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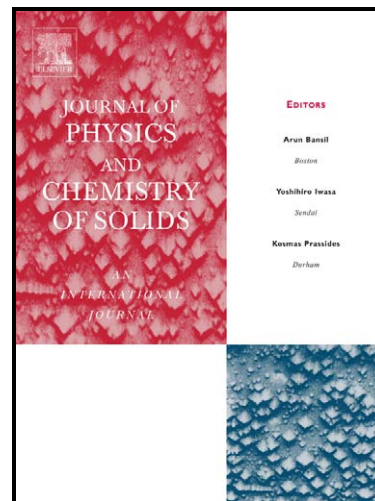
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Anomalous temperature dependence of elastic constant c_{44} in V, Nb, Ta, Pd, and Pt

L. Huang[1], M. Ramzan[1], L. Vitos[1,2,3], B. Johansson[1,2], and R. Ahuja[1,2*]

[1]*Condensed Matter Theory Group, Department of Physics,*

Uppsala University, BOX 530, SE-751 21, Uppsala, Sweden

[2]*Applied Materials Physics, Department of Materials and Engineering,*

Royal Institute of Technology (KTH), SE-100 44, Stockholm, Sweden

[3]*Research Institute for Solid Stade Physics and Optics,*

P.O. Box 49, H-1525 Budapest, Hungary

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Abstract

The anomalous temperature dependence of elastic constant c_{44} for elements V, Nb, Ta, Pd, and Pt, has been calculated using first-principles theory. It is shown that the variation of elastic constant for simple elements can be approximated as the sum of thermal expansion and electronic components. The thermal expansion contributes the normal linearly decreasing effect to the elastic constant with temperature, while electronic contribution is determined by the unique character of electronic structure of elements and leads to the anomalous effect to the elastic constant with temperature.

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*Corresponding author. E-mail: `rajeev.ahuja@fysik.uu.se`

I. INTRODUCTION

The elastic constants are perhaps the most fundamental property of condensed matter. In general, due to the thermal expansion of lattice, the elastic constants show a monotonically decreasing trend with increasing temperature. However, with the pronounced effect of electronic entropy, an anomalous temperature dependence of the shear elastic constant c_{44} has been observed for transition metals V, Nb, Ta, Pd, and Pt [1–7].

In this letter, by applying a simple quasi-harmonic approximation [8], the electronic effect is separately calculated from the normal thermal expansion effect. In this way, the subtle contribution of electronic structure on the temperature dependence of elastic constant can be precisely evaluated. Our theoretical results show a good agreement with the previous experimental measurements. Compared with other theoretical methods [9, 10], which can be used for the calculation of elastic constant with temperature, our model shows a good calculation efficiency and a transparent physical picture.

II. METHODS

The isothermal elastic constants c_{ij} (simplified as c) are derived from the second order strain derivative of the Helmholtz free energy of the system, which can be separated as

$$F(V, T) = E_e(T, V) + F_v(T, V) - TS_e(T, V). \tag{1}$$

where E_e is the electronic energy, F_v is the phonon vibrational free energy, and S_e is the electronic entropy given by

$$S_{el} = -2k_B \int \{f(E)lnf(E) + [1 - f(E)]ln[1 - f(E)]\}N(E)dE. \tag{2}$$

where $f(E)$ is the Fermi-Dirac distribution, $N(E)$ is the density of states (DOS), and k_B is the Boltzman constant. The function inside the big brackets is sharply peaked around the chemical potential μ, thus only $N(E)$ around μ gives the contribution to the electronic entropy. The electronic energy E_e and entropy S_e were calculated using the finite temperature density functional theory [11]. Including explicitly the Fermi-Dirac statistics, the temperature dependent charge density and chemical potential μ are calculated to determine E_e and S_e. The variation of the elastic constants from zero temperature $T_0 = 0$K to temperature

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T is equal to $\Delta c(T, V) \equiv c(T, V) - c(T_0, V_0).\Delta c(T, V)$ can be calculated as the sum of a constant temperature and volume component[8]

$$\Delta^T c = c(T, V) - c(T, V_0) \quad and \quad \Delta^V c = c(T, V_0) - c(T_0, V_0). \tag{3}$$

In Fig. 1, the c_{44} of Nb, at the constant temperature, shows a closely linear decreasing dependence on increasing volume. The linear dependences for various temperatures are differed by less than 2% up to the melting temperature. Furthermore, we observed the same behavior with all the other calculated elements. Therefore, in this study, we take an approximation assuming $\Delta^T c(T, V)$ shows a constant linear dependence of V, thus can be calculated by equation

$$\Delta^T c(T, V) \approx \frac{\partial c}{\partial V}|_{V_0, T_0}[V(T) - V_0], \tag{4}$$

The thermal expansion can be calculated by the equation

$$V(T) - V_0 = \int_{T_0}^{T} V(T')\alpha dT', \tag{5}$$

where α, the thermal expansion coefficient, is calculated using a Debye theory combined with the *ab-initio* equation of state (EOS) [12]. We neglect the phonon contributions at fixed volume and use the electronic free energy $F_e(T, V_0)$ to compute $\Delta^V c(T, V_0)$, which only contains the electronic contribution from Fermi-Dirac distribution and its function with T is closely related with the variation of density of states around the Fermi level induced by the distortion matrix of c. The electronic free energies F_e are calculated using the exact muffin-tin orbitals (EMTO) method [13, 14]. When compared to the conventional muffin-tin or nonoverlapping approach, the exact crystal potential is more accurately described by the overlapping spheres in EMTO method. The generalized gradient approximation (GGA) [15] was used for treating exchange correlation potential. The s, p, d, and f orbitals (l_{max}=3) are used to solve the one electron equations with the soft-core approximations. To obtain the good accuracy for the calculation of elastic constants, we used about 30 000 uniformly distributed k points in the irreducible wedge of the Brillouin zones. The shear elastic constant c_{44} in cubic lattice is calculated from a volume conserving monoclinic deformation,

$$\begin{pmatrix} 1 & \epsilon & 0 \\ \epsilon & 1 & 0 \\ 0 & 0 & 1/(1-\epsilon^2) \end{pmatrix}. \tag{6}$$

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The corresponding strain energy

$$E(\epsilon) = E(0) + 2Vc_{44}\epsilon^2 + O(\epsilon^4) \tag{7}$$

for four distortions $\epsilon = 0.00,\ 0.01,\ 0.02,\ 0.03$ is calculated. The c_{44} were determined from the linear function in ϵ^2 fitted to the total energy $E(\epsilon)$.

III.   RESULTS AND DISCUSSIONS

The table I shows the calculated equilibrium volume V_0, bulk modulus B, elastic constant c_{44}, and the thermal expansion coefficient α compared with experimental values [16]. The good agreement between theoretical and experimental data shows that our calculation method can give an accurate description on the ground state properties.

Fig. (2 and 3) shows the calculated temperature dependence of c_{44} for the elements Nb and Pd, respectively. In there, the electronic and thermal expansion contributions are shown in (a) and (b), respectively. The total variations of c_{44} with temperature are shown in (c) and compared with previous experimental data. The previous reported theoretical results are also plotted.

Δc_{44}^V contains the electronic contribution and is closely related with the density of states around Fermi level. Fig. 4 shows calculated density of states (DOS) around Fermi level for five elements in their equilibrium lattice and in the corresponding c_{44} typed monoclinic distorted lattice. The common feature that all the Fermi levels for the five elements are located at the right side of valence band peak can be clearly noticed. The DOS for c_{44} typed distorted lattice show subtle variations from the equilibrium lattice. As for the variation of Δc^V with temperature, it can be easily deduced that the lower DOS by distorted lattice will give an increasing effect, while the higher DOS by the distorted lattice will give a decreasing effect. Our calculation on the elastic constant can precisely capture the subtle effect of electronic structure of each elements. According to the equation 2, only the density of states around Fermi energy has a contribution to the electronic entropy. When temperature increases, the wider range of density of states around Fermi level will be included to contribute the electronic entropy. For V, Nb, and Ta, the density of states for distorted lattice within $\pm$ 0.1 eV around Fermi level show higher than the density of states for bcc lattice, while become lower at the wider energy range. Thus from the Fig. 2 (a) $\Delta^V c_{44}$ first shows a

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decrease at lower temperature and then an increase at higher temperature. For fcc elements Pd and Pt, the DOS for c_{44} distorted lattice around Fermi energy are always lower than the DOS for fcc lattice. Thus seen in the Fig. 3 (a), $\Delta^V c_{44}$ always increase when temperature is increased from 0 K.

The temperature dependence of the second component $\Delta^T c_{44}$ is much simple. As seen in Fig 2 and 3 (b), when temperature higher than the debye temperature, $\Delta^T c_{44}$ always shows a linearly decreasing trend with increasing temperature and this behavior is the so called normal temperature dependence of elastic constants. Our calculated thermal expansions α for five elements show certain deviation from the experimental values. Using the experimental α, we made recalculation of $\Delta^T c_{44}$, indicated by the dashed line in Figure (b). As is seen, the results of $\Delta^T c_{44}$ using Debye model show good agreement with the $\Delta^T c_{44}$ calculated using experimental α, especially at the lower temperature range.

The over all variations of c_{44} with temperature are compared with experimental data in Fig 2 and 3 (c), which show that the main temperature dependence trend for each elements are closely agreed between experiments and our theory. Especially, for the fcc Pd, the flat curves of c_{44} as a function of temperature at lower temperature range is closely captured by our theoretical calculations.

IV. CONCLUSIONS

To summarize, we have shown by approximating the variation of elastic constants with temperature as the sum of thermal expansion and electronic contributions, the anomalous temperature dependence of c_{44} for five transition metals V, Nb, Ta, Pd, and Pt, can be accurately captured by our theoretical model. The separating treatment for the different contributions can provide a transparent physical picture on how the each parameters will influence the total variation of elastic constants.

[1] E. Walker, Solid State Commun. **28**, 587 (1978).

[2] Y. Talmor, E. Walker and S. Steinemann, Solid state Commun. **23**, 649 (1977).

[3] E. Walker and P. Bujard, Solid State Commun. **34**, 691 (1980).

[4] J. A. Rayne, Phys. Rev. **118**, 1545 (1960).

[5] R. E. MacFarlane, J. A. Rayne and C. K. Jones, Phys. Lett. **18**, 91 (1965).

[6] P. Bujard, R. Sanjines, E. Walker, J. Ashkenazi and M. Peter, J. Phys. F: Metal Phys., **11**, 775 (1981).

[7] J. Ashkenazi, M. Dacorogna, M. Peter, Y. Talmor, and E. Walker, Phys. Rev. B **18**, 4120 (1978).

[8] L. Huang, L. Vitos, S. K. Kwon, and B. Johansson, Phys. Rev. B **73**, 104203 (2006).

[9] A. R. Oganov, J. P. Brodholt, and G. D. Price, Nature, **411**, 934 (2001).

[10] R. E. Cohen and O. Gülseren, Phys. Rev. B **63**, 224101 (2002).

[11] N. D. Mermin, Phys. Rev. **137**, A1441 (1965).

[12] P. Söderlind and B. Johansson, Thermochim, Acta **218**, 145 (1993).

[13] L. Vitos, Phys. Rev. B **64**, 014107 (2001).

[14] O. K. Andersen and T. Saha-Dasgupta, Phys . Rev. B **62**, 16219 (2000).

[15] J. P. Perdew, Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[16] V. L. Moruzzi and J. F. Janak, and K. Schwarz, Phys. Rev. B **37**, 790 (1988).

[17] R. J. Wolf, K. A. Mansour, M. W. Lee, R. R. John, Phys. Rev. B **46**, 8027 (1992).

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TABLE I: Theoretical and experimental [16] equilibrium volume V_0, bulk modulus B, shear elastic constant c_{44}, and thermal expansion coefficient α.

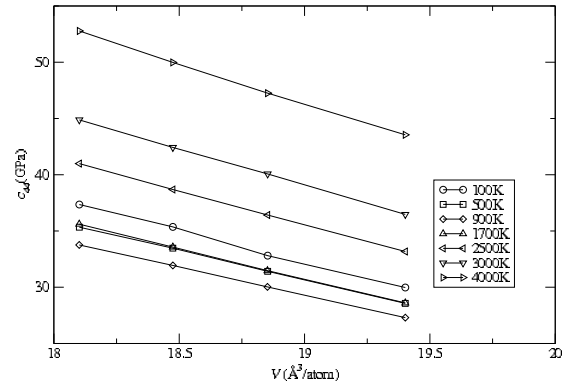|		V_0 (Å^3)	B(GPa)	c_{44}(GPa)	α(x10^{-6}K^{-1})
V	EMTO	13.47	175	35.69	6.6
	Exp.	13.77	162	45.87	7.8
Nb	EMTO	18.13	161	37	6.0
	Exp.	17.98	170	30	7.1
Ta	EMTO	18.41	185	95.8	4.6
	Exp.	18.13	200	87.6	6.3
Pd	EMTO	15.48	165	85.15	12.59
	Exp.	14.72	181	71.17	11.6
Pt	EMTO	15.84	244	98.72	8.13
	Exp.	15.06	230	77.4	8.9

FIG. 1: Elastic constant c_{44} as a function of volume at different constant temperatures from 100 K to 4000 K.
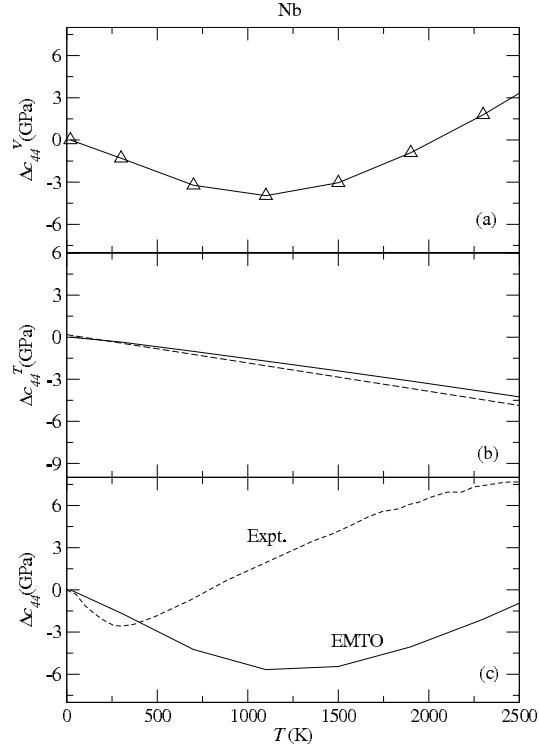
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FIG. 2: The calculated temperature dependence of c_{44} of bcc Nb. The electronic contribution Δc_{44}^V, the thermal expansion contribution Δc_{44}^T, and the total Δc_{44} with function of temperature are ploted in (a), (b), and (c) respectively. In the Fig (b), the dashed line represent the calculated Δc_{44}^T using the experimental thermal expansion coefficient α. The previous theoretical and experimental data [6] are compared with our theoretical result.
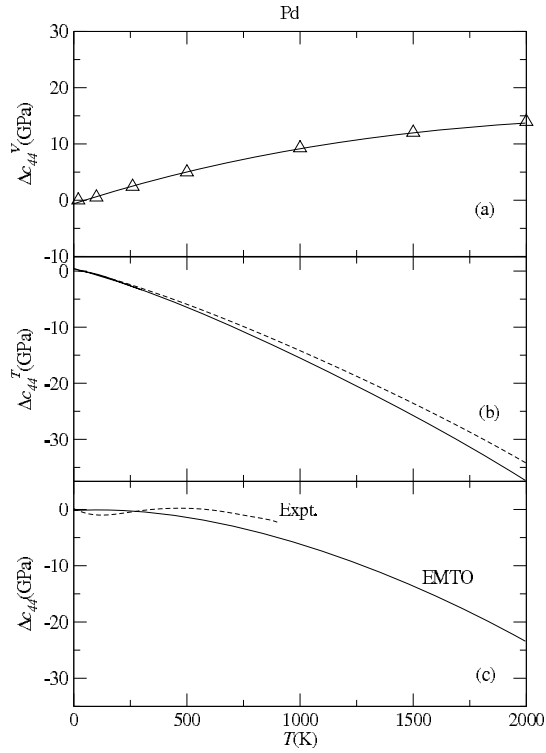
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FIG. 3: The calculated temperature dependence of c_{44} of fcc Pd. The experimental data [4] are compared with our theoretical result. Other description is the same as in Fig. 2.
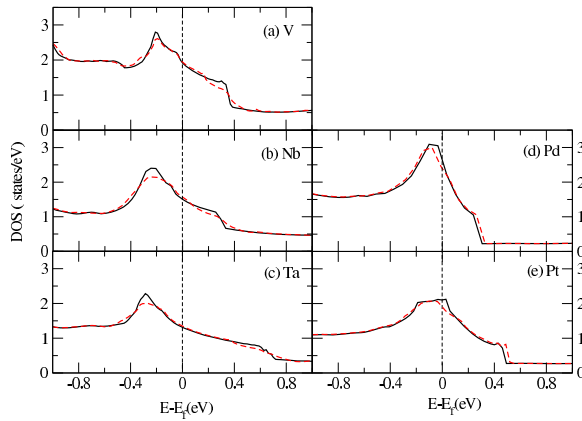

FIG. 4: (Color online). Density of states (DOS) for V, Nb, Ta, Pd, and Pt in equilibrum lattice (solid line) or in c_{44}-type monoclinic distorted lattice (dashed line).