raised. This also helps to get a more accurate calibration.

Zhokhovskii's papers [16, 17] have developed the idea of creating a pressure scale based on phase equilibrium phenomena in single-component systems, i.e., regarding the pressure as the thermodynamic parameter which determines the state of the substance. Making an experimental determination of how the melting points of a number of materials vary with the pressure, representing the data as a functional relationship, and making a reasonable extrapolation of the function to the higher pressure range is a practical way of setting up such a pressure scale. However, the uncertainty in the pressure in an extrapolation from 30,000-100,000 kg/cm² or higher may turn out to be just as great as the spread in the values of the polymorphic transition pressures given above. At these high pressures, phenomena may be encountered which are completely new and unforeseen by the theory. An example of this is provided by the maxima in the melting curves observed for rubidium, cesium, and tellurium at high pressures, which is hard to explain, even if there are polymorphic transitions under pressure in these elements. It is therefore more nearly right to construct a superhigh pressure scale which is not based on any single phenomenon but on a number of independent phenomena occurring under pressure, for example the variation of electrical resistance with pressure, melting points, compressibility, etc., as has already been pointed out in Zhokhovskii's papers and in the discussion in [2]. A pressure scale constructed in this way will evidently be much more reliable.

In conclusion, I tender profound gratitude to E. G. Ponyatovskii for furnishing data on the phase diagram of InSb, as well as to Yu. N. Ryabinin, L. D. Livshits, and V. K. Markov for discussion of the work and valuable comments.

Summary

1. It is shown that for phase transitions accompanied by hysteresis, the mean values found from going "up" and "back" (raising and lowering the temperature or pressure) are not the same as the equilibrium thermodynamic parameters of the transitions, because of the fact that superheating and supercooling (transition from a more dense to a less dense phase and the other way around) are not equally probable. The true thermodynamic phase equilibrium line will gravitate toward the "hot" boundary, i.e., toward the superheating line (transition from a more dense to a less dense phase).

‡ In [13] impurities were found to have a large effect on the transition pressure in bismuth, which may serve to explain the well known discrepancies between the transition parameters found with different samples.

** The effect which the medium used to transmit the pressure has on the mean values found for the transition pressures been shown by Boyd and England [3]. In investigating the transitions Bi I – Bi II – Bi III in experiments where the pressure-transmitting media were AgCl, talc, Bn and pyrophyllite, they observed that there was a substantial change in the transition hysteresis, principally as a result of shift in the "cold" boundary, i.e., the transition pressure when the pressure was being raised. Thus, the mean transition pressures change in value, depending on the solid medium used to transmit the pressure. Even in work where the test substance itself is the medium transmitting the pressure, it is obvious that the transition parameters found will be functions of the various stresses occurring in the sample, i.e., they will be functions of the apparatus used to make the tests.

2. The discrepancies between the values for the polymorphic transition pressures in solids, in particular in Cs, Tl, and Ba, as found from different samples by different authors, may be accounted for by the hysteresis in these transitions of the first kind, which is essentially dependent on the experimental conditions (nature of the stresses produced in the sample).

3. In view of this, a pressure scale based on fixed values of the transition pressures in solids is very arbitrary, and depends on the type of apparatus used to measure the transition parameters.

4. Calibrating high pressure apparatus from the changes in a number of independent physical phenomena occurring under pressure, such as the change in electrical resistance with pressure, melting points, compressibility, etc., will obviously be more reliable.

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