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Scaling Behavior between Heat Capacity and Thermal Expansion in Solids

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We experimentally analyze the heat capacity and thermal expansion of reference solids in a wide temperature range from several Kelvin to melting temperature, and establish a universal double-linear relation between the experimental heat capacity C_p and thermal expansion β, which is different from the previous models. The universal behavior between heat capacity and thermal expansion is important to predict the thermodynamic parameters at constant pressure, and is helpful for understanding the nature of thermal properties in solids.

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Heat capacity (HC) and coefficient of thermal expansion (CTE) can be used to characterize changes in macroscopic variables, for example, temperature-dependent enthalpy and volume. They are the most fundamental and important thermodynamic parameters for solids, and have been widely studied by many theoretical and experimental methods.[1,2] In general, heat capacity depends upon temperature T and conditions of heating: at constant-volume C_v or constant-pressure C_p. Conventionally, C_v is smaller than C_p. HC data are usually obtained under constant, generally atmospheric, pressure, i.e. experimental HC usually refers to C_p. At low temperatures, HC is very sensitive to the atomic structure of the solids and to the quantum mechanical nature of the atomic motions, which was developed by Einstein and Debye.[3,4] HC of solids near room temperature is usually close to a constant $3R$ (R: gas constant), which is the Dulong–Petit law. HC of solids at high temperatures is larger than the theoretical value $3R$, which is due to thermal expansion and is usually explained by anharmonic effect.[5] However, direct relationship between experimental HC and CTE is rarely reported.

There is a well-known relationship between C_v and C_p:

$$C_p = C_v + KVT\beta^2, \tag{1}$$

where V is the molar volume, β the coefficient of volumetric thermal expansion at constant pressure and is defined as $\beta = \frac{1}{V} \cdot \frac{dV}{dT}$, T is the temperature, and K is the isothermal bulk modulus.[6] Values of C_p, β, K, T and V are measured by experiments, C_v can only be determined according to Eq. (1) or theoretical models. Another relationship in terms of the C_v and β, suggested by Grüneisen, is

$$C_v = KV\beta/\gamma, \tag{2}$$

where γ is the Grüneisen constant.[7] From Eqs. (1) and (2), the relation of C_p and β should be quasi-parabolic. Actually, the Grüneisen constant is calculated by Eqs. (1) and (2). Because values of C_v and γ cannot be directly measured by experiments, the correlative behavior between C_p and β cannot be determined by the relationships or the models.

By studying the experimental results, Bodryakov reported the linear behavior between the HC and CTE for some materials at low temperatures or low HC (below $3R$).[8,9] He also reported a trilinear behavior between the HC and CTE for solid KCl from zero to melting temperature.[10] Andritsos *et al.* analyzed the anharmonic effect on the C_v by molecular dynamics simulation, and shows that the C_v is dependent on the temperature and CTE.[5] Askerov and Cankurtaran theoretically studied the temperature-dependent C_p and β by Debye approximation, and the relationship between the C_p and β is complicated and temperature-dependent.[11] Drebushchak *et al.* studied the relationship between the C_p and β by the Lennard–Jones potential, and the pressure-dependent C_p.[12,13] Garai theoretically predicted a linear correlation between the C_p and β below the Debye temperature.[14] The studies of Raju *et al.* show that the ratio β/C_p is approximated by a temperature-independent constant, the temperature-dependent bulk modulus, enthalpy and volume are estimated, and are close to the experimental data.[15] Although there are some experimental results or models about the correlation between the C_p and β, the systemic studies about the universal relationship between the experimental C_p and β for general solids in wide temperature ranges are lacking.

Our previous study shows a new heat capacity model by the correlation between the experimental heat capacity C_p and coefficient of thermal expansion (β) in Al_2O_3 and Cu.[16] In this work, we quantitatively analyze the experimental HC C_p and the

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coefficient of volumetric thermal expansion (β) in a series of reference solid materials with the melting temperature T_m from 3695 K to 84 K, and find that there is a critical HC C_{p0} for each of the reference solids: the experimental C_p is linearly dependent on the CTE β, below or above the critical value, respectively. The linear behavior is different from the quasi-parabolic result by Eqs. (1) and (2). The average value of the critical HC C_{p0} in the reference solid materials is $25.17\pm0.91\,\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$, which is close to the Dulong–Petit value $3R$. The universal thermodynamic behaviors are helpful to predict the macroscopic physical properties in general solids.

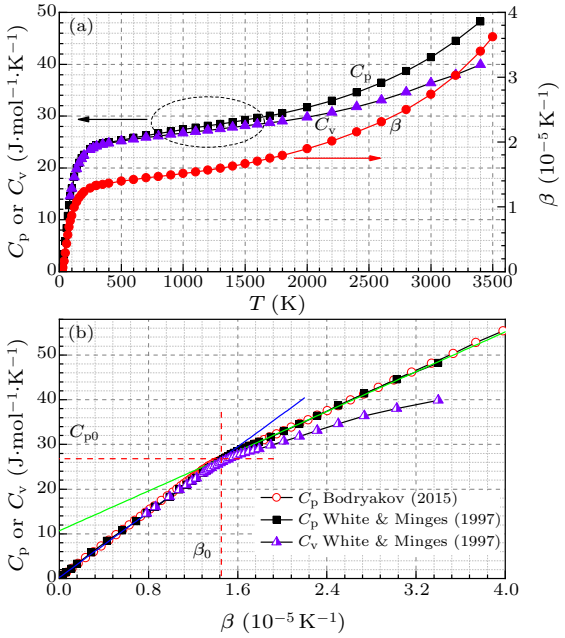

Fig. 1. (a) Temperature-dependent heat capacity C_p (or C_v) and the coefficient of volumetric thermal expansion β for tungsten (data from White and Minges); (b) correlation between the C_p (or C_v) and β for tungsten (square and triangle: data from White and Minges;[17] circle: data from Bodryakov[8]), solid lines: linear-fitting results (blue line: C_p is below about $3R$; green line: C_p is above about $3R$); dashed lines: the coordinates of the intersection of the blue and green solid lines.

Collating and Analyzing the Experimental Data. The experimental heat capacity C_p, the calculated constant-volume heat capacity C_v, and the coefficient of volumetric thermal expansion (β) of pure metal: tungsten (W) up to melting temperature are shown in Fig. 1(a).[17] When the temperature is close to zero, both HC and CTE are close to zero. Above zero Kelvin, both HC and CTE quickly increase with increasing temperature. After the HC is close to the Dulong–Petit value $3R$, both HC and CTE still gradually increase with temperature, but the changes in both HC and CTE with temperature obviously decrease. Thus, the CTE varies with temperature in the same manner as the experimental HC. The constant-volume heat capacity C_v is close to the experimental heat capacity C_p below $3R$. Above $3R$, the difference between the C_p and C_v gradually increases with the increasing temperature. By the temperature-dependent heat capacity C_p (or C_v) and thermal expansion β, we can obtain the C_p (or C_v) and β at same temperatures, and determine the correlation between the C_p (or C_v) and β. Figure 1(b) shows the correlative behavior between the C_p (or C_v) and β of tungsten (data from Refs. [8,17]). There is an inflection in the C_p (or C_v) vs β data of tungsten. The value of HC at the inflection is a critical HC: C_{p0}. The constant-volume heat capacity C_v is linearly dependent on the CTE β below the critical HC C_{p0} (or at low temperatures), and deviates from the linear behavior above the critical HC C_{p0}, which is different from the theoretical models.[7] Therefore, from the correlative behavior between the C_v and β for tungsten, the Grüneisen parameter in Eq. (2) cannot keep a constant in the wide temperature range, and the Grüneisen model is effective only below the critical HC (or at low temperatures).

Above or below the critical HC, the experimental HC C_p exhibits linear behavior with the CTE β:

$$C_p = C + E\cdot\beta, \tag{3}$$

where C and E are constants. The parameters C_1 and E_1 (or C_2 and E_2) in Eq. (3) for tungsten are determined by linear fitting below (or above) the critical HC C_{p0}, respectively (the solid lines), and are listed in Table 1. The value of the critical HC C_{p0} for tungsten, quantitatively determined by the intersection of the solid fitting lines (blue and green), is about $26.95\,\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$.

Previous studies mainly focused on the correlation between the HC and CTE at low temperatures. In order to study the universal correlative behavior between the C_p and β in solids, we survey the experimental heat capacity C_p and the coefficient of volumetric thermal expansion (β) in a series of reference solid materials.[9,17–29] The experimental data of the C_p and β were measured at constant pressure, and were obtained in a wide temperature range from several Kelvin to melting temperature. The investigated solid materials include metals (W, Ta, Mo, Pt, Be, Cu, Al, and Hg), oxides (MgO and Al_2O_3), and inert monatomic solids (Xe, Kr, and Ar). Their melting temperatures are in the range from 3695 K to 84 K (as listed in Table 1).[30]

The correlative behavior between the C_p and β in the reference solid materials is shown in Fig. 2(a). The CTEs of inert monatomic solids are much larger than those of other solids. Figure 2(b) exhibits the correlative behavior between the C_p and β for the reference solid materials at low CTE. Similarly to tungsten, all

of the reference solids show an inflection in the C_p vs β data. The critical HCs C_{p0} at the inflection for the reference solids are close to $3R$, and the HC exhibits linear behavior with the CTE above or below the critical HC, respectively. The linear behavior is different from the previous common belief: the quasi-parabolic relation by Eqs. (1) and (2).

Table 1. Thermodynamic parameters of some reference solid materials (mol: a mole of atoms): T_m: melting temperature (see Ref. [30]); parameters C_1 and E_1 (or C_2 and E_2) obtained by the equation $C_p = C + E\beta$ (C_p: the experimental heat capacity; β: the coefficient of volumetric thermal expansion) when C_p is below (or above) about $3R$, respectively; C_{p0}: the critical heat capacity; V: the molar volume at room temperature (see Ref. [30]); K: the isothermal bulk modulus at room temperature (see Ref. [30]); P_2: the equivalent pressure (calculated by E_2/V).

Materials	T_m (K)	C_1 ($J\cdot mol^{-1}\cdot K^{-1}$)	E_1 (10^6 J/mol)	C_2 ($J\cdot mol^{-1}\cdot K^{-1}$)	E_2 (10^6 J/mol)	C_{p0} ($J\cdot mol^{-1}\cdot K^{-1}$)	V (cm^3/mol)	K (GPa)	P_2 (GPa)	Refs.
W	3695	0.24(6)	1.827(9)	10.69(14)	1.112(7)	26.95	9.47	310	117	[17]
Ta	3293	0.007(1)	1.3060(2)	6.322(6)	0.9752(2)	24.93	10.85	200	90	[18]
MgO	3125	0.17(12)	0.5914(41)	13.26(50)	0.2745(102)	24.60	5.52	162	50	[19]
Mo	2896	−0.008(30)	1.583(4)	11.10(7)	0.9142(25)	26.28	9.38	230	97	[20]
Al_2O_3	2327	−0.020(7)	0.94085(7)	14.27(4)	0.4060(14)	25.12	5.14	252	79	[21]
Pt	2042	0.27(33)	0.9550(218)	8.88(36)	0.6007(89)	23.49	9.09	230	66	[22]
Be	1560	0.00006(19)	0.46509(1)	6.209(12)	0.3494(2)	24.96	4.85	130	72	[23]
Cu	1357	0.19(5)	0.4997(23)	12.78(48)	0.2394(73)	24.36	7.11	140	34	[17]
Al	934	−0.11(3)	0.3608(9)	14.17(87)	0.1618(96)	25.79	10.00	76	16	[24–26]
Hg	264	0.011(7)	0.2239(1)	19.96(6)	0.0510(4)	25.84	14.09	25	3.6	[9]
Xe	161	0.057(24)	0.04712(9)	17.43(9)	0.01391(9)	24.70				[27]
Kr	116	0.30(5)	0.0319(1)	17.35(13)	0.01041(9)	25.60				[28]
Ar	84	0.10(3)	0.02112(6)	12.95(7)	0.01004(4)	24.59				[29]

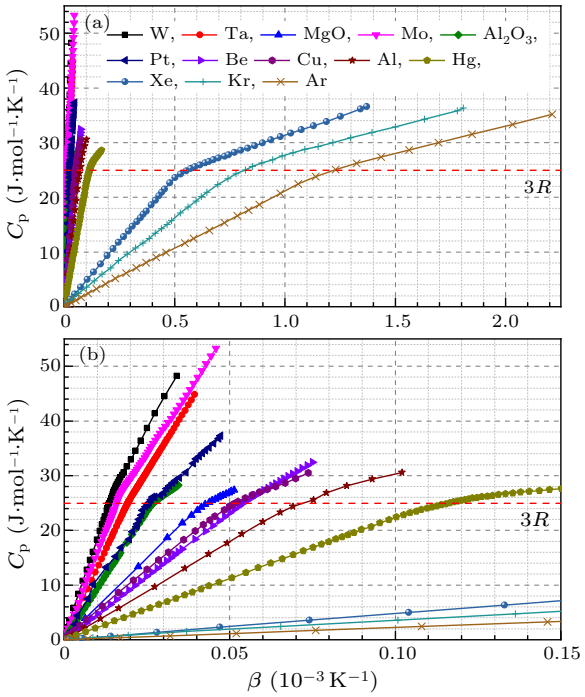

Fig. 2. (a) Correlative behavior between the C_p and β for the reference materials listed in Table 1. (b) C_p and β for the reference materials at low coefficient of volumetric thermal expansion. The dashed line is the Dulong–Petit value $3R$.

The parameters C_1 and E_1 (or C_2 and E_2) of the reference solid materials, shown in Table 1, are the fitting results by Eq. (3) below (or above) the critical HC, respectively. The values of the critical HC C_{p0} for the reference solid materials, determined by the intersection of the fitting lines, are shown in Fig. 3. The average value of C_{p0} (the blue line in Fig. 3, the blue dashed lines are the errors) is $25.17 \pm 0.91\,J\cdot mol^{-1}\cdot K^{-1}$, which is close to the Dulong–Petit value $3R$ (the red line in Fig. 3).

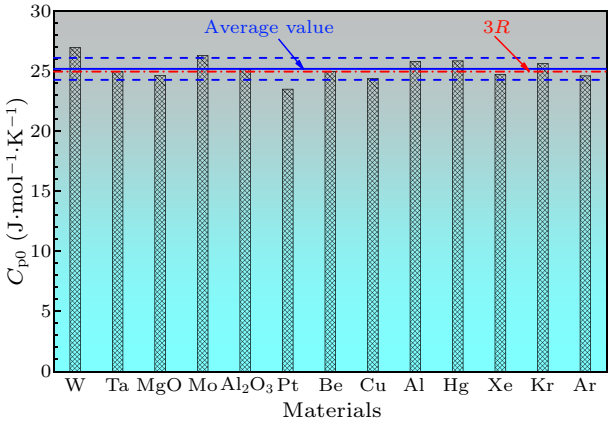

Fig. 3. Critical heat capacity C_{p0} for the reference solid materials, which is determined by the intersection of the linear fitting lines. The blue line is the average value of C_{p0}, the dashed blue lines are the errors, and the dot-dashed red line is the Dulong–Petit value $3R$.

The parameters C_1 for the reference solid materials are close to 0, which are in agreement with the experimental results: both HC and CTE increase from zero at 0 K with the increasing temperature. The CTE is scaled by the parameter E_1, and all of the reference solid materials present the same linear behavior between the C_p and scaled β below the critical HC C_{p0}, as shown in Fig. 4(a). Similarly, the CTE is scaled by the parameters C_2 and E_2, and the linear behavior be-

tween the C_p and scaled β above the critical HC C_{p0} for the reference solid materials is shown in Fig. 4(b). Therefore the linear correlative behavior between the experimental C_p and β below or above the critical HC C_{p0} is a universal property in solids.

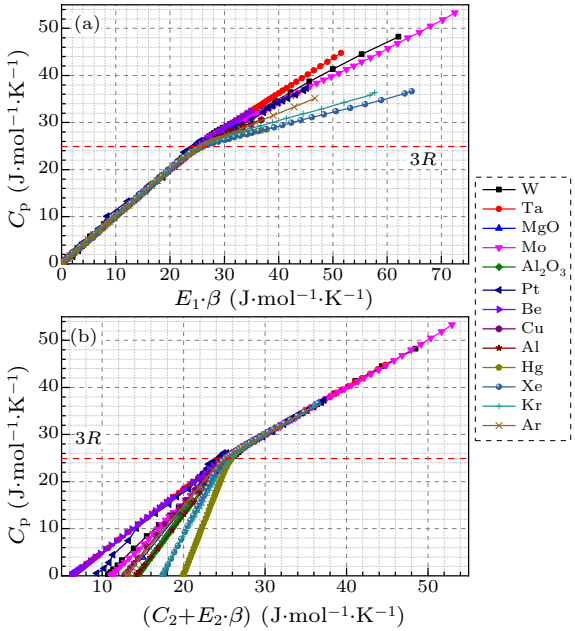

Fig. 4. Linear behavior between the C_p and different scaled β: (a) $E_1 \cdot \beta$ and (b) $C_2 + E_2 \cdot \beta$, for the reference materials listed in Table 1. The dashed line is the Dulong–Petit value $3R$.

Discussions. In metals, the heat capacity usually includes the contributions of the phonon (or lattice) and electron. The electronic heat capacity is linearly temperature-dependent at low temperatures, and is usually a small fraction of the phonon (or lattice). However, at very low temperatures, the situation reverses and the electronic specific heat becomes dominant.[31] The oxides and inert monatomic solids are insulated. The electronic heat capacity of insulated solids is zero. In this study, the reference solids include metals, oxides, and inert monatomic solids. Above several Kelvin, all of reference solids, including metals and insulated solids, show the same scaling behavior between the HC and CTE. Thus, the electronic heat capacity may be negligibly small in the temperature range, or the free electrons may induce the thermal expansion like the phonon (or lattice), and the electronic heat capacity and electronic thermal expansion also follow the scaling behavior.

We define the equivalent pressure $P_2 = E_2/V$, (V: the molar volume). Usually, the change of volume in solids from zero to melting temperature is less 5%. The values of P_2 in the reference solid materials are determined by the molar volume V at room temperature, as listed in Table 1. The equivalent pressure P_2 are close to their isothermal bulk modulus K at room temperature (also shown in Table 1). The equivalent pressure P_2, determined by the correlation between the C_p and β, is four orders of magnitude larger than the experimental pressure (one atmospheric pressure). Thus, compared to the equivalent pressure, the low experimental pressure weakly affects the heat capacity or thermal expansion of solids, and the scaling behavior between the C_p and β in solids is still effective at atmospheric pressure or low pressure.

Our result shows that there is a universal correlation between the experimental heat capacity and thermal expansion in solids at constant pressure. The thermodynamic variables can be predicted by the universal properties or Eq. (3). For example, the temperature-dependent thermal expansion or volume can be predicted by the heat capacity, and the temperature-dependent heat capacity or enthalpy can be predicted by the thermal expansion in solids. On the other hand, we can also predict the internal energy function at constant pressure. The HC is defined in thermodynamics: $C_p = (\frac{dQ}{dT})_P$ at constant pressure P with Q being the heat and T the temperature. By the basic relation in thermodynamics at constant pressure $dQ = dU + PdV$ (dQ: the change of the heat, dU: the change of the internal energy, and dV: the change of the volume), the temperature-dependent change of the parameters can be written as $(\frac{dQ}{dT})_P = (\frac{dU}{dT})_P + P(\frac{dV}{dT})_P$. By $\beta = \frac{1}{V} \cdot (\frac{dV}{dT})_P$ and Eq. (3), the equation can be written as

$$\left(\frac{dU}{dT}\right)_P = C + \left(\frac{E}{V} - P\right)V\beta. \tag{4}$$

Hence, we can obtain the internal energy function $U(T, V)$ at low constant pressure P by Eq. (4) as follows:

$$U = CT + E\ln\left(\frac{V}{V_0}\right) - P(V - V_0), \tag{5}$$

where V_0 is the molar volume at zero Kelvin, and $U = 0$ at zero Kelvin.

In quantum statistical physics, one of the central and most recognizable results is that the heat capacity of a solid increases from zero gradually up to near $3R$ with increasing the temperature. However, the experimental heat capacity at high temperatures usually exceeds the theoretical value $3R$, even is double value of $3R$. For example, the heat capacities of W and Mo are about 48 and 53 J·mol^{-1}·K^{-1} near their melting temperatures, respectively. The anharmonic effect of interatomic interaction is induced by the thermal expansion, and is used to explain the excess heat capacity.[1,32–34] The anharmonicity may govern many properties of solids, including the heat capacity, the thermal expansion and conductivity, phase transitions, melting, and so on. When the heat capacity is

up to $3R$, the phonon heat capacity is close to a constant. The heat capacity continues to increase with the thermal expansion. Thus, the anharmonicity can be quantified by the universal correlation between the heat capacity and thermal expansion in solids.

In summary, we have, for the first time, found that the experimental $C_{\rm p}$ is linearly dependent on the β above or below the critical HC $C_{\rm p0}$ in the reference solid materials, and discussed the universal scaling behavior between the $C_{\rm p}$ and β. The average value of the critical HC $C_{\rm p0}$ in solids is $25.17 \pm 0.91\,{\rm J\cdot mol^{-1}\cdot K^{-1}}$. The universal scaling behavior is effective at low pressure in both metals and insulated solids, and can be used to quantitatively determine the internal energy and anharmonicity in solids.

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