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Applicability of equation of state for prediction of mechanical properties of nanomaterials

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ABSTRACT

Nanomaterials have been the subject of enormous interest since last few years due to extremely small feature size and have the potential for wide-ranging industrial, biomedical, and electronic applications In the present research work the high pressure behaviour of nanomaterials like 67 nm and 37 nm γ*-*Al_2O_3*, 3C-SiC, nanocrystalline Ni, nano* ε*-Fe are studied using potential free equations of state (EOS). The calculated values of mechanical properties such as compression, bulk modulus for the nanomaterials come out to be in reasonable good agreement with the available experimental data. It has been observed that Tait's EOS is suitable for predicting the mechanical properties of nanomaterials successfully.*

Keywords: Nanomaterials, Equation of State, mechanical properties.

INTRODUCTION

Recently, nanomaterials in the field of physics, chemistry, and engineering with dimensions less than 100 nm have attracted much attention [**1, 2, 3**]. Nanomaterials have large surface to volume ratio as compared to their bulk counterpart and surface effects have significant role in enhancement of properties of nanomaterials. The quantum phenomenon play important role at nano level. The properties like hardness, sintering ability, melting temperature, and electronic structure dependent upon size of the particle [**4-5**]. The barrier height between two phases of a material has been found to depend on the size of the nanocrystals [**6**]. Due to novel and enhanced compared to traditional materials, nanomaterials open up possibilities for new technological applications.

There are many theoretical and experimental work on nanocrystalline iron (n-Fe).Researchers have investigated different properties magnetic, mechanical, thermal, electrical properties, surface passivation, and mechanical properties of ε-Fe [**7- 11**].

The wide applications of nanocrystalline γ-Al_2O_3like catalyst, catalyst carrier, absorbent, coating, and soft abrasive have attracted much attention. A lot of synthesis approaches like microwave sintering, plasma-assisted sintering, and high-pressure sintering have been used , to explore to produce highly dense γ-Al_2O_3 without excessive grain growth [**12-14**]. Fully dense nanocrystalline alumina can be obtained using high-pressure sintering [**15**].

In recent years, nanocrystalline nickel (n-Ni), a nanocrystalline metal, has been studied widely using experimental and theoretical approaches [**16,17**]. The properties like diffusion coefficient and vibrational modes,magnetic, mechanical, and electrical behavior of n-Ni have been widely studied [**16**]. Transmission electron microscopy, X-ray diffraction, and small-angle neutron scattering have been used to understand the physical properties of n-Ni, the internal strain and grain boundary structure of n-Ni [**16**].

Nanocrystalline 3C-SiC sample considered in the present study was synthesized by laser induced vapour phase reactions [**18**], and was characterized as nearly spherical particles with mean grain size about 30 nm. In the present work compressibility of 30 nm 3C-SiC nanocrystals is reported.

In the present investigation, we have analyzed the pressure dependence of compressional behaviour of n-γ-Al_2O_3,3C-SiC,n-Ni and n-ε-Fe .For this purpose, we have used usual Tait's Equation of State to predict the change in unit cell volume as a function of pressure. The results achieved from usual Tait's Equation of State are found in good agreement with the available experimental data.

2. Mathematical Formulation

The Usual Tait equationis mostuseful non-linear relation of compression and pressure for different class of solids and liquids [**19**]. Kumar [**20**] presented the derivation of this equation taking the product of the thermal coefficient of volume thermal expansion (α) and bulk modulus (K_T) to remain constant under the effect of pressure [**21-23**] i.e.

$$\alpha K = \text{constant} \quad ...(1)$$

Differentiation of equation (1) with respect to volume at constant temperature gives

$$\alpha\left(\frac{dK}{dV}\right)_T + K\left(\frac{d\alpha}{dV}\right)_T = 0 \quad ...(2)$$

Which yields

$$\delta_T = \frac{V}{\alpha}\left(\frac{d\alpha}{dV}\right)_T = -\frac{V}{K}\left(\frac{dK}{dV}\right)_T \quad ...(3)$$

Where δ_T is Anderson-Gruneisen parameter.at constant temperature

$$\frac{dK}{K} = -\delta_T \frac{dV}{V} \quad ...(4)$$

Integrating equation (4) with $K=K_0$, when $V=V_0$. Assuming that δ_T is independent of V, we get

$$\frac{K}{K_0} = \left(\frac{V}{V_0}\right)^{-\delta_T} \quad ...(5)$$

Since

$$K = -V\left(\frac{dP}{dV}\right)_T$$ Then equation (5) becomes

$$\frac{V}{K_0}\left(\frac{dP}{dV}\right) = \left(\frac{V}{V_0}\right)^{-\delta_T} \quad ...(6)$$

Or

$$\frac{dV}{V^{\delta_T+1}} = -\frac{1}{K_0 V_0^{\delta_T}} dP \quad ...(7)$$

The integration of equation (7) gives us the following relation

$$P = \frac{K_0}{K_0^{'}}\left[\exp\left\{-K_0 \ln \frac{V}{V_0}\right\} - 1\right] \qquad \ldots(8)$$

Equation (8) is the same relation as given by Murnaghan [**24**] in 1944 in a slightly different way, assuming that bulk modulus depends linearly on pressure.

Due to simplicity of equation (8), it had been widely used in the literature [**19, 25**]. it noted that the Murnaghan approximation and the approximation that δ_T is independent of V are equivalent to each other because $\delta_T = \left(\frac{dK}{dP}\right)_T = K_0^{'}$. However, the more recent studies in high-pressure research demonstrate that the Anderson parameter δ_T is related to η=V/V$_0$ (where V$_0$ is the initial volume) as given below [**26**].

$$\frac{(\delta_T + 1)}{\eta} = A \qquad \ldots(9)$$

Where A is a constant for a given solid. Thus equation (3) takes the following form

$$\frac{dK}{K} = \left[-\frac{A}{V_0} + \frac{1}{V}\right]dV \qquad \ldots(10)$$

Integrating above equation we get

$$\frac{K}{K_0} = \frac{V}{V_0}\exp A\left[1 - \frac{V}{V_0}\right] \qquad \ldots(11)$$

Since $K = -V\left(\frac{dP}{dV}\right)_T$ equation (11) may be rewritten as

$$\frac{K}{K_0}\exp A\left[1 - \frac{V}{V_0}\right]dV = -dP \qquad \ldots(12)$$

On integration equation (12) gives

$$P = \frac{K_0}{A}\left[\exp A\left(1 - \frac{V}{V_0}\right) - 1\right] \qquad \ldots(13)$$

Here K$_0$ is the zero pressure bulk modulus and the constant A is determined from the initial conditions, viz at V=V$_0$, $A = \delta_T^0 + 1$

Equation (13) is the Usual Tait's Equation (UTE) and it can be written as follows

$$\frac{V}{V_0} = \left[1 - \frac{1}{K_0^{'} + 1}\ln\left\{1 + \left(\frac{K_0^{'} + 1}{K_0}\right)P\right\}\right] \qquad \ldots(14)$$

Using usual Tait's equation (UTE) the expression for isothermal bulk modulus K(P) is written as[**27**]

$$K = K_0 \frac{V}{V_0}\left\{1 + \frac{K_0' + 1}{K_0} P\right\} \quad \ldots(15)$$

From equation (14)

$$1 + \frac{K_0' + 1}{K_0} P = \exp\left\{\left(1 - \frac{V}{V_0}\right)\left(K_0' + 1\right)\right\} \quad \ldots(16)$$

Putting equation (16) in equation (15) we get

$$K(P) = K_0 \frac{V}{V_0} \exp\left\{\left(K_0' + 1\right)\left(1 - \frac{V}{V_0}\right)\right\} \quad \ldots(17)$$

This is the equation for isothermal bulk modulus.

Using the well-established thermo dynamic approximation that is [**21,22,23**] under the effect of pressure the product of α (P) and K(P) remains constant. i.e.

$$\alpha K_P = \alpha_0 K_0 \quad \ldots(18)$$

Where α_0 and K_0 are the value of α and K at zero pressure. We have another approximation for Anderson- Gruneisen parameter **[28]**

$$\delta_T = -\frac{1}{\alpha K}\left(\frac{dK}{dT}\right)_P = \frac{dK}{dP} \quad \ldots(19)$$

at P=0, we have $\delta_T^0 = K_0'$. So the equation (15) with the help of equation (18) can be written as

$$\frac{\alpha}{\alpha_0} = \left(\frac{V}{V_0}\right)^{-1}\left\{1 + \frac{\delta_T^0 + 1}{K_0} P\right\}^{-1} \quad \ldots(20)$$

Using equation (17) we get

$$\alpha(P) = \alpha_0 \left(\frac{V}{V_0}\right)^{-1} \exp\left\{-\left(K_0' + 1\right)\left(1 - \frac{V}{V_0}\right)\right\} \quad \ldots(21)$$

Equation (20) and equation (21) are useful relation for predicting the pressure dependence of α along isotherm.

RESULTS AND DISCUSSION

Equation 14,17 and 21 have been used for the calculation of compression, isothermal bulk modulus and relative isothermal expansion coefficient, respectively for like 67 nm and 37 nm γ-Al_2O_3, 3C-SiC, nanocrystalline Ni, nano ε-Fe.The input parameters which are required are given in Table 1.We have plotted the variation of compression (V/V_0) , isothermal bulk modulus (K_T) and relative isothermal expansion coefficient $\alpha(P)/\alpha_0$) with pressure for nanocrystalline γ-Al_2O_3 with an average particle sizes 67 nm and 37 nm, nanocrystalline Ni (mean particle size 20 nm), 30 nm 3C-SiC and ε-Fe in figures 1-15. It may be noted from figures 1, 4, 7, 10 and 13 that the values of relative compression calculated from usual Tait's equation of state represent excellent agreement with the available experimental data. It is found in the present study that the 37 nm nanocrystalline γ-Al_2O_3 is more compressible at high pressure as compare to the 67nm nanocrystalline γ-Al_2O_3 (figures 1 and 4). It is clear that the variations of relative isothermal expansion coefficient ($\alpha(P)/\alpha_0$) and compression with pressure decreases and the variation of isothermal bulk modulus (K_T) increases with pressure for these nanomaterials. It may thus be concluded that the usual Tait's Equation of state explains the compressional behaviour of nanomaterials satisfactorily. The variation of isothermal bulk modulus and the variation of relative isothermal expansion coefficient with pressure could not be compared with the experimental values since the experimental data on these physical properties of nanomaterials under study are not available so far.

Table1: Input parameters

Materials	K_0(GPa)	K'_0
67 nm Al_2O_3	248[29]	3.2[29]
37 nm Al_2O_3	151[29]	5.7[29]
3C-SiC	220.6[30]	4[30]
Nano-ε-Fe	179[31]	3.6[31]
Nano Ni	185.4[32]	4[32]

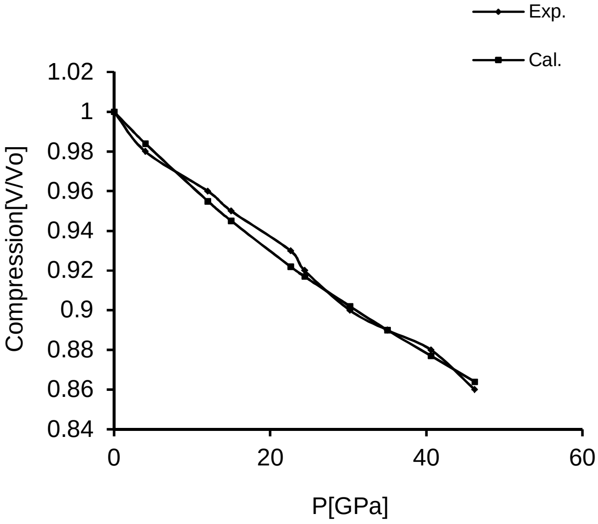

Figure 1: V/V_0 Vs pressure for 67 nm nanocrystalline γ-Al_2O_3.Exp. Ref.[29]

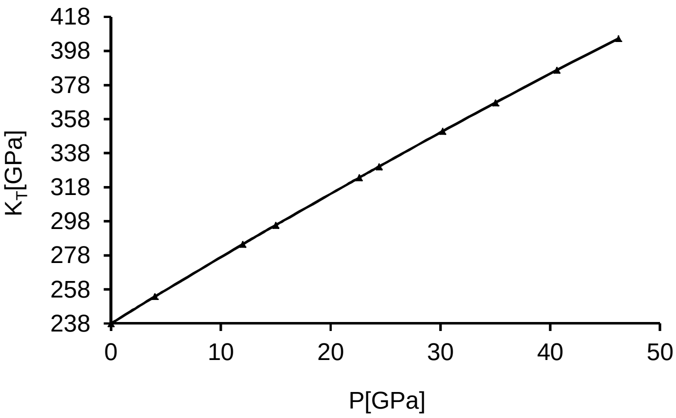

Figure 2: K_T vs pressure for 67 nm n- γ-Al_2O_3

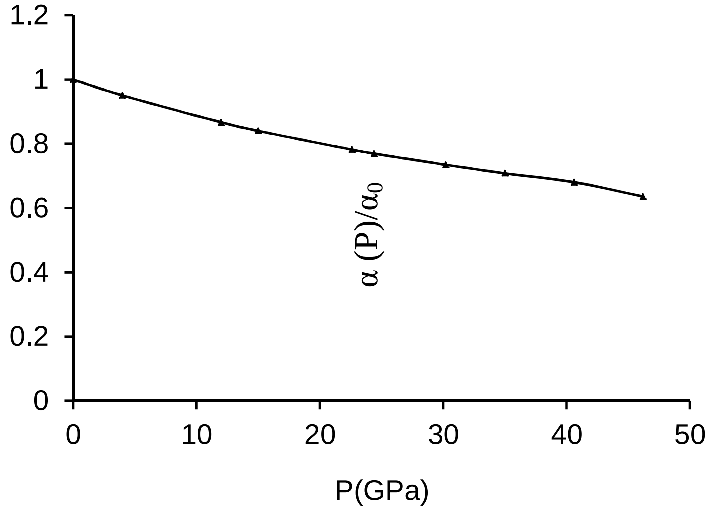

Figure 3:Relative isothermal expansion coefficient with pressure for 67 nm nanocrystalline γ-Al_2O_3

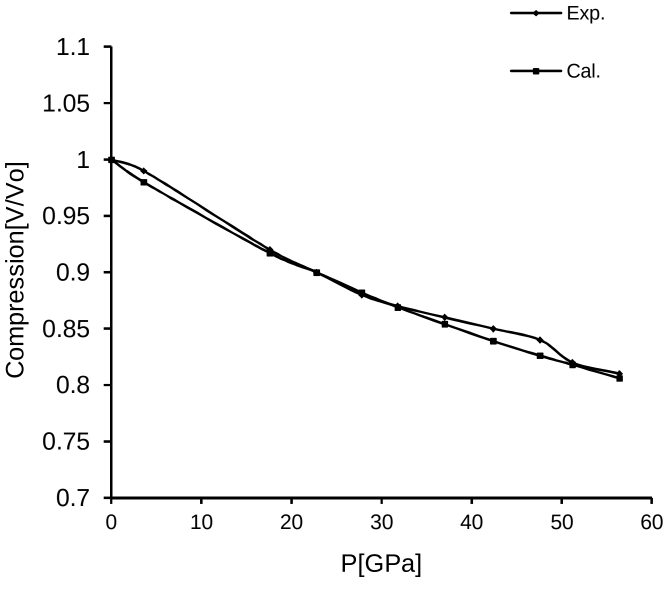

Figure 4:V/V0 vs pressure for 37 nm nanocrystalline γ-Al_2O_3. Exp. Ref.[29]

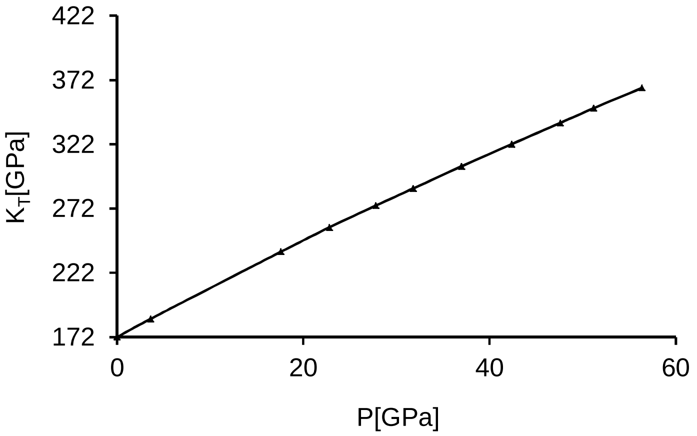

Figure 5: K_T vs pressure for 37 nm n-γ-Al_2O_3

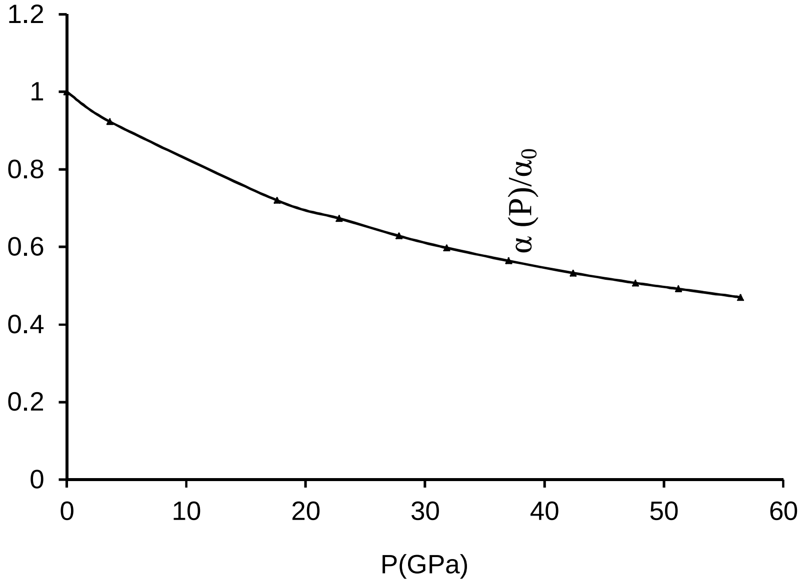

Figure 6: Relative isothermal expansion coefficient with pressure for 37 nm nanocrystalline γ-Al_2O_3

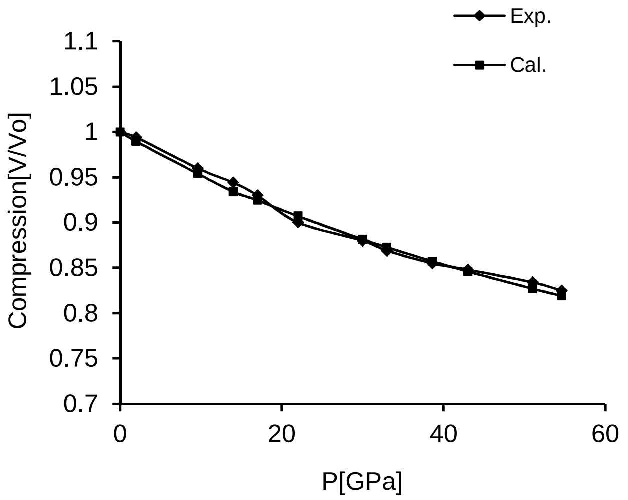

Figure 7: V/Vo vs pressure for 20 nm nanocrystalline Ni. Exp. Ref. [32]

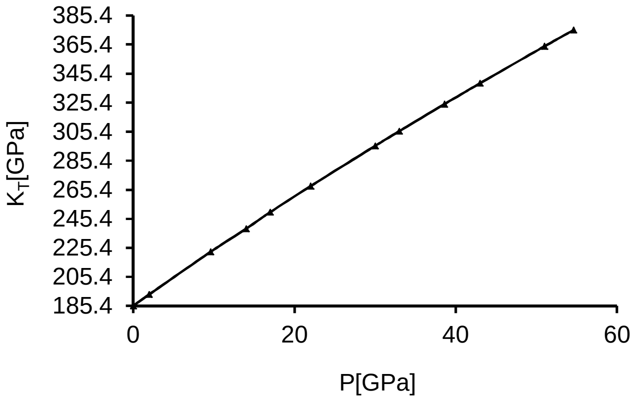

Figure 8: K_T vs pressure for 20 nm n- Ni

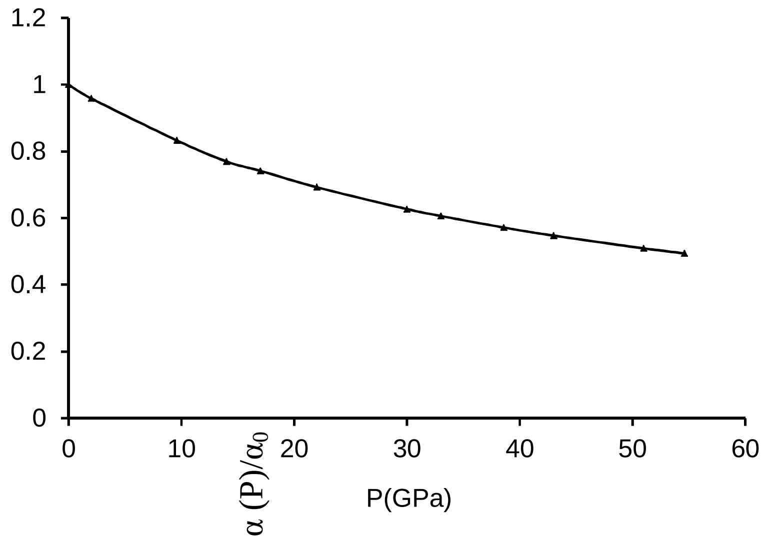

Figure 9: Relative isothermal expansion coefficient vs pressure for 20 nm n- Ni

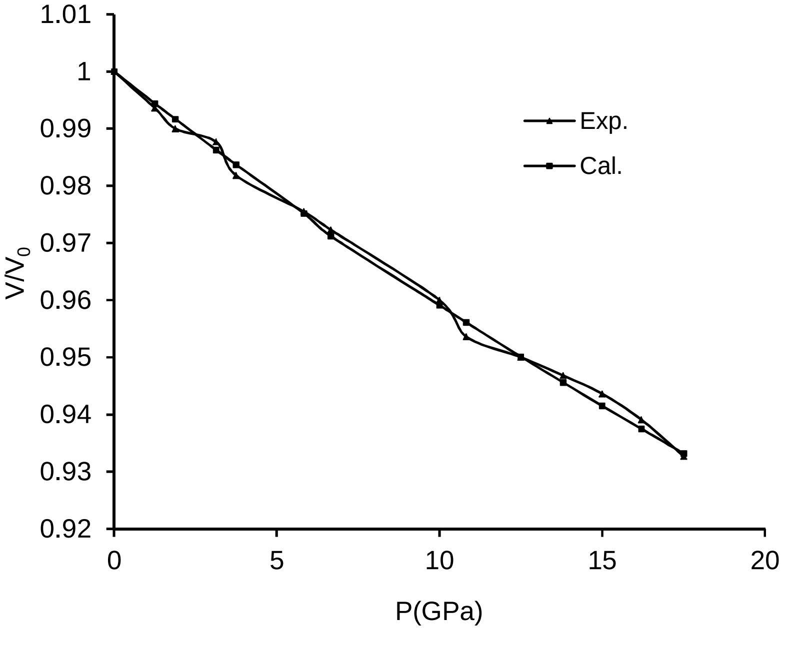

Figure 10: V/Vo vs pressure for 30 nm nanocrystalline 3C-SiC.Exp. Ref.[30]

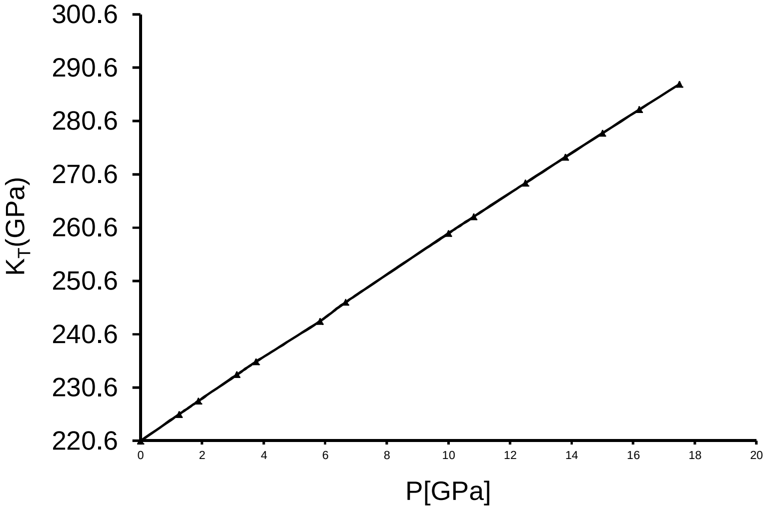

Figure 11: K_T vs pressure for 30 nm 3C-SiC

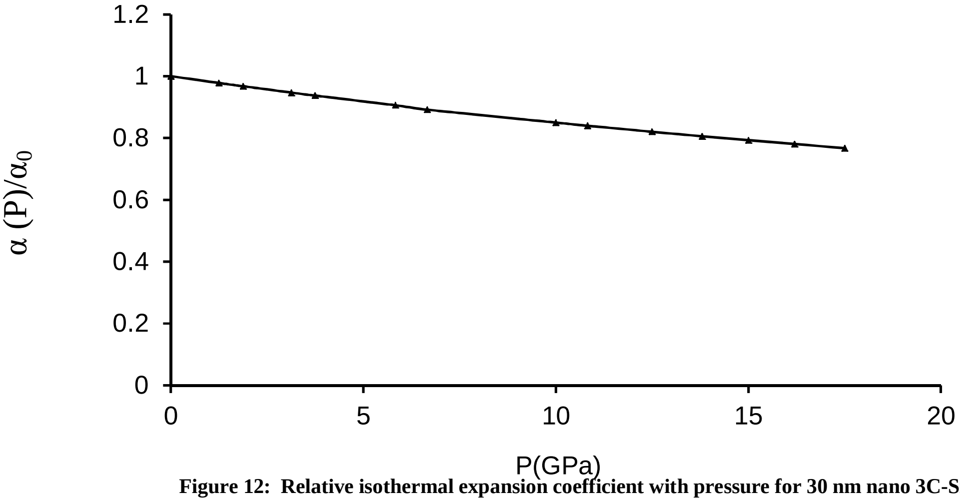

Figure 12: Relative isothermal expansion coefficient with pressure for 30 nm nano 3C-SiC

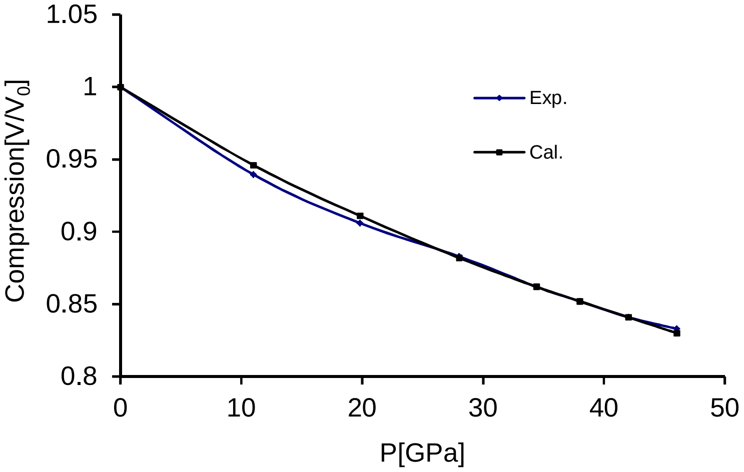

Figure 13: V/V_0 vs pressure n-ε-Fe.Exp. Ref.[31]

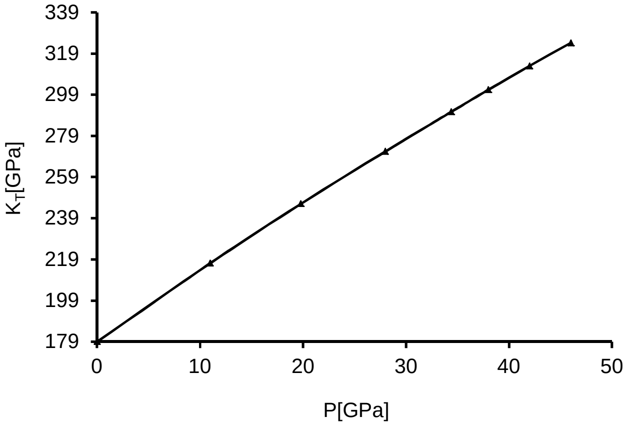

Figure 14: K_T vs pressure for n-ε-Fe

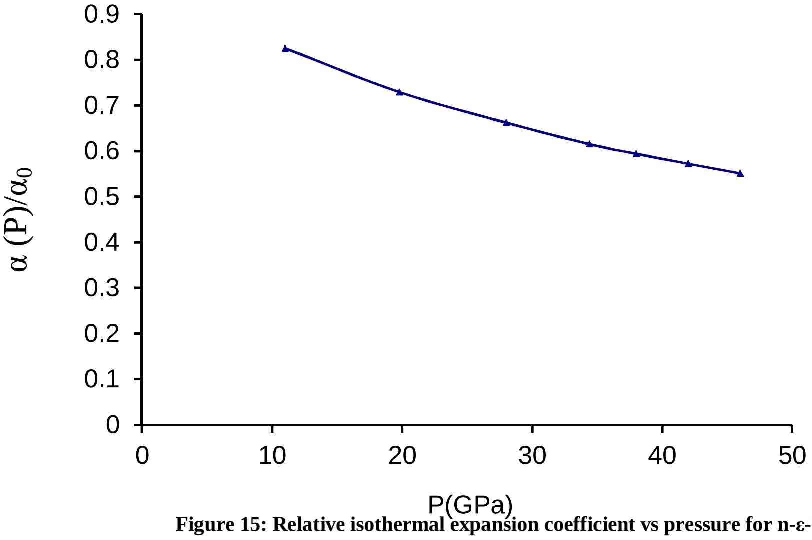

Figure 15: Relative isothermal expansion coefficient vs pressure for n-ε-Fe

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