effect of thermal excitation of conduction electrons becomes important. In simple metals this effect has conventionally been taken into account by adding the "electronic terms" $\varepsilon_e = \frac{1}{2}\beta\theta^2$, $p_e = \frac{1}{2}(\gamma_e/v)\beta\theta^2$ to the energy and pressure sums, respectively, appearing in the Mie–Grüneisen equation [71Z2, 66Z1]. These contributions follow from the fact that internal energy and pressure increase as θ^2 for a degenerate electron gas and in approximately this manner to temperatures of 30 000 to 50 000 K following other models. Assuming the θ^2 dependence to be exact, the coefficients β and γ_e, called the *electronic specific heat* and *electronic Grüneisen parameter*, respectively, are functions only of specific volume. The values of γ_e suggested (usually $\frac{1}{2}$ or $\frac{2}{3}$) are not too different from the lattice γ at large compression, so neglect of this term may not greatly influence the estimation of $p_c(v)$ from Hugoniot data. Proper inclusion of the electronic excitation is necessary, however, if temperatures exceeding a few thousand kelvins are to be estimated accurately.

It has been known for some years that this simple treatment is inadequate for ionic crystals and transition metals [65A2] and, indeed, for many other substances. Since γ_e actually depends on the details of the electronic band structure of the material, it can vary significantly.

The particular case of rubidium has been considered by Grover [71G4] and Ross [72R2]. Interest arose in this case because of a disagreement between static and shock measurements of compressibility. The possibility that anomalous electronic behavior was involved was suggested by the occurrence of an electronic transition in cesium at 4.5 GPa. Ross was able to show that the shock compression of rubidium produced a sufficiently great change in the band structure of this material that the high temperatures also present were sufficient to excite electrons into an upper band and thus significantly lower the thermal pressure.

3.2.7. Extended equations of state

The development of digital computers and the associated software necessary for solving complex flow problems has given rise to the need for equations of state covering extended ranges of the state variables. Such equations of state are developed on the basis of a broad range of theoretical and experimental information. Usually they cover the entire range of solid behavior, and extend to molten and vaporized states. Shock-compression experiments cover only a small portion of the range of interest, but are unique in providing the only data at both high temperature and high density. Since shock-compressed solids may melt or vaporize on decompression, access is also provided to states of high temperature and low density.

It is usual to represent the most extreme states of high temperature and both high and low density by the relatively simple theoretical models valid in these regions, while the states that are both more accessible to experimental observation and more difficult to describe theoretically are represented by semi-empirical models fit to experimental data. Because of the range of states covered by these models, they are presented in the form of distinct functional or tabular relations covering various regions. Emphasis is laid on thermodynamic consistency and validity under various limiting conditions of temperature and density. Two widely used families of equations of state of this sort are implemented in the CHART D [72T2] and GRAY [71R4] computer codes.

Shock-compression and other data are also used to develop more detailed equations of state for various materials on a case-by-case basis. Andrews [73A2] has marshaled a variety of theoretical and experimental information to construct a detailed equation of state for the α and ε phases of iron. Johnson et al. [74J2] have developed a simple but very satisfactory description of the solid I, solid II and liquid phases of bismuth using the Mie–Grüneisen model with γ/v and C_v held constant. Equations of state describing the behavior of a number of solids are included in the SESAME

[78B2] library. Skidmore and Morris [62S2] and Barnes [75B2] have described applications of shock-compression data to the development of equations of state of uranium and sodium, respectively, in low pressure, high temperature regions of interest in nuclear reactor analyses.

3.2.8. Comparison of shock-compression and other data

Matter can be compressed by static means as well as shock loading, and comparison of the data obtained by these two methods permits testing the basic assumptions made in each case. Agreement, as a whole, is sufficiently good and wide-spread that significant disagreement in a particular instance is possible evidence for occurrence of unrecognized or unquantified physical phenomena. The comparability of shock- and static-compression data takes on a particular significance when the former are involved in determination of pressure standards for static measurements. This standardization takes two forms: (1) use of phase-transformation pressures measured in shock-compression experiments for fixed-point calibration and (2) use of isotherms calculated from Hugoniot data to calibrate marker materials for use as continuous-reading internal standards when static measurements are made by X-ray diffraction (for recent reviews of this work, see Decker et al. [72D2] and Bassett and Takahashi [74B1]).

Static- and shock-compression data are commonly compared on the basis of the pressure along room-temperature isotherms although a more sensitive, and perhaps more revealing, comparison can be made in terms of the bulk modulus and its various pressure derivatives. Comparison of pressure is most appropriate in the case of calibration standards and for certain geophysical investigations, whereas comparison of moduli is necessary in more basic equation-of-state studies.

The use of phase transformation pressures determined by shock compression for fixed-point calibration of static measurements is an important application that is presently a subject of some debate. Duvall and Graham [77D6] carefully compared determinations of the onset of phase transformations by the two methods and found good agreement in most cases. Nevertheless, there is abundant evidence that shock-induced transformations are subject to influences other than pressure and temperature so that particular cases must be critically examined before the shock data are used to establish fixed-point calibrations.

Isotherms derived from shock data have been compared with Bridgman's isotherms since the earliest days of this research, but the improved static and ultrasonic methods developed in recent years have now provided much more dependable sources of data for comparison. Some recent comparisons to Bridgman's pressures occur in works of Carter et al. [71C2], Fritz et al. [71F2], and Carter [73C3]. Similar comparisons to more recent data are those of Drickamer et al. [66D4]. Their static data were taken by X-ray diffraction methods and were compared to a few very early shock experiments [57C1] on alkali halides. The compressions reach about 40 per cent in the more compliant materials and the disagreement in compression at a given pressure is a few per cent. The data of Drickamer et al. on NaCl and LiF have since been found to be in excellent agreement with more recent shock data of Fritz et al. [71F2] and Carter [73C3], respectively, but their data on NaF fail to agree with most other data on this substance and are also in poor agreement with Carter's [73C3] shock isotherm. Carter's (p, v) data on NaF are in good agreement with those of Olinger and Jamieson [70O2] and Spieglan and Jamieson [74S6], although a systematic divergence at high pressure is apparent, so the agreement of the pressure derivative of the modulus is much less satisfactory.

The extensive group of static-compression experiments of Vaidya and Kennedy [70V1, 71V2] and Vaidya et al. [71V1] have been compared to shock-compression data and this comparison