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Critical Evaluation of the Thermodynamic Properties of Cobalt

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The thermodynamic properties and the pressure–temperature phase diagram of Co have been evaluated from experimental information using thermodynamic models for the Gibbs energy of the various phases. For hcp and fcc Co the model describes the magnetic contribution to the molar volume, expansivity, and compressibility and the efect of pressure upon the Curie temperature. Experimental data of many different types are satisfactorily described by the evaluated model parameters.

KEY WORDS: cobalt; compressibility; density; enthalpy; Gibbs energy; heat capacity; molar volume; thermal expansion; transition temperature.

1. INTRODUCTION

The thermodynamic properties of Co have been studied experimentally in considerable detail. Most of the studies have been performed at atmospheric pressure and consist of measurements of the thermodynamic properties of the hcp and fcc phases. Some thermodynamic data obtained at high pressures concerning the effect of pressure on the volume of the hcp phase and the hcp/fcc equilibrium temperature have also been published.

The thermodynamic data have been reviewed several times. The data available in 1960 were reviewed in the *Cobalt Monograph* [1] together with data on other physical properties. Specific compilations of the thermodynamic data were performed by Hultgren et al. [2], Touloukian and Buyco [3], and Hultgren et al. [4]. The thermodynamic and general physical properties were reviewed by Betteridge in two recent works [5, 6], and finally, the most recent review of thermodynamic data was performed by Nishizawa and Ishida [7].

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The thermal expansion data have been reviewed by Touloukian et al. [8], and the compressibility data by Kennedy and Keeler [9]. Finally, the experimental information on the P–T diagram has been reviewed by Young [10] and, more recently, by Nishizawa and Ishida [7].

These previous assessments of experimental data were performed by considering separately each type of information and by comparing the accuracy of the pieces of information from various sources. An alternative procedure is used in the present work. It is based upon the fact that all the measurable properties of the substance can be expressed in terms of first and second derivatives of the Gibbs energy with respect to T and P and may thus be treated simultaneously if a model for the Gibbs energy of the substance as a function of T and P is adopted. A model of that type is used in the present work. It is based upon the phenomenological description of the magnetic [11] and the nonmagnetic [12] contributions to the Gibbs energy of the substance. Hence, the model is particularly useful for the treatment of the thermodynamic properties of the 3d-ferromagnetic elements Fe, Ni, and Co. In a recent work it was shown that the model can describe satisfactorily the thermodynamic properties and the P–T diagram of Fe [13]. We now present the results of a similar treatment of the properties of cobalt.

2. THERMODYNAMIC MODELS

2.1. General Considerations

The Gibbs energy per mole of cobalt is written as the sum of two contributions, a nonmagnetic and a magnetic one:

$$G_{\mathrm{m}}(T, P) = G_{\mathrm{m}}^{\mathrm{nmg}}(T, P) + \Delta G_{\mathrm{m}}^{\mathrm{mg}}(T, P) \tag{1}$$

The magnetic contribution represents the effect upon $G_{\mathrm{m}}(T, P)$ of variations in the degree of magnetic ordering, and the nonmagnetic contribution describes the effects of change in T and P upon the nonmagnetic energy and entropy of the assembly of the metal ions and conduction electrons. For describing the effects of T and P upon these contributions, a phenomenological approach is adopted, using the following expression:

$$\begin{aligned} G_{\mathrm{m}}(T, P) - H_{\mathrm{m}}^{\mathrm{SER}} = {} & [H_{\mathrm{m}}(T_0, 0) - H_{\mathrm{m}}(T_0, P_0) - S_{\mathrm{m}}(T_0, 0)T] \\ & - \int_{T_0}^{T} \left(\int_{T_0}^{T} \frac{C_{\mathrm{P}}^{\mathrm{nmg}}(T, 0)}{T} \, dT \right) dT \\ & + \int_{0}^{P} V_{\mathrm{m}}^{\mathrm{nmg}}(T, P) \, dP + \Delta G_{\mathrm{m}}^{\mathrm{mg}}(T, P) \end{aligned} \tag{2}$$

The first term involves the properties of the substance at the reference temperature T_0 and pressure P_0 and also at $P=0$. In the present assessment the reference state recommended by the SGTE (Scientific Group Thermodata Europe) [14] is adopted. It is denoted by the superscript SER (stable element reference) and is defined as the stable state at $T_0=298.15$ K and $P_0=0.1$ MPa.

2.2. The Nonmagnetic Contribution to the Gibs Energy

Below the melting point the nonmagnetic contribution to the heat capacity, $C_\mathrm{P}^\mathrm{nmg}(T, 0)$, is described by a polynomial with positive and negative powers whose coefficients are evaluated from experimental data.

$$C_\mathrm{P}^\mathrm{nmg}(T, 0) = -(c+2dT+6eT^2+2fT^{-2}) \tag{3}$$

The term with T^{-2}, which may be related to the leading term of the Thirring–Stern [15] high-temperature expansion for the lattice heat capacity, was included in Eq. (3) in order to describe the C_P data for hcp Co below room temperature. The quadratic term was included in order to describe the deviation from the linear behavior caused by anharmonicity and vacancy formation, which are appreciable when approaching the melting point.

Due to the lack of information for hcp Co at high temperatures and for fcc Co at low temperatures, it is not possible to evaluate all four parameters, c, d, e, and f, for either of the phases. As a reasonable approximation, it was instead assumed that they all had the same values in the two phases.

Above the melting point T_f a method of extrapolation recently adopted by the SGTE organization [14] is used which makes the heat capacity of a solid phase approach the value of the liquid

$$C_\mathrm{P}^\mathrm{s}(T) = C_\mathrm{P}^\mathrm{liq}(T) + [C_\mathrm{P}^\mathrm{s}(T_\mathrm{f}) - C_\mathrm{P}^\mathrm{liq}(T_\mathrm{f})]\left(\frac{T}{T_\mathrm{f}}\right)^{-10}, \qquad T > T_\mathrm{f} \tag{4}$$

The properties of the liquid phase have been studied only between the melting point and 1873 K. For this reason Eq. (3) was simplified by assuming a temperature independent heat capacity. For the extrapolation of C_P below the melting point the procedure adopted by the SGTE was again adopted. In this case the heat capacity of liquid Co below T_f was assumed to approach C_P of the hcp phase according to the expression

$$C_\mathrm{P}^\mathrm{liq}(T) = C_\mathrm{P}^\mathrm{hcp}(T) + [C_\mathrm{P}^\mathrm{liq}(T_\mathrm{f}) - C_\mathrm{P}^\mathrm{hcp}(T_\mathrm{f})]\left(\frac{T}{T_\mathrm{f}}\right)^{6}, \qquad T < T_\mathrm{f} \tag{5}$$

The results of compression studies made on solid and liquid phases have often [16] been described by expanding the isothermal bulk modulus [$B(T, P)$] in powers of P and retaining only the linear term

$$B(T, P) = B(T, 0) + nP \tag{6}$$

where $B(T, 0)$ is the bulk modulus at zero pressure. Equation (6), usually known as the Murnaghan [17] approximation, was adopted in the present work for describing the effect of pressure upon $V_m^{\text{nmg}}(T, P)$. By integrating Eq. (6) we obtain

$$V_m^{\text{nmg}}(T, P) = V_m^{\text{nmg}}(T, 0)[1 + nK^{\text{nmg}}(T, 0)P]^{-1/n} \tag{7}$$

where $V_m^{\text{nmg}}(T, 0)$ and $K^{\text{nmg}}(T, 0)$ are nonmagnetic contributions to the molar volume and to the isothermal compressibility at zero pressure, respectively. The parameter n was treated as temperature independent, an approximation previously suggested by Swenson [18] and used successfully in the recent assessments of the thermodynamic properties and the phase diagram of various transition metals, Fe [13], Mo [19], W [20], Cr [21], and Zr [22]. The parameter n for hcp Co was evaluated from the high-pressure data producted by static [23] and dynamic [9] methods. Lacking information for fcc Co its n parameter was assumed to be the same as for hcp Co, an approximation also used when treating hcp and fcc Fe [13].

The general lack of information on the compressibility of liquid metals makes it difficult to estimate the effect of melting upon the parameter n. However, its value can be evaluated from the fcc/liquid equilibrium line, as was successfully done in the case of liquid Fe. The same procedure was now adopted for evaluating n for liquid Co.

The effect of temperature of $V_m^{\text{nmg}}(T, 0)$ was described in the following way:

$$V_m^{\text{nmg}}(T, 0) = V_m^{\text{nmg}}(T_0, 0) \exp\left[\int_{T_0}^{T} \alpha^{\text{nmg}}(T, 0)\, dT\right] \tag{8}$$

where T_0 is the reference temperature and $\alpha^{\text{nmg}}(T, 0)$ is the nonmagnetic contribution to the isothermal expansivity at zero pressure. It dependence upon T for all the condensed phases of Co was described by means of the linear expression

$$\alpha^{\text{nmg}}(T, 0) = \alpha_0 + \alpha_1 T \tag{9}$$

The α parameters for hcp and fcc were evaluated from the available X-ray and dilatometric data, whereas for liquid Co they were evaluated from data on the effect of temperature on density.

Finally, the temperature dependence of $K^{\text{nmg}}(T, 0)$ remains to be discussed. Whereas data by Bridgman [23] may be used to evaluate the compressibility of hcp Co at room temperature, no direct information on the compressibility of the Co phases at higher temperatures could be found. However, the following expresion for the temperature dependence of $K^{\text{nmg}}(T, 0)$ was adopted:

$$K^{\text{nmg}}(T, 0) = K_0 + K_1 T + K_2 T^2 \tag{10}$$

and the K parameters were determined by combining the data available with estimates of the compressibility at very high temperatures. Equation (10) was also used to describe the compressibility of the liquid phase. However, experimental data for a direct evaluation of all three parameters are not available. For this reason Eq. (10) was simplified by setting the parameter K_2 to zero. The other two were evaluated from a consideration of the fcc/liquid equilibrium.

2.3. The Magnetic Contribution to the Gibbs Energy

A phenomenological description of the temperature dependence of the magnetic Gibbs energy has recently been presented by Hillert and Jarl [11]. It is based upon a series expansion of an expression suggested by Iden [24]:

$$\begin{aligned}\Delta G_{\text{m}}^{\text{mg}} = {} & -k_{\text{Co}}^{\beta} RT_{\text{c}}(79/140 - 518\tau/1125) - k_{\text{Co}}^{\alpha} RT_{\text{c}}(\tau^4/6 + \tau^{10}/135 \\ & + \tau^{16}/600 + 71/120 - 518\tau/675), \qquad \tau < 1\end{aligned} \tag{11}$$

and

$$\Delta G_{\text{m}}^{\text{mg}} = -k_{\text{Co}}^{\beta} RT_{\text{c}}(1/10\tau^4 + 1/315\tau^{14} + 1/1500\tau^{24}), \qquad \tau > 1 \tag{12}$$

where

$$\tau = T/T_{\text{c}} \tag{13}$$

$$k_{\text{Co}}^{\alpha} = 1.0469 \ln({}^0\beta + 1) \tag{14}$$

$$k_{\text{Co}}^{\beta} = 0.4269 \ln({}^0\beta + 1) \tag{15}$$

T_{c} is the Curie temperature and the quantity ${}^0\beta$ plays the same role as the Bohr magneton number n_{B} in Weiss and Tauer's approach to the magnetic entropy [25]. In the present work the model by Hillert and Jarl is applied. However, the identification of ${}^0\beta$ with n_{B} depends upon the localized spin model [26]. In the present work ${}^0\beta$ was thus not set equal to n_{B}. Instead, it was evaluated from heat capacity and enthalpy data at high temperatures.

A direct evaluation of the model parameters for the hcp phase is not possible because the transformation to fcc Co takes place before the transformation to the paramagnetic state. Its parameters were thus defined during the assessment work in the way described in Section 3.

The effect of pressure is described through the pressure dependence of T_c. A linear variation was assumed:

$$T_c(P) = T_c(0) + \omega P \tag{16}$$

ω can be related to the ratio between the magnetic volume and the enthalpy,

$$\omega = \left(\frac{dT_c}{dP}\right)_{P=0} = T_c(0)\,\frac{\Delta V_m^{mg}(T, 0)}{\Delta H_m^{mg}(T, 0)} \tag{17}$$

The parameter ω was assumed to have the same value for fcc and hcp Co.

A more complete discussion of Eq. (17) and its consequences is given elsewhere [27].

2.4. The Total Gibbs Energy

The contributions to the Gibbs energy discussed in the preceding sections given, when combined as indicated in Eq. (1), the following type of analytical expression for the Gibbs energy in solid and liquid cobalt as a function of temperature and pressure:

$$\begin{aligned} G_m(T, P) - H_m^{SER} &= a + bT + cT\ln(T) + dT^2 + eT^3 + fT^{-1} \\ &\quad + jT^{(i+1)} + \int_0^P V_m^{nmg}(T, P)\,dP + \Delta G_m^{mg}(T, P) \end{aligned} \tag{18}$$

where

$$\begin{aligned} \int_0^P V_m^{nmg}(T, P)\,dP &= \frac{A \cdot \exp[\alpha_0 T + (\tfrac{1}{2})\alpha_1 T^2]}{(K_0 + K_1 T + K_2 T^2)(n-1)} \\ &\quad \times \{[1 + nP(K_0 + K_1 T + K_2 T^2)]^{1-1/n} - 1\} \end{aligned} \tag{19}$$

$\Delta G_m^{mg}(T, P)$ is given by Eqs. (11) and (12), with τ defined by Eq. (13) and T_c given by Eq. (16). A is a parameter of the dimension volume. The exponent i is equal to -10 for solid phases and equal to 6 for the liquid. Finally, j is equal to zero for the solid phases below T_f and for the liquid phase above T_f. Otherwise j is equal to unity.

3. SELECTED EXPERIMENTAL INFORMATION FROM ATMOSPHERIC PRESSURE

3.1. Transition Temperature for hcp/fcc

The temperature for the hcp/fcc transition in Co has been determined many times. A survey of the values published after 1948 is given in Ref. 28 and earlier values were reviewed by Fine and Ellis [29].

A value of 695 ± 5 K was now selected, in essential agreement with the values reported by Jeanjean et al. [30] using thermal analysis, by Adams and Altstetter [31] using calorimetry, by Lvov and Chirkov [32] using internal friction, by Nelson and Altstetter [33] using dilatometry under various compression loads, by Hess and Barrett [34] by studying the effect of plastic deformation upon the transition, and finally, by Fine and Ellis [29] from a study of the thermal expansion of Co.

3.2. Transition Temperature for fcc/Liquid

The melting point of Co has been determined only a few times. The data available in 1947, six measurements published between 1905 and 1914, were reviewed by Van Dusen and Dahl [35] and are not considered here. In the same paper, Van Dusen and Dahl presented new determinations of the melting point. Their value, 1768 K, recently [36] included in a list of secondary reference points for the IPTS'68, was also accepted in the present work.

3.3. Molar Volume of hcp Co

Information on the molar volume of hcp Co can be obtained from two sources, X-ray determinations of the lattice parameters at various temperatures and dilatometric studies. The X-ray data available in 1958 were reviewed by Pearson [37], who preferred the data by Taylor and Floyd [38]. A survey of the data published after Pearson's review is presented in Ref. 28. The values recently presented by Müller et al. [39] were selected in the present work. From their results, the molar volume of hcp Co was evaluated at 295.65, 258.65, 234.15, 197.65, 172.15, and 146.15 K, and these values were included in the optimization in the present work. Dilatometric information of hcp Co at higher temperatures is available from the X-ray studies of Marick [40], Owen and Jones [41], Bolgov et al. [42], and Petrov [43] and from the dilatometric studies by Fine and Ellis [29], Bibring and Sebilleau [44], Arbuzov and Zelenkov [45], and Krajewski et al. [46]. From these data, the following pieces of information were selected. Thermal expansivity values at 373, 473, and 573 K were taken from the

X-ray work by Owen and Jones, and from the work by Petrov, values of the relative expansion $\Delta V_m/V_m$ were selected at 473, 573, and 673 K. Finally, some data on the hcp phase obtained by Petrov above the equilibrium temperature according to the present work were also selected. Values at 773, 873, 973, and 1073 K were included in the optimization.

3.4. Molar Volume of fcc Co

When reviewing the lattice parameter data on fcc Co at room temperature, Pearson [37] selected the values due to Taylor and Floyd [38]. From a survey of the data now available, presented in Ref. 28, the values presented by Müller and Scholten [47] were now preferred. The molar volume of fcc Co at 298.15, 773.15, 875.15, 930.15, and 1176.15 K was evaluated from their lattice parameter data and included in the optimization. In addition, a value at 1180.15 K was taken from another recent work by Kohlhaas et al. [48].

Expansivity data from dilatometric studies were also selected in the same temperature range. From the work by Arbuzov and Zelenkov [45], values of the thermal expansion coefficient at 823, 873, 921, 975, and 1024 K were selected, and from the recent dilatometric work by Richter and Lotter [49] a thermal expansivity value at 1173 K was taken. Above 1200 K, the X-ray data by Müller and Scholten indicate higher values than the data by Kohlhaas et al., although both sources are in better agreement at the highest temperatures, about 1600 K. The earlier data obtained by Bolgov et al. [42] support the values by Müller and Scholten. Thus, the molar volume of fcc Co at high temperatures was now defined by including in the optimization volume values from Müller and Scholten at 1277, 1338, 1349, 1374, 1373, and 1623 K, from the work by Kohlhaas et al. at 1585 and 1623 K, and finally, $\Delta V_m/V_m$ from the work by Bolgov et al. at 1379, 1411, 1489, 1524, and 1564 K.

3.5 Molar Volume of Liquid Co

The density of liquid Co as a function of temperature has been determined several times [28]. In a review in 1974 Crawley [50] preferred the results presented by Saito et al. [51] using the maximum bubble pressure method and the levitated drop method. Two additional pieces of information are now considered. The first one comes from the study made by Lucas [52] using the Archimedean technique at temperatures up to about 2023 K, and the second, which is the most recent one, is the work by Drotning [53] using the gamma attenuation technique at temperatures up to about 2370 K. Most of the sources agree on a value between 7.7 and 7.8 for the density at the melting point, but the discrepancy on its temperature derivative is large. There is essential agreement between the two most recent studies by Lucas and Drotning, and the density data obtained by Drotning were preferred in the present work. Values at 1768, 1800, 1900, 2000, 2100, 2200, 2300, and 2370 K were selected and included in the optimization.

3.6. Thermochemical Data on hcp Co

The thermochemical information on hcp Co at temperatures above 150 K, the lowest temperature considered in the present work, consists of measurements of the heat capacity by various methods and of drop-calorimetric measurements of the enthalpy. Heat capacity values were selected from Clusius and Schachinger [54] at 150.48, 160.67, 200.4, 205.94, 249.31, and 269.83 K , from Armstrong and Grayson-Smith [55] at 473 K, from Tret'jakov et al. [56] at 413, 523, and 673 K, from Braun and Kohlhaas [57] at 450 and 750 K, and from Normanton [58] at 707 K. Finally, the enthalpy and entropy of hcp Co at 298.15 K obtained by Hultgren et al. [4] from their analysis of the low-temperature data were accepted in the present work.

3.7. The hcp/fcc Transformation Enthalpy

The enthalpy of the hcp/fcc transition has been determined several times, and a survey of the available data is presented in Ref. 28. The most recent calorimetric data are due to Jeanjean et al. [30] and Normanton [58], but the most extensive experimental study is the one performed by Adams and Altstetter [31]. They studied the phase transformation on heating and on cooling by means of a constant heat flux calorimeter and specimens of various types. The value $400 \pm 40\ \mathrm{J \cdot mol^{-1}}$, in agreement with their data, was selected in the present work.

3.8. Thermochemical Data for fcc Co

In addition to the works already reviewed in connection with hcp Co, heat capacity data for fcc Co are provided by the recent work by Peletskii and Zaretskii [59]. The properties of fcc Co were now evaluated by including in the optimization heat capacity values from Armstrong and Grayson Smith [55] at 750, 850, 1000, 1100, 1200, 1250, 1300, 1320, 1340, 1360, 1390, 1400, 1480, 1500, 1600, 1700, and 1768 K. In addition, enthalpy values were selected from the drop-calorimetry work by Jaeger et al. [60] at 929.25, 1183.5, and 1678.65 K and from Jaeger and Zuithoff [61] at 1149.95, 1353.05, and 1569.05 K.

3.9. Thermochemical Data for Liquid Co

Two quantities were used to define the thermochemical properties of liquid Co, the enthalpy of melting and the heat capacity. A survey of the available information on the enthalpy of melting of Co is presented in Table I. It consists of the drop-calorimetry data by Wüst et al. [62], Umino [63], and Kubaschewski [64], the adiabatic calorimetry data by Vollmer et al. [65], and the data obtained by Seydel et al. [66] in a recent study using a pulse-heating technique. The high value reported by Umino was not supported by the results obtained by Kubaschewski using drop calorimetry, and the adiabatic calorimetry study by Vollmer et al. gave a value in between. This value, $16.2 \pm 0.25\ \mathrm{kJ \cdot mol^{-1}}$, was selected in the present work. However, it should be emphasized that in the recent pulse-heating study performed by Seydel et al., a melting enthalpy of about $17.8\ \mathrm{kJ \cdot mol^{-1}}$ was obtained. They used a submicrosecond technique and, in the same work, reported data for other elements, V, Fe, Ni, Mo, Pd, and W. All their data are considerable higher than earlier results.

Very little is known about the heat capacity of liquid Co. In the only recent study, Vollmer et al. [65] obtained $40.5\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ by adiabatic calorimetry, a value which is in line with the ones recently proposed for various metals of the 3d-transition series, Fe [13], Cr [21], 4d-transition series, Mo [19], Zr [22], and 5d-transition series, W [20]. The value due to Vollmer et al. was thus accepted in the present work.

3.10. Magnetic Properties of hcp and fcc Co

As already mentioned, the ${}^{0}\beta$ parameter in the magnetic model was used as an adjustable parameter in order to fit thermochemical data at high temperatures. However, in view of the limited high-temperature information on HCP Co, the assessment was simplified by using the same ${}^{0}\beta$ values as for FCC Co. A reason for this approximation is that the Bohr magneton number, n_B, which is identical to ${}^{0}\beta$ according to the localized spin model, is practically the same for the two structures, 1.7 and 1.745 according to Meyer and Taglang [67].

A survey of the available information on the Curie temperature is presented in Ref. 28. For fcc Co various techniques have given different results. In effect, a representative value from the magnetic studies is 1399 ± 7 K, whereas from the heat capacity data available in 1980, the value is 1375 ± 5 K. However, from a very recent study of various thermophysical properties of Co reported by Peletskii and Zaretskii [59] the value 1396 K may be evaluated. This value is well within the experimental scatter band of the magnetic measurements, and in particular, it is in

Table I. The Enthalpy of Melting of Co According to Various Sources

Source of information	Enthalpy of melting: Reported value ($J \cdot mol^{-1}$)	Enthalpy of melting: Error limits ($J \cdot mol^{-1}$)	Ref. No.	Comments
Wüst et al. (1918)	14,815		62	Drop calorimetry
Umino (1926)	17,034		63	Drop calorimetry (specimen purity, 98.135% Co)
Kubaschewski (1950)	15,690	±1,200	64	Drop calorimetry (ice calorimeter)
Hultgren et al. (1963)	17,155		2	Assessment. The selected value is a compromise between the results by Umino [63] and the enthalpy of melting given by Richard's rule with $\Delta S_f = 1.17\, R$.
Vollmer et al. (1966)	16,200	±250	65	High-temperature adiabatic calorimetry. Two types of specimens: (a) spectroscopically pure Co (Johnson-Matthey); (b) 99.5% Co
Hultgren et al. (1973)	16,192	±250	4	Assessment. The results by Vollmer et al. [65] were accepted.
Seydel et al. (1979)	17,797		66	Submicrosecond pulse-heating method. Data on V, Fe, Ni, Mo, Pd, and W are also reported in the same work.
Present work	16,200	±250		Selected values. The adiabatic calorimetry data presented by Vollmer et al. [65] were selected.

excellent agreement with the results by Myers and Sucksmith [68]. It was thus accepted in the present work.

Estimate values for the Curie temperature of metastable hcp Co are given by Meyer and Taglang [67] and by Sucksmith [69]. Meyer and Taglang studied several Fe–Ni–Co alloys and evaluated 1090 K by extrapolation to pure Co, whereas Suchsmith performed various extrapolations of the low-temperature data for hcp Co and obtained two values, 1130 and 1150 K. In the present work, a preliminary evaluation of the relative stabilities of hcp and fcc Co was performed using a value for T_c of 1150 K and the value for ${}^0\beta$ obtained from data on fcc Co. The lower T_c for hcp Co was then found to make hcp more stable than fcc Co above 1067 K. This result indicated that either (a) the magnitude of the magnetic contribution should be decreased or (b) the difference between the Curie temperatures for those phases should be lower. Alternative a was not accepted for two reasons. The first reason is the very small difference between the Bohr magneton numbers for these phases, as discussed above. The second reason is that a lower ${}^0\beta$ value would result in a higher entropy of melting of hcp Co. Some calculations indicated that a sufficient lowering of the ${}^0\beta$ value would result in entropies of melting for hcp Co much higher than the expected ones [70]. Alternative b was thus preferred and T_c for hcp Co was simply set equal to T_c for fcc Co, i.e., 1396 K.

4. SELECTED DATA FROM HIGH PRESSURES

4.1. Compressibility Data

The available information on the pressure dependence of V_m for Co has been reviewed by Kennedy and Keeler [9]. It consists of determinations of V_m at room temperature and pressures up to about 3 GPa reported by Bridgman [23] and of values of V_m at 298.15 K and pressures up to 120 GPa obtained by Kennedy and Keeler by the so-called reduction of shock-wave data. From the work by Bridgman molar volume values were selected at 2.026, 2.533, and 3.039 GPa, and from the data from shock-wave studies, molar volume values were selected at 26, 36, 46, 55, 65, 75, 85, 95, 100, and 120 GPa. Direct measurements of the compressibility of Co at high temperatures are not available. However, some information may be extracted from the Young modulus data reported by Köster [71]. This was made in the present work by taking into account the slight temperature dependence of Poisson's number for Co treated by Schramm [72]. Values for the compressibility of hcp Co were selected at 373 and 473 K and for fcc Co at 773, 873, 973, 1073, and 1173 K. The selected data were included in the optimization. Information on the compressibility of hcp above 695 K is not available because of the hcp/fcc transformation. For fcc Co no data were found above 1173 K, and nothing is known about the compressibility of the liquid phase. However, this information is necessary for describing the stability of the various phases at high temperatures and pressures, and thus an extrapolation of the low-temperature data was attempted in the present work. Whereas the compressibility of the liquid phase is considered in the next section in connection with the fcc/liquid equilibrium, the extrapolation of the compressibility of solid Co to high T is now discussed. The consideration of the effect of temperature on the compressibility and the estimation of data is conveniently made in terms of the dimensionless quantity usually called called the Anderson–Grüneisen parameter [73]

$$\delta(T, 0) = \frac{1}{\alpha(T, 0)\, K(T, 0)} \frac{dK(T, 0)}{dT} \tag{20}$$

In effect, the information on δ for various metals at room temperature indicates that this parameter varies from about 3 to 10, and Bohlin [74] has observed that for many substances at room temperature the value of δ is roughly equal to twice the value of n, defined by Eq. (6). The behavior of δ at higher temperatures is less known and Anderson [73] has used the approximation $\delta = n$ when treating data on certain oxides and silicates. Whereas the application of his approximation at high pressures is discussed in a recent paper [75], $\delta(T, 0)$ was evaluated in the present work for metals whose properties at high temperatures have recently been assessed, W [20] and Zr [22]. The evaluation seems to confirm that $\delta(T, 0)$ is a decreasing function of T, which approaches the value $\delta = n$ at temperatures near their melting points. By assuming a similar behavior for δ of solid Co, the following values for $\delta(T, 0)$ were estimated at 2000, 2800, and 4000 K: 5.5, 4.5, and 3. These values were assumed to hold for hcp and fcc Co and were included in the optimization.

4.2. The fcc/Liquid Equilibrium at High Pressures

The fcc/liquid equilibrium line for Co has not been reported but a rough estimate is now attempted. A previous estimate has been given by Nishizawa and Ishida [7] using the Clapeyron equation and treating dT/dP as pressure independent for values of P lower than 2 GPa. However, a more realistic extrapolation to high P and T should take into account the effect of these variables upon ΔV_m and ΔS_m, i.e., the curvature of the liquidus line. The effect of pressure on compressibility is now estimated by adopting for the liquidus curve a similar curvature as for fcc Fe, on which

Table II. Summary of Optimum Parameters for Cobalt[a]

Element	Mass	Stable element reference (SER)	Thermodynamic properties at the reference state	
Co	58.9332	Hcp Co at 298.15 K and 10^5 Pa	$H_m^{SER} - H_m(0, P_0)$	$S_m^{SER} - S_m(0, P_0)$
			4765.567	30.03

HCP

298.15 K < T < 1768 K

$$G_m^{hcp} - H_m^{SER} = 309.57525 + 133.36601T - 25.0861T\ln(T) - 2.6547387\ 10^{-3}T^2$$
$$- 1.7348\ 10^{-7}T^3 + 72526.92\ T^{-1} + \Delta G_m^{mg} + \int_0^P V_m^{hcp}\,dP$$

1768 K < T < 6000 K

$$G_m^{hcp} - H_m^{SER} = -17198.3318 + 253.28374T - 40.5T\ln(T) + 9.3488246\ 10^{30}T^{-9} + \int_0^P V_m^{hcp}\,dP$$

FCC

298.15 K < T < 1768 K

$$G_m^{fcc} - H_m^{SER} = 737.166 + 132.750762T - 25.0861T\ln T - 2.6547387\ 10^{-3}T^2 - 1.7348\ 10^{-7}T^3 + 72526.92T^{-1} + \Delta G_m^{mg} + \int_0^P V_m^{fcc}\,dP$$

1768 K < T < 6000 K

$$G_m^{fcc} - H_m^{SER} = -16770.741 + 252.668487T - 40.5T\ln(T) + 9.34883246\ 10^{30}T^{-9} + \int_0^P V_n^{fcc}\,dP$$

Liquid

298.15 K < T < 1768 K

$$G_{\mathrm{m}}^{\mathrm{liq}} - H_{\mathrm{m}}^{\mathrm{SER}} = 15394.612 + 124.434078T - 25.0861T\ln(T) - 2.6547387\ 10^{-3}T^2 - 1.7348\ 10^{-7}T^3 + 72526.92T^{-1} - 2.19804786\ 10^{-21}T^7 + \int_0^P V_{\mathrm{m}}^{\mathrm{liq}}\,dP$$

1768 K < T < 6000 K

$$G_{\mathrm{n}}^{\mathrm{liq}} - H_{\mathrm{n}}^{\mathrm{SER}} = -847.2758 + 243.599944T - 40.5T\ln(T) + \int_0^P V_{\mathrm{m}}^{\mathrm{liq}}$$

where $\Delta G_{\mathrm{m}}^{\mathrm{mg}}$ is given by Eqs. (11) to (15) and

$$^0\beta^{\mathrm{hcp}} = {}^0\beta^{\mathrm{fcc}} = 1.35$$

$$T_{\mathrm{c}}^{\mathrm{hcp}} = T_{\mathrm{c}}^{\mathrm{fcc}}(P) = 1395.988 + 2.10^{-8}P$$

$$\int_0^P V_{\mathrm{m}}\,dP = \frac{A\exp(\alpha_0 T + \frac{1}{2}\alpha_1 T^2)}{(K_0 + K_1 T + K_2 T^2)(n-1)}\{[1 + nP(K_0 + K_1 T + K_2 T^2)]^{1-1/n} - 1\}$$

and the constants in the expressions of $\int_0^P V_{\mathrm{m}}\,dP$ for the various phases have the following values:

Phase	A $(\mathrm{m}^3 \cdot \mathrm{mol}^{-1})10^6$	α_0, $(\mathrm{K}^{-1})10^5$	α_1, $(\mathrm{K}^{-2})10^9$	K_0, $(\mathrm{m}^2 \cdot \mathrm{N}^{-1})10^{12}$	K_1, $(\mathrm{m}^2 \cdot \mathrm{N}^{-1} \cdot \mathrm{K}^{-1})10^{15}$	K_2, $(\mathrm{m}^2 \cdot \mathrm{N}^{-1} \cdot \mathrm{K}^{-2})10^{20}$	n
hcp	6.7198750	3.45819359	5.58753394	4.51215767	1.60731053	4.66728911	4.0070
fcc	6.7529274	3.20701588	5.86834503	4.66591978	1.45932922	5.17368742	4.0070
liquid	6.4650793	10.12169928	−8.3	5.06841984	4.32537907	0	4.5925

[a] All data in SI units. Temperature values according to IPTS 68. Atmospheric pressure (P_0) is 101,325 Pa. The ranges of validity of the given expressions correspond to $P = P_0$.

there is some experimental information. This was achieved by selecting values for the melting temperature of fcc Fe at 11.8 and 20 GPa from the work by Liu and Bassett [76] and substracting the difference between the melting point of fcc Fe, 1801 K, and that of fcc Co, 1768 K. These values, 2144 ± 100 K at 11.8 GPa and 2290 ± 100 K at 20 GPa, were included in the optimization.

4.3. The hcp/fcc Equilibrium Line at High Pressures

The only source of information on the fcc/hcp equilibrium boundary is the work by Kennedy and Newton [77]. They used DTA and studied pressures up to about 5 GPa. Their results were accepted in the present work. Values for the hcp/fcc equilibrium temperature were thus selected from their work at 2.17, 3.0, 4.09, 4.35, 4.61, and 4.87 GPa and included in the optimization. The extrapolation to even higher pressures was performd by comparison with the hcp/fcc equilibrium line for Fe. In the optimized *P–T* diagram for Fe [13] the lines for the fcc/fcc and fcc/liquid equilibria are essentially parallel between 10 and 20 GPa. This feature was assumed to hold for Co even at higher pressures, and the hcp/fcc line was assumed to become parallel to the fcc/liquid line at very high pressures.

5. ASSESSMENT PROCEDURE

The treatment of the selected experimental information was performed by using PARROT, a computer program for the optimization of thermodynamic model parameters developed by Jansson [78]. It works by minimizing an error sum where each data point has been given an

Table III. Assessed Thermodynamic Properties of hcp and fcc Cobalt at 298.15 K and 101,325 Pa

Property	hcp	fcc
C_P ($J \cdot mol^{-1} \cdot K^{-1}$)	25.175	25.275
C_V ($J \cdot mol^{-1} \cdot K^{-1}$)	24.732	24.811
Enthalpy relative to 0 K ($J \cdot mol^{-1}$)	4765.576	5193.185
Entropy relative to 0 K ($J \cdot mol^{-1} \cdot K^{-1}$)	30.040	30.655
Molar volume ($m^3 \cdot mol^{-1}$) 10^6	6.669120	6.697499
Thermal expansion coefficient (K^{-1}) 10^5	3.722254	3.474611
Isothermal compressibility ($m^2 \cdot N^{-1}$) 10^{12}	5.088292	5.199997
Grüneisen parameter, γ_G	1.9726	1.8037

Table IV. Changes in the Thermodynamic Properties of hcp, fcc, and Liquid Cobalt at the Stable and Metastable Phase Transitions at 101,325 Pa

	hcp/fcc	fcc/liquid	hcp/liquid
Transition temperature (K)	695.0	1768.0	1700.41
Enthalpy change ($J \cdot mol^{-1}$)	427.594	16200.	16602.1
Entropy change ($J \cdot mol^{-1} \cdot K^{-1}$)	0.615	9.163	9.763
Heat capacity change ($J \cdot mol^{-1} \cdot K^{-1}$)	0.00	0.896	−0.144
Volume change ($\Delta V_m/V_m$)(%)	0.329	5.992	5.815
Thermal expansivity change ($\Delta\alpha/\alpha$)(%)	−5.511	86.75	78.07
Isothermal compressibility change ($\Delta K/K$)(%)	0.93	69.16	65.42

appropriate weight. Since the data are of many different types, the weights were selected by personal judgment and they were changed by trial and error until reasonable agreement was obtained for most of the information. Some information was given such high weights that they were reproduced exactly. These pieces were the temperature of transformation of hcp/fcc and fcc/liquid at atmospheric pressure and the enthalpy of melting. The resulting thermodynamic parameters are given in Table II. Values of the thermodynamic properties of solid Co at 298.15 K and 101,325 Pa are given in Table III, whereas the changes in the thermodynamic properties associated with the hcp/fcc, fcc/liquid, and hcp/liquid transitions are given in Table IV. Comparisons between measured and calculated quantities are given in the figures. The results are discussed in the next section.

6. DISCUSSION

6.1. Thermochemical Properties

The calculated enthalpy and heat capacity of hcp and fcc Co showed excellent agreement with the available experimental data.

In Fig. 1 the assessed enthalpy of fcc and liquid Co up to 2100 K is compared with the experimental data. The data by Jaeger et al. [60, 61] and Wüst et al. [62] for fcc Co are well reproduced, but the old measurements by Umino [63] indicate higher values above 1460 K. The assessed enthalpy of melting is also given in Table I. It reproduces the value by Vollmer et al. [65]. The enthalpy of the liquid phase according to the present work falls in between the values reported by Umino [63] and by Wüst et al. [62].

Figure 2 shows the heat capacity close of the Curie temperature. Beween 1100 and 1300 K the assessed heat capacity for fcc Co is higher

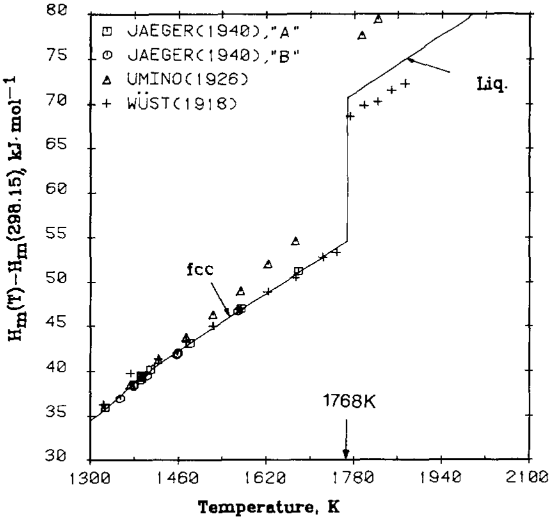

Fig. 1. The assessed enthalpy of fcc and liquid Co between 1300 and 2100 K compared with the available experimental data. The fcc/liquid equilibrium temperature is indicated. A and B denote the data presented by Jaeger et al. [60] and Jaeger and Zuithoff [61], respectively. The assessed enthalpy of melting, based upon the data by Vollmer et al. [65], is compared in Table I with the values according to various sources.

than the experimental values, but between 1300 and the Curie temperature the present calculation is supported by the results by Peletskii and Zaretskii [59] and Braun et al. [57]. Above the Curie temperature, the assessed values reproduce the data by Braun et al. [57].

In Fig. 3, the assessed molar Gibbs energy of fcc and liquid Co relative to hcp Co is given as a function of T at one atmosphere. The metastable melting point for hcp Co is also indicared, while the entropy of melting is given in Table IV. These quantities are now be compared with the predictions of the empirical relations due to Ardell [80] and to Katz and Chekovskoi [70], which are frequently [81] used for estimating melting data for metastable phases. Following Ardell we may estimate the melting point of hcp Co as

$$T_{\mathrm{f}}^{\mathrm{hcp}}=\frac{\Delta H_{\mathrm{m}}^{\mathrm{hcp/fcc}}(695)+\Delta H_{\mathrm{m}}^{\mathrm{fcc/liq}}(1768)}{\Delta S_{\mathrm{m}}^{\mathrm{hcp/fcc}}(695)+\Delta S_{\mathrm{m}}^{\mathrm{fcc/liq}}(1768)} \tag{21}$$

Application of Eq. (21) with the data given in Table III gives 1700.51 K, which is almost identical to the present value. The entropy of melting of

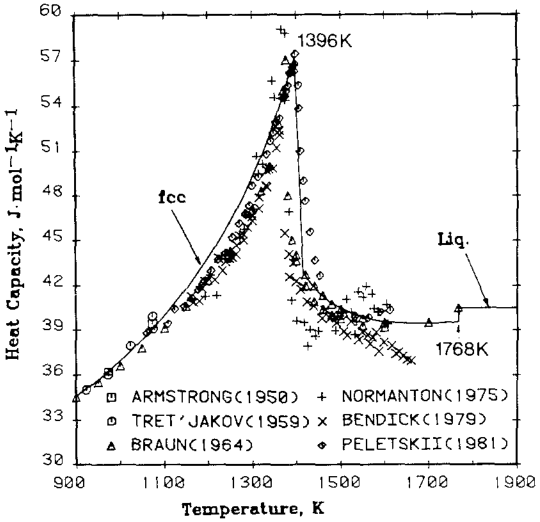

Fig. 2. The assessed heat capacity of fcc and liquid Co between 900 and 1900 K compared with the available experimental data. The Curie temperature selected in the present work, 1396 K, is compared in Ref. 28 with data from various sources. The fcc/liquid equilibrium temperature is indicated. The assessed heat capacity of liquid Co is based upon data presented by Vollmer et al. [65].

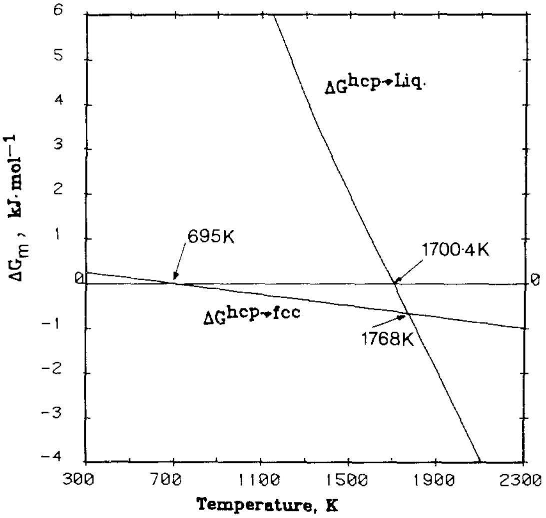

Fig. 3. The assessed Gibbs energy of fcc and liquid Co relative to hcp Co between 300 and 2300 K at 101325 Pa. The temperatures for the hcp/fcc, fcc/liquid, and hcp/liquid equilibrium are indicated. The assessed changes in the thermodynamic properties at these various transitions are given in Table III.

hcp Co given in Table III is higher than for fcc Co but lower than the value predicted by the relation between entropy of melting and melting temperature given by Katz and Chekovskoi [70]:

$$\Delta S_m = 4.9748 + 3.38393\ 10^{-3}\ T_f \qquad (22)$$

With the present value for the melting point of hcp Co, Eq. (22) gives 10.7 $J \cdot mol^{-1} \cdot K^{-1}$ for the entropy of melting, which is about 10% higher than the value assessed in the present work. The discrepancy is not surprising in view of the fact that Eq. (22) also predicts a higher entropy of melting for fcc Co.

6.2. Molar Volume, Density, and Thermal Expansivity of Solid Co at 101,325 Pa

An important feature of the present treatment of the thermodynamics of Co is the coupling between the magnetic enthalpy, ΔH_m^{mg}, and the magnetic contribution to the molar volume, ΔV_m^{mg}, established by Eq. (17) through the quantity dT_c/dP. In consequence, the assessed V_m versus T curve should show similar variations in curvature as the assessed integral enthalpy. This is indeed the case, and Fig. 4 shows the assessed molar volume of fcc Co compared with the values obtained from the reported lat-

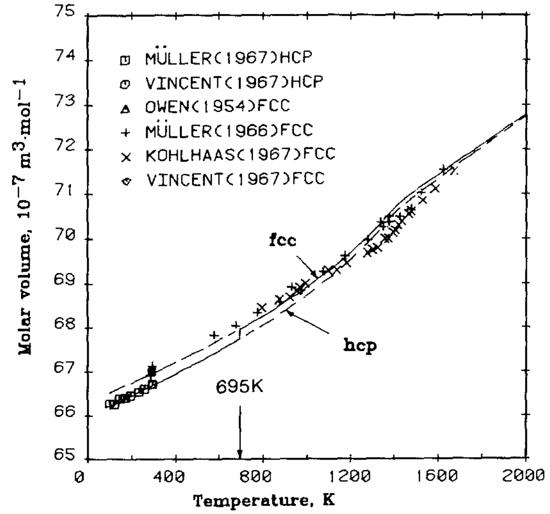

Fig. 4. The assessed molar volume of hcp and fcc Co compared with experimental data according to various sources. The hcp/fcc equilibrium temperature is indicated.

tice parameter data. The results by Müller and Scholten [47], which show the magnetic contribution and were given a low weight in the evaluation by Nishizawa and Ishida [7], are well reproduced by the calculation. Some data points for hcp Co are also presented in Fig. 4. They are well reproduced. Besides, Fig. 4 shows that the assessed volume difference between hcp and fcc Co decreases with increasing *T*.

Finally, the thermal expansion coefficient, α, is considered. A comparison between the calculated and the reported values is made in Fig. 5. The values for hcp Co given by Owen and Jones [41] below 600K are well reproduced and so are the values for fcc Co given by Arbuzov and Zelekov [45]. The points due to Richter and Lotter [49] hold for temperatures close to the Curie point and could thus be expected to show very high values. This essentially confirmed by they do not reproduce the sharp peak in the calculated curve.

6.3. Density of Liquid Co at 101,325 Pa

The assessed density of liquid Co is compared with the experimental data in Fig. 6. The assessed values reproduce well the data obtained by Drotning [53] using the gamma technique. The values obtained by Kirshenbaum and Cahill [83] indicate a larger temperature effect, as do

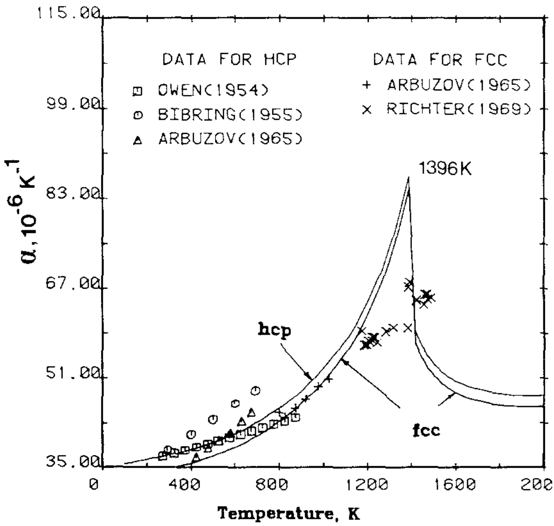

Fig. 5. The thermal expansion coefficient (α) of hcp and fcc Co assessed in the present work compared with data according to various sources.

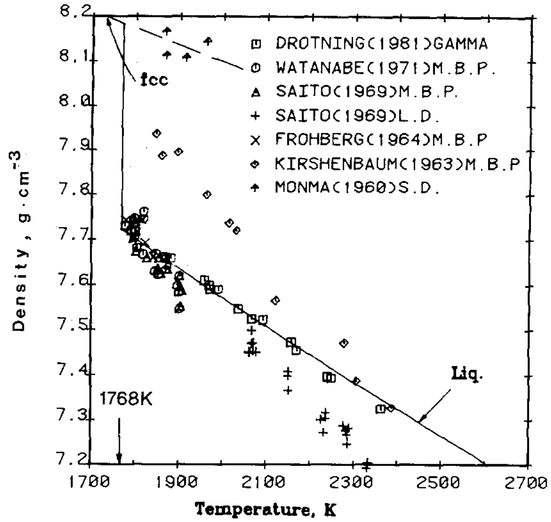

Fig. 6. The assessed density of fcc and liquid Co compared with experimental data according to various sources. In these experiments various techniques were used, gamma attenuation (gamma), maximum bubble pressure (M.B.P.), levitated drop (L.D.), and sessile drop (S.D.). The fcc/liquid equilibrium temperature is indicated.

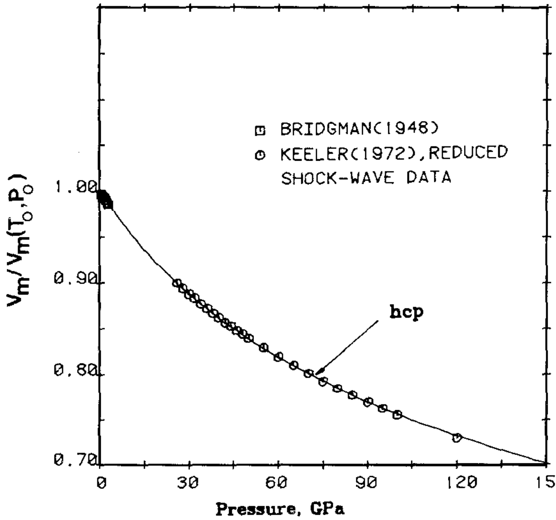

Fig. 7. The assessed molar volume of hcp Co up to 150 GPa, relative to the volume of hcp phase at $T_0 = 298.15$ K and $P_0 = 101{,}325$ Pa compared with the static compression data reported by Bridgman [23] and the values obtained by Kennedy and Keeler [9] from shock-wave data above 26 GPa.

the points by Saito et al. [51], who used the levitation drop technique. Finally, Fig. 6 shows four data points obtained by Monma and Suto [84] using the sessile-drop method. Their points, which evidently correspond to superheated fcc Co, bracket the present extrapolation of density for fcc Co.

Extrapolation to very high temperatures using the present assessment shows a more modest decrease in the density than earlier expressions proposed by Crawley [50] and Drotning [53].

6.4. Molar Volume at High Pressure and Compressibility

The assessed molar volume of hcp Co at 298.15 K reproduce well the static compression data reported by Bridgman [23].

In Fig. 7, the assessed molar volume of hcp Co at 298.15 K is compared with the data reported by Bridgman an values obtained by Kennedy and Keeler [9] through the so-called reduction of shock-wave data. All the data points are well reproduced. Finally, the pressure dependence of the bulk modulus of solid Co at room temperature is compared in Table V

Table V. The Pressure Derivative of the Bulk Modules for hcp and fcc Cobalt According to Various Sources and the Present Assessment

Source of information	$(\partial B/\partial P)_T$		Comments
	hcp	fcc	
Slater (1939)	4.2785	3.9407	Evaluated in the present using the relation $(\partial B/\partial P)_T = 2\gamma_G + \frac{1}{3}$ due to Slater [87]. γ^{hcp} and γ_G^{fcc} were evaluated at 298.15 K and 101,325 Pa (see Table III).
Dugdale (1953)	4.9450	4.6074	Evaluated in the present work using the relation $(\partial B/\partial P)_T = 2\gamma_G + 1$ due to Dugdale and MacDonald [88]. γ_G^{hcp} and γ_G^{fcc} were evaluated at 298.15 and zero pressure: $\gamma_G^{hcp} = 1.9725$, $\gamma_G^{fcc} = 1.80372$.
Bohlin (1973)	3.9452	3.6074	Evaluated in the present work using the relation $(\partial B/\partial P)_T = 2\gamma_G$ due to Bohlin [74]. γ_G^{hcp} and γ_G^{fcc} were evaluated at 298.15 K and 101,325 Pa (see Table III).
Fisher (1975)	6.228	6.208	Evaluated in the present work using the linear relation between $(\partial B/\partial P)_T$ and $1/V_m$ proposed by Fisher et al. [89]
Steinberg (1982)	4.74		Estimated by Steinberg [90] from shock-wave data
Present work	4.007	4.007	Assessed values

with values according to various estimates. Most of the prediction methods give higher values, but lower values are obtained by the method due to Bohlin [74].

The calculated compressibility of Co at higher temperatures is compared in Fig. 8 with the values evaluated from the Young modulus data by Köster [71]. The data points for hcp Co are systematically higher than the present ones, but the difference starts at lower temperatures, where the calculated values are based upon Bridgman's data. It seems necessary to accept that there is a systematic difference. In can be due either to some systematic error in the data by Köster or to an error in the assumption of isotropy in the polycrystalline sample, which was introduced in the evaluation of the points in Fig. 8.

The assessed values for fcc Co reproduce reasonably well the data points from Köster's work. In particular, the rapid increase in compressibility which takes place above 800 K, when approaching the Curie temperature, is well reproduced by the present model of the magnetic contribution to the compressibility. Data from higher temperatures are not available to compare with the drastic decrease in K above T_c predicted by the present calculation. However, it is easy to see that a linear extrapolation of the data by Köster up to the melting point would give a

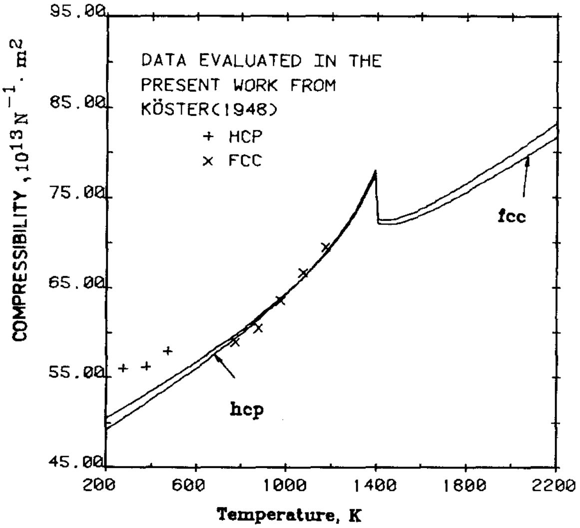

Fig. 8. The assessed compressibilities of hcp and fcc Co between 200 and 2200 K compared with data evaluated in the present work from the study presented by Köster [71].

value for K about 70% higher than at room temperature, which would be unusual, in the view of increments from 20 to 30% observed for other metals [91]. The present compressibility value at the melting point, which is 45% higher than at room temperature, is also high but more in line with the expected trend.

6.5. The Temperature–Pressure Phase Diagram

The assessed T–P phase diagram for Co up to 20 GPa and 2300 K is compared in Fig. 9 with the experimental data on the hcp/fcc boundary reported by Kennedy and Newton [77]. Their data are reproduced within the experimental error, but the points for pressures below 2 GPa indicate higher equilibrium temperatures. It should be noted that the hcp/fcc transition point at one atmosphere was selected by considering information from several other sources.

Due to the various assumptions involved in the present calculation, necessitated by the lack of thermophysical data for Co, the phase diagram is considered only as a tentative one. It is included here in the hope that it will make the design of new experiments easier.

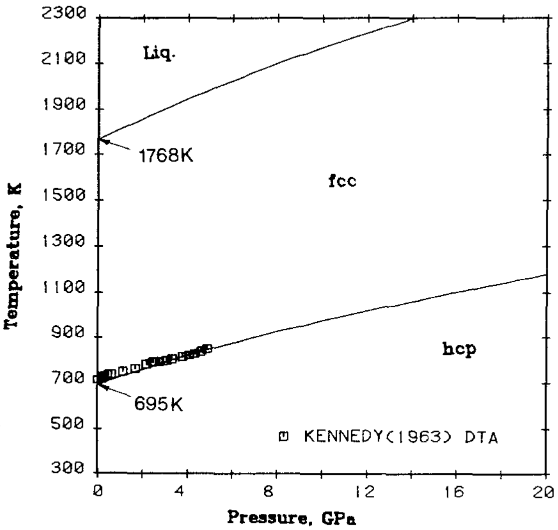

Fig. 9. The assessed temperature–pressure phase diagram for Co up to 2300 K and 20 GPa compared with DTA data on the hcp/fcc equilibrium boundary reported by Kennedy and Newton [77]. The hcp/fcc and fcc/liquid equilibrium temperatures at 101,325 Pa are indicated.

6.6. Pressure Dependence of the Curie Temperature

The comparisons made in sections 6.2 and 6.3 showed that the present treatment of the pressure contribution to $\Delta G_m^{mg}(T, P)$ can account for the magnetic contribution to the molar volume, expansivity, and compressibility within the experimental error. The coupling is made through ω in Eq. (17), the pressure derivative of T_c, which was treated as a free parameter. Its value, obtained from the optimization, was controlled by the volume and expansivity data from zero pressure. It will thus be interesting to compare the resulting value, $\omega = 2\ \mathrm{K \cdot kbar^{-1}}$, with the ones according to other sources, $\pm 1\ \mathrm{K \cdot kbar^{-1}}$ [92]. In fact, it has been observed [93] that at high P the thermocouples indicate a temperature which is somewhat too low. In a more recent work, Leger et al. [94] also reported no effect of P upon T_c, but in their work no corrections for the pressure effect upon the emf of the thermocouples were performed above 800 K. The uncertainty they gave to their data should thus be considered as too small. Besides, in the same work they report measurements on various Ni–Co alloys, showing an increasing effect of P on T_c up to 55 w/o Co and then a drastic change in slope for the alloy with 70 w/o Co. Their data are shown in Fig. 10 together with their selected line. It is evident that the negligible

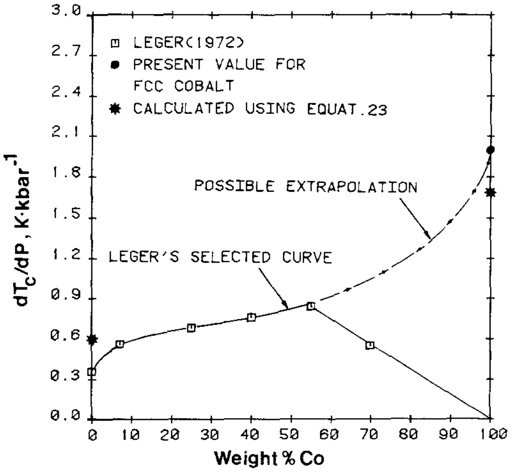

Fig. 10. The pressure derivative of the Curie temperature of Ni–Co alloys according to Leger et al. [94]. The solid line is the adopted by Leger et al. to describe their data. The dotted line represents a possible extrapolation which ignores the result from the alloy Ni–70 w/o Co but takes into account the value of dT_c/dP for Co evaluated in the present work. The values of dT_c/dP for Ni and Co predicted by Eq. (23) are also given.

pressure effect on T_c for 100 w/o Co was obtained by relying on the odd results from the alloy with 70% Co. However, the Curie temperature for this alloy is very high, 1219 K, and the reported value for this alloy should probably be given a lower weight. In particular, an extrapolation which ignores the value from this alloy is indicated in Fig. 10 using a dotted line. It suggests that the high effect for pure Co obtained in the present work could be reconciled with the trend shown by all the other points. In Fig. 10 we also show two points calculated from an equation based upon the so-called itinerant-electron model [95]:

$$dT_c/dP = (5/3)KT_c \tag{23}$$

where K is the isothermal compressibility. The point for Ni is reasonably close to their masured value, whereas the point for Co is close to our result.

Another alternative explanation for the discrepancy between the present and the previous values for dT_c/dP is our neglect of any pressure dependence in the other model parameters for ΔG_m^{mg}, Eqs. (11) and (12), necessitated by the lack of thermochemical data at high pressures.

7. CONCLUSIONS

The results show that the models used in our work are adequate for describing the available data within the experimental accuracy. However, simplifications introduced in the description of certain temperature and pressure dependencies of $G_m(T, P)$ limit the possibilities of making reliable extrapolations outside the range studied experimentally. Such extrapolations are reliable only if they are based on more physically based models.

The present assessment has revealed the lack of experimental data on the thermophysical properties of Co. At atmospheric pressure, more compressibility data for fcc and liquid Co are necessary. At higher pressures, values for the hcp/fcc equilibrium temperature above 5 GPa are necessary, as well as data on the melting curve. Finally, the effect of pressure upon the Curie temperature for Co should be reconsidered.

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