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ANHARMONIC PROPERTIES AND sp-d HYBRIDIZATION IN BARIUM AT HIGH TEMPERATURES

N. K. Bhatt* and A. R. Jani

Department of Physics, Sardar Patel University, Vallabh Vidyanagar – 388120, Gujarat

ABSTRACT

Heavy alkaline metals are characterized by close proximity of empty d-bands to the Fermi energy E_F . Effect of closeness of E_F to d-bands on different physical properties is highest in barium with substantial sp-d hybridization, which is further influenced by the application of pressure and temperature. While the *evanescent* form of pseudopotential is sufficient to deduce physical properties at ambient condition, it is combined to mean-field potential (MFP) approach to estimate some anharmonic physical properties of Ba at finite temperatures. Ion-motional free energy (F_{ion}), temperature variations of bulk modulus and anharmonic contribution to specific heat at constant volume are obtained. Most pronounced anharmonic property, the volume-thermal expansion is also obtained, but results overestimate the experimental data. Discrepancy in thermal expansion is discussed and rectified by including sp-d hybridization into the description but without considering the d-band filling effect. Good accordance of thermal expansion with the experimental findings reveals promising applicability of the present potential to investigate several other physical properties at high-T and high-P regime.

Key words: Anharmonicity, mean-field potential, Barium.

INTRODUCTION

Close proximity of d-bands to the Fermi level (E_F) in heavy alkaline metals, e.g., barium, makes their physical properties quite sensitive to external parameters like temperature and pressure [1, 2]. Unfortunately, however, finite temperatures thermophysical properties of barium are very scanty [2, 3], where the effects of anharmonicity play vital role in deciding physical properties.

Experimentally, in order to observe anharmonic effects, it is necessary to make measurements for higher order Bragg reflections at elevated temperatures. Under these experimental conditions, the thermal diffusion scattering (TDS) contributes substantially, and is a function of both temperature and reciprocal lattice vectors. The TDS results from interactions between the incident photons and phonons present in the lattice, but the relative energy change ($\sim 10^{-2}$ – 10^{-3} eV) is so small that it is very difficult to separate from elastically scattered Bragg component, and, if measured, involves large uncertainty. On the other hand, theoretically, to account for anharmonicity in lattice dynamics and thereby in different thermodynamic properties is difficult due to its many-body nature, and complete *ab initio* computations at high temperatures pose challenges. To circumvent these practical difficulties, mean-field potential (MFP) approach is employed [4-8], which models vibrational contribution of lattice ions to the total free energy in terms of 0K cohesive energy. Robustness of the MFP approach, in conjunction with the *evanescent* local pseudopotential [9], has been verified and confirmed by accurate calculations of thermodynamic properties of some elemental metals at high-T and high-P. [e.g., see Ref. 1,7,8].

In view of aforesaid facts, we in the present paper estimated some anharmonic properties at elevated temperatures for bcc-barium. It is shown that the simple *evanescent* potential [9] is not sufficient to account for anharmonicity at high-T, and we have improved the potential by incorporating hybridization into the description.

Next section briefly discusses theory and computational scheme. Results for some anharmonic properties including volume-thermal expansion are presented, and the discrepancy observed in thermal expansion is also discussed. Improvement

over *evanescent* potential is sought and examined, while important inferences are drawn in the final section.

THEORY AND COMPUTATION

For non-magnetic metals total or Helmholtz free energy can be given by

$$F(\Omega, T) = E_C(\Omega) + F_{ion}(\Omega, T) + F_{eg}(\Omega, T). \quad (1)$$

Here, E_C represents the static energy at 0K which is calculated within the framework of pseudopotential [9] theory, corrected to second order in energy, while F_{eg} is the free energy due to electronic excitation. The vibrational free energy due to lattice ions within the MFP formalism is given as follows [4-8].

$$\frac{F_{ion}(\Omega, T)}{k_B T} = - \left[\left(\frac{3}{2} \right) \ln \left(\frac{mk_B T}{2\pi\hbar^2} \right) + \ln \{v_f(\Omega, T)\} \right], \quad (2)$$

where

$$v_f(\Omega, T) = 4\pi \int \exp \left[- \frac{g(r, \Omega)}{k_B T} \right] r^2 dr. \quad (3)$$

Here, $g(r, \Omega)$ is known as the mean-field potential (MFP) experienced by the lattice ions. It is given by

$$g(r, \Omega) = \frac{1}{2} [E_C(a_0 + r) + E_C(a_0 - r) - 2E_C(a_0)] + \left(\frac{1}{2} \right) \left(\frac{r}{a_0} \right) [E_C(a_0 + r) - E_C(a_0 - r)], \quad (4)$$

where r is the distance that the lattice ion deviates from an equilibrium position, and a_0 is the lattice constant with respect to volume Ω . Now, the problem of evaluating vibrational free energy is reduced to compute one-dimensional integration in Eq. (3) only. By calculating Helmholtz free energy $F(\Omega, T)$ using Eq. (1), as an explicit function of atomic volume (\equiv pressure) and temperature, it is now straight forward to obtain different anharmonic physical properties numerically.

We have used local pseudopotential due to Fiolhais et al [9] to evaluate E_C in eq. (1). These authors have proposed density-parameter based *evanescent* form of local pseudopotential for sp-bonded metals including heavy alkaline metals. It was demonstrated that the cohesive properties at ambient condition are better compared to non-local norm-conserving pseudopotentials for some metals [9]. We have

* Corresponding author: bhattsniarg@hotmail.com

combined this local potential within the MFP description to account for vibrating ionic contribution to the total free energy. Resulted lattice ion-motional free energy (F_{ion}) is plotted in the Fig. 1. In absence of other reported data, we judge our results as follows. Figure reveals that for $T > \theta_D$ (where $\theta_D = 110\text{K}$ for Ba is the Debye temperature) F_{ion} is non-linear, which suggests that lattice vibrations do not respond to temperature in proportion. This observation contradicts and proves that the usually taken value for $F_{ion} = -3k_B T$ is just the crude estimate.

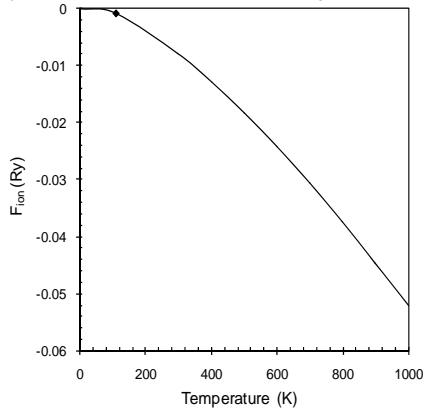


Fig. 1 Free energy due to vibrating lattice ions is shown as a function of temperature. Symbol in the graph is the result corresponding to Debye temperature.

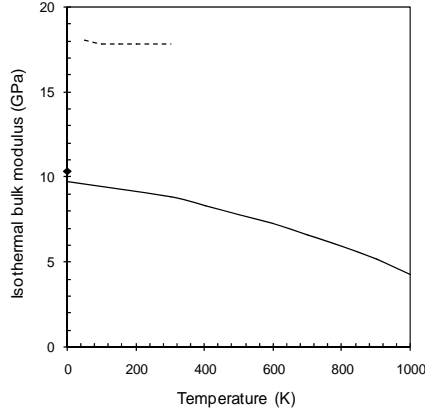


Fig. 2 Present estimate for B_T at different temperatures is compared to theoretical results (B_T at different temperatures) due to Pandya [10]. Symbol (solid diamond) represents experimental datum at 0K from Kittel [11].

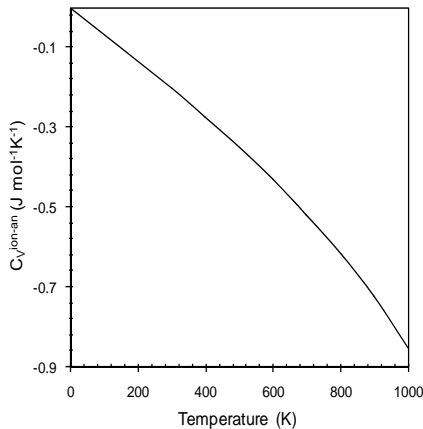


Fig. 3 Temperature variation of anharmonic contribution to ionic specific heat at constant volume.

Figs. 2 and 3 depict temperature variation of isothermal bulk modulus (B_T) and anharmonic contribution to the ionic specific heat at constant volume (C_v^{ion-an}). Again, downward declination near melting observed in these properties show better account of intrinsic anharmonism. Probably, there is an elastic softening at high temperatures, which results into internal anharmonism. It was shown [1, 5] that the conventional quasiharmonic approximation (QHA) is not sufficient to incorporate true anharmonicity at and close to melting. Again due to unavailability of the experimental and *ab initio* results, we compared our results for B_T with local pseudopotential employed within harmonic approximation (HA) based findings [10]. Discrepancy (no decrease in B_T with respect to temperature) observed in results due to Pandya [10] clearly manifest inadequacy of HA at high temperatures.

Finally, we compared present estimates for volume-thermal expansion with the experimental results [12] in the Fig. 4. Our results largely overestimate the experimental trend and are unphysical. Re-examination of the problem reveals that the discrepancy observed in thermal expansion is due to neglect of sp-d hybridization. For barium, even at 0K there is substantial admixture of 5d-band with the Fermi energy [2]. With temperature, this overlap effect is further influenced and insisting hybridization to be included into the description [1, 2, 9]. Following Harrison's [13] generalized OPW pseudopotential method; a parametric representation for sp-d hybridization is used. Results corresponding to improved potential (*evanescent* + sp-d hybridization) show good correlation with the experimental findings with maximum deviation of $\sim 6\%$ at $T = 550\text{K}$. Also, effect of hybridization on pair-potential and form factors are checked, and are found to be consistent to the prediction due to Moriarty [2] through his GPT calculations. Encouraged by these observations, we have calculated several other thermodynamic properties at high-T and high-P regime for Ba, and results will be published elsewhere.

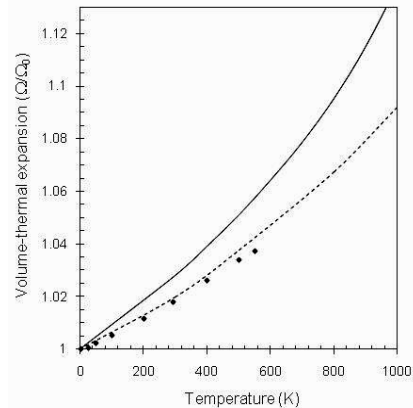


Fig. 4 Relative volume-thermal expansion for bcc-Ba, with (broken line) and without (continuous line) sp-d hybridization, is compared with experimental results due to Ref [12].

SUMMARY AND CONCLUSIONS

We have calculated some anharmonic properties of elemental bcc-Ba within the MFP + pseudopotential formalism. All results clearly suggest proper account of anharmonism at finite temperatures (i.e. non-linearity), which is very important,

particularly, close to melting. Local pseudopotential due to Fiolhais et al [9], which reasonably reproduces the cohesive properties at ambient condition, has expected limitations at higher temperatures. In order to improve this potential, sp-d hybridization is included. Good agreement for thermal expansion hence obtained is the confirmation to this assertion. We also conclude that the potential at high temperatures should be angle-independent, and the use of local potential is thus justified. Present results for thermal expansion also infer that barium is showing empty d-band – transition-metal character. In fact, with compression d-band progressively increases in energy [2,14] and d-band filling should be required, but is not the case at high temperatures. In contrast, hybridization is only sufficient to mimic anharmonicity at finite temperatures, as observed from results for thermal expansion. In absence of high-T study for this metal, we believe that present study may serve as guideline and means of comparison for future study.

ACKNOWLEDGEMENT

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