

curves in certain of their porous samples which were more nearly consistent with the properties of coesite.

An equation of state for stishovite was first constructed from Wackerle's data by McQueen *et al.* (1963). These authors felt that the high-pressure phase was probably a dense silica glass whose short-range order was stishovite. Other authors, Anderson and Kanamori (1968), Ahrens *et al.* (1969), and Ahrens *et al.* (1970), have constructed different equations of state for stishovite based on alternative formulations or on newer thermodynamic data. The various shock loading, static loading, and thermodynamic data on stishovite are summarized by Davies (1972), who constructed a new equation of state for both stishovite and the "coesite-like" phase observed by Trunin *et al.* (1971b). All equations of state rely heavily on the shock compression data; there are unresolved differences among the various treatments and the measured thermodynamic constants of stishovite.

High-pressure x-ray diffraction studies on stishovite and coesite by Bassett and Barnett (1970) showed a bulk modulus for stishovite which was in significant disagreement with that derived from the shock data, constrained to an initial density of 4.29 Mg/m<sup>3</sup>. They suggested that the high-pressure shock-loaded material might be a mixture of small stishovite crystallites and a short-range order glass. Consideration of heterogeneous melting for quartz just above the HEL, discussed in Sec. VI.C, lends credence to this view and raises questions as to whether the high-pressure phase obtained under shock loading is a pure solid stishovite phase. Primak (1975) has expressed the opinion that the high-pressure phase is not stishovite, but is most likely a dense ordered array of oxygen atoms with disordered silicon atoms.

Finite transformation rates for the 14.4 GPa transition are indicated in the sample thickness dependence measurements of Al'tshuler *et al.* (1965) and the unusually small compressibility in the mixed phase region. Podurets and Trunin (1971) have given qualitative consideration to reaction rates to account for Wackerle's data in the mixed phase region. Podurets and Trunin (1974) have used the data in the mixed phase region to calculate nuclei sizes. Calculations of this sort are clouded by the heterogeneous melting upon yielding described in Sec. VI.C.

Attempts by DeCarli and Jamieson (1959) to recover dense quartz from shock-loaded single crystals were unsuccessful; however, they did recover amorphous quartz. DeCarli and Milton (1965) successfully recovered stishovite but no coesite from shock-loaded crystalline quartz. Deribas *et al.* (1968) have recovered both stishovite and quartz in shock-loaded porous quartz samples. Stishovite is apparently easier to recover than coesite under shock loading. It is noteworthy that the opposite is true of dense quartz recovered from meteorite craters. German *et al.* (1973) have recently reported recovery of a dense orthorhombic form of quartz from samples shock-loaded between 35 and 90 GPa.

Both coesite and stishovite have been recovered from meteorite craters. The discovery of naturally occurring coesite by Chao *et al.* (1960) and of naturally oc-

curing stishovite by Chao *et al.* (1962) was in Meteor Crater, Arizona. A summary of coesite and stishovite recovered from meteorite craters is given by Stoffler (1971). Coesite has been found in seven craters, whereas stishovite is found in only two. Coesite is also found to be more abundant than stishovite. The broader area of changes in quartz rocks in meteorite craters is summarized by Chao (1967) and in a very comprehensive review by Stoffler (1972).

Wackerle's observation of compacted fused quartz recovered after shock loading to 25 GPa is similar to that observed by Roy and Cohen (1961), who observed permanent densification of fused quartz above hydrostatic pressures of 2 GPa. A comprehensive treatment of compaction phenomena in fused quartz is given by Primak (1975).

Evidence for a low-pressure transition in fused quartz is reported by Graham (1971), who determined second-, third-, and fourth-order longitudinal elastic constants from shock loading experiments of Barker and Hollenbach (1970). Above a compression of 6% the elastic constants were found to increase with stress in the normal manner. Similar behavior has been observed by Bridgman (1948). This is apparently a higher-order transition.

The  $\alpha$ - $\beta$  quartz transition under shock loading has been investigated by Gauster *et al.* (1973), who used stress pulse measurements in crystalline quartz samples, pulse heated in 50 ns with a high-energy electron beam machine. Their observations between 250 MPa and 2 GPa at temperatures from 495 to 1635 K are consistent with the high-pressure phase measurements of Cohen and Klement (1967).

## K. Hydrogen

The possibility of producing metallic hydrogen at very high pressures has long been a subject of interest and speculation. Wigner and Huntington (1935) appear to have been the first to suggest that such a transition might occur; they estimated the pressure of transition to be not less than 25 GPa. When 100 GPa pressures began to be achieved in shock waves, there was some hope that they might provide a means for direct observation of the metallic state. In order to achieve the required pressures in a shock wave, it is necessary to precompress the hydrogen to a substantial density. Even so, it turns out that the heating that accompanies shock compression is so great as to eliminate any possibility of producing the required transition. This difficulty has in turn led to consideration of implosion techniques for isentropic compression (Hawke, *et al.*, 1972; Hawke, 1977; Lubkin, 1976; Grigor'ev *et al.*, 1972). Shock compression experiments have helped to improve theoretical estimates of the transition pressure, but there still exists no definitive answer to the question of metallic transition. Shock experiments and their interpretation have been summarized by Ross (1974), Van Thiel *et al.* (1974), and Ross *et al.* (1975). In the meanwhile Vereshchagin *et al.* (1975) has reported observations of a conducting phase in hydrogen under static compression to about 100 GPa.



## V. SECOND-ORDER PHASE TRANSITIONS

In contrast to first-order phase transitions, which are characterized by discontinuities in volume and entropy, second-order phase transitions involve phases for which volume and entropy are continuous, but higher derivatives of energy, specific heat, compressibility, and thermal expansion are discontinuous. The Ehrenfest relations, which interrelate the variables changing at the transition, are

$$\Delta\beta_T = \Delta\alpha(dT_C/dP),$$

$$\Delta C_p = TV\Delta\alpha(dT_C/dP)^{-1}, \quad (76)$$

where  $\beta_T$  is isothermal compressibility,  $\alpha$  is volume thermal expansion coefficient,  $T_C$  is critical temperature,  $P$  is pressure,  $C_p$  is specific heat at constant pressure,  $T$  is temperature,  $V$  is specific volume, and  $\Delta$  indicates the change at the critical temperature and pressure.

Based on Eqs. (76), the most apparent manifestation of a second-order phase transition in a shock-loaded solid will be a pronounced change in compressibility at the critical pressure and temperature. This change in compressibility should be apparent from stress-volume measurements that characterize the compressibility both below and above the transition. In situations where compressibility decreases, the transition should also be indicated with time-resolved detectors by a sudden decrease in rise time of a plastic wave above the critical pressure.

If the transition is to be significant enough to be detected, it is apparent from Eqs. (76) that the critical

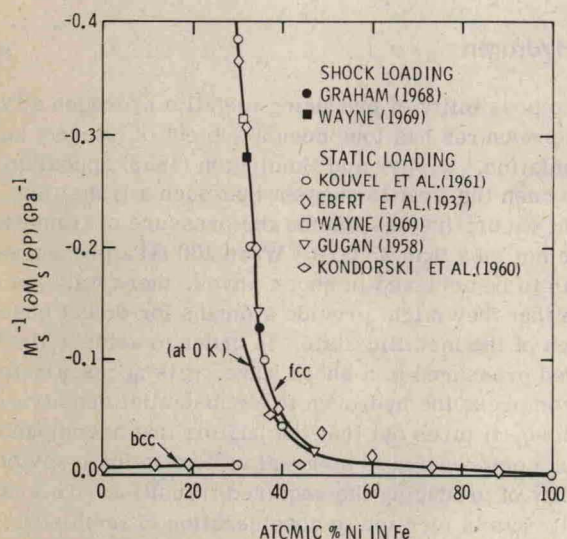


FIG. 29. The relative change in saturation magnetization with pressure is a strong function of composition for the iron-nickel alloy system. Alloys with nickel contents less than about 28 at. % are stable in the bcc phase and have magnetizations that are insensitive to pressure. Alloys with nickel contents greater than about 28 at. % are stable in the fcc phase, and for compositions between 28 and 40 at. % Ni the magnetizations are very sensitive to pressure. A similar effect is noted for the pressure dependence of the Curie temperature. Pressure sensitive magnetic properties lead to higher-order phase transitions, which have been observed under shock and static loading.

temperature must be sensitive to pressure. Such behavior is not common, but certain ferromagnetic alloys have Curie temperatures that are highly sensitive to pressure. Figure 29 shows measurements of the pressure derivative of the saturation magnetization of the iron-nickel alloy system. (The change in saturation magnetization with pressure is directly related to the change of Curie temperature with pressure. See Kouvel, 1963.) For compositions less than 28 at. % Ni, the alloys are stable in the bcc phase and are characterized by magnetizations that are insensitive to pressure. From the previous discussions of bcc iron alloys, it is apparent that these alloys would be expected to go through polymorphic phase transitions at pressures much less than the Curie point transition. On the other hand, alloys with Ni content greater than 28 at. % Ni are stable in the fcc phase and, in the vicinity of 28 at. % Ni, show unusually large sensitivity of magnetization to pressure. Accordingly, fcc Fe-Ni alloys with compositions in the vicinity of 28 at. % Ni are the most likely candidates to undergo pressure-induced, second-order phase transitions.

Curran (1961) considered the possibility of second-order phase transitions in iron and in Invar, a 36 wt. % Ni-Fe alloy. His analysis was directed toward the possibility that a multiple shock wave structure would be produced by the transition. His experiments on Invar under explosive loading did not show a multiple wave structure; however, the stress-volume curve showed a gradual decrease in compressibility as the stress was increased. The experiments did not positively identify a second-order phase transition.

Graham *et al.* (1967) reported an investigation of the stress-volume relation of a 28.4 at. % Ni-Fe alloy under impact loading. This alloy was chosen for study because the Curie temperature is highly sensitive to pressure and the expected transition at 2.5 GPa is well within the stress range for which the quartz gauge can provide accurate, time-resolved wave profile measurements. Furthermore, with projectile impact loading, data could be obtained in the immediate vicinity of the transition.

The stress-volume curve obtained by Graham *et al.* is shown in Fig. 30. A pronounced decrease in compressibility is observed at 2.5 GPa. Furthermore, the decrease in compressibility is manifested by a dramatic decrease in rise time of the plastic wave for input stresses just above 2.5 GPa. After a correction for shear strength at the HEL, the computed value for  $dT_C/dP$  from the shock loading investigation is in excellent agreement with static compression measurements. Thus, this study provides quantitative identification of the pressure-induced, second-order, ferromagnetic-to-paramagnetic transition in this fcc iron alloy and provides thermodynamic data on the change in variables at the transition. Given these data on 28.4 at. % Ni, it is apparent that the behavior of Invar observed by Curran was a consequence of a similar ferromagnetic-to-paramagnetic transition. For some unknown reason, the change in compressibility in that alloy is more gradual.

To further investigate the behavior of Invar, Graham (1968) measured the magnetization change under impact loading from 3 to 20 GPa. The measured coefficient is