# Theoretical examination of whether phonon dispersion in $Nb_3Sn$ is anomalous

H. M. Tütüncü,[1,2] G. P. Srivastava,[2] S. Bağcı,[1] and S. Duman[1]
[1]*Fen-Edebiyat Fakültesi, Fizik Bölümü, Sakarya Üniversitesi, Mithatpaşa, 54100, Adapazarı, Turkey*
[2]*School of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, United Kingdom*
(Received 24 July 2006; published 21 December 2006)

*Ab initio* psuedopotential calculations have been performed for the electronic structure and lattice dynamics of $Nb_3Sn$. It is found that electronic states near the Fermi level show anomalous dispersion. In agreement with the experimental measurement by Pintschovius *et al.* [Phys. Rev. Lett. **54**, 1260 (1985)] it is found that the dispersion of the longitudinal acoustic branch along [111] does not exhibit a sinusoidal form, and thus can be said to be anomalous. However, our work clearly disproves the presence of a dip in the dispersion curve predicted by Weber in 1984 [Physica B & C **126**, 217 (1984)]. Our results further provide a quantitative estimate of strong interaction of electronic states near the Fermi level with the longitudinal acoustic and a group of phonon modes with average frequency of 4.5 THz along the [111] direction. The calculated electron-phonon mass enhancement parameter is 1.51 and the resulting superconducting critical temperature is 17.7 K.

DOI: 10.1103/PhysRevB.74.212506 PACS number(s): 74.70.Ad, 63.20.Kr, 74.25.Jb, 74.25.Kc

## I. INTRODUCTION

Compounds with the A15 crystal structure have been the subject of much interest, partly because many such materials exhibit high superconducting transition temperatures. One such material is $Nb_3Sn$, whose elastic, vibrational, and superconducting properties have been investigated through considerable experimental efforts. The elastic constants of $Nb_3Sn$ were determined using ultrasonic measurement technique.[1] Several groups have employed the inelastic neutron scattering measurement technique to obtain the phonon dispersion curves.[2–5] The electron-phonon interaction in this material was studied using the electron tunneling of technique.[6] A time-constant measurement was performed to calculate the low-temperature specific heat of this material.[7] More recently, it has been observed that $Nb_3Sn$ is a new example of two-gap superconductor, with the superconducting transition temperature close to 18 K.[8] Multigap superconductors are characterized by Fermi level crossing of more than one electronic band and weak interband scattering (see, e.g. Ref. 8). On the theoretical side, the structural and electronic properties of this material has been studied by several groups, employing different theoretical schemes: a self-consistent augmented-plane-wave method (APW),[9,10] a tight-binding method,[11–13] plane-wave pseudopotential method with the local density approximation (PWPP-LDA),[14] and linearized augmented-plane-wave method within the local density approximation (LAPW-LDA).[15,16]

In contrast to the wealth of theoretical works presented on the structural and electronic properties of $Nb_3Sn$, to the best of our knowledge the only theoretical calculation of the full phonon dispersion relations in this material has been based on a tight-binding method.[12,13] This work predicted pronounced dips at the zone-edge $R$ and at nearly $0.5\Gamma$-$R$ in the dispersion along the longitudinal acoustic (LA) branch. Experimental measurements by Pintschovius *et al.*,[5] did not find any clear evidence of any dip in the dispersion of this branch along the [111] direction. The experimental results were also found to lie at appreciably higher energies than the theoretical prediction for all values of the phonon wave vector from $0.1\Gamma$-$R$ to $R$. However, the experimental group by Pintschovius *et al.* reported to have verified the anomalous behavior predicted by Weber.

In the past 20 years there has been no progress in either proving or disproving the existence of the dip behavior. In fact, there has been no physical reasoning presented for the departure of the LA dispersion from the sinusoidal form. It is clear that an accurate knowledge of the lattice dynamics of this compound is essential in order to assess the role of electron-phonon coupling in explaining its superconductivity. In this paper, we present results of *ab initio* calculations of the electronic structure, lattice dynamics, and superconductivity parameters (electron-phonon mass enhancement parameter and transition temperature) for $Nb_3Sn$.

## II. THEORY

The electronic band structure of $Nb_3Sn$ was calculated using the density functional theory in its gradient-corrected functional approximation. We treated the electron-electron exchange and correlation interactions within the Kohn-Sham[17] and Perdew-Wang[18] schemes, respectively. Ion-electron interactions were treated by using Vanderbilt ultrasoft pseudopotentials.[19] Single-particle wave functions were expanded in a plane-wave basis set up to 20 hartree kinetic energy cutoff. The electronic charge density was evaluated up to 80 hartree kinetic energy cutoff, by employing 176 special **k** points within the irreducible part of the Brillouin zone. The phonon dispersion curves were obtained within the framework of the density functional perturbation theory, as explained in Ref. 20. Essentially, dynamical matrices were evaluated on a $4\times4\times4$ **q**-points mesh within the irreducible part of the Brillouin zone. These were then Fourier interpolated to obtain the phonon dispersion curves along various symmetry directions.

In order to calculate the electron-phonon mass enhancement parameter $\lambda$, we used a denser **k**-point mesh with $24\times24\times24$ Monkhorst-Pack divisions. This parameter is defined as the first reciprocal moment of the spectral function $\alpha^2F(\omega)$,[20]

$$\lambda = 2\int_0^\infty \frac{\alpha^2F(\omega)}{\omega}d\omega \approx \sum_{\mathbf{q}j} \lambda_{\mathbf{q}j} W(\mathbf{q}), \qquad (1)$$

 

TABLE I. Calculated structural parameters of $Nb_3Sn$. The obtained results are also compared with previous experimental and theoretical results.

| Parameters | This work | Expt. (Ref. 1) | Expt. (Ref. 8) | Expt. (Ref. 23) | APW (Ref. 10) | PWPP-LDA (Ref. 14) | LAPW-LDA (Ref. 15) |
|---|---|---|---|---|---|---|---|
| $a$ (Å) | 5.31 | 5.29 | 5.29 | | 5.28 | 5.26 | |
| $B$ (GPa) | 161 | 154 | | 160 | | | 159 |
| $B'$ | 4.15 | | | | | | |

where $j$ indicates a phonon polarization branch, and $W(\mathbf{q})$ is the weight of a $\mathbf{q}$ point in the first Brillouin zone. The mode-dependent coupling constant $\lambda_{qj}$ is given as[20]

$$\lambda_{qj} = \frac{\gamma_{qj}}{\pi \hbar N_{E_F} \omega_{qj}^2}. \quad (2)$$

Here $\gamma_{\mathbf{q}j}$ is the linewidth of the phonon mode $\mathbf{q}j$ due to electron-phonon interaction and $N(E_F)$ is the electron density of states per atom and spin at the Fermi level $E_F$. All calculations were performed by using the code *pwscf*.[21]

## III. RESULTS

### A. Structural and electronic properties

In order to calculate electronic structure, we have performed a geometry optimization of $Nb_3Sn$. The equilibrium lattice constant $a$, the static bulk modulus at zero pressure $B$, and the first-order pressure derivative of the bulk modulus $B'$ have been determined by fitting the calculated static total energies as a function of volume to the Murnaghan equation of state.[22] The bulk properties ($a$, $B$, and $B'$) from the total energy calculations are summarized in Table I, together with previous experimental and theoretical results. The resulting theoretical lattice constant and bulk modulus are 5.31 Å and 161 GPa, which compare well with the experimental values[8,23] of 5.29 Å and 160 GPa, respectively.

The upper panel in Fig. 1 shows the electronic band structure of $Nb_3Sn$. Along the cube-axis direction $\Gamma$-$X$ there is a clear separation between occupied and unoccupied energy bands, with the highest occupied band lying slightly but clearly below the Fermi energy $E_F$. Along the symmetry directions $\Gamma$-$M$, $\Gamma$-$R$, and $R$-$M$, up to three bands cross the Fermi level towards the corresponding zone edges. Throughout the direction $R$-$M$ three bands cross the Fermi level. Along $\Gamma$-$X$ the highest occupied band is of symmetry $\Gamma_{12}$ and gently disperses downwards towards the zone edge. Along $\Gamma$-$M$ and $\Gamma$-$R$ the $\Gamma_{12}$ state shows a nonmonotonous dispersion and occupies energy above $E_F$ at the zone edges. While the dispersion of this band can be considered as normal along $\Gamma$-$M$, it is certainly anomalous along $\Gamma$-$R$, as it is characterized by a shallow dip at the zone center and another dip at a point more than one-half way along the zone edge. The dispersion of this band calculated in our work differs from that presented in the work of Mattheiss and Weber,[11] according to which this band lies at a significantly higher energy than $E_F$ at $R$ and there is just a hint of a dip at the zone center. The wavy nature of the electronic bands near the Fermi level in Fig. 1 is similar to that calculated by Sadigh *et al.*[14] who employed the plane-wave pseudopotential method and the local density approximation.

Consistent with these features, the lower panel in Fig. 1 shows a finite density of states at the Fermi level. The density of states peaks at around $E_F-0.005$ hartree and drops to a minimum at around $E_F+0.01$ hartree. States close to $E_F$ show hybridization between the states (of zone-center symmetries) $\Gamma_{12}$, $\Gamma_1$, and $\Gamma'_{25}$, with dominant contribution from the band with symmetry $\Gamma_{12}$. In other words, the peak in the density of states near $E_F$ has a dominant contribution from the $p$ and $d$ orbitals of the Nb atoms. Our band structure and density of states results are generally similar to the results obtained from previous calculations by Mattheiss and Weber[11] using a nonorthogonal tight binding scheme, and Mattheiss[9] using the augmented-plane-wave scheme.

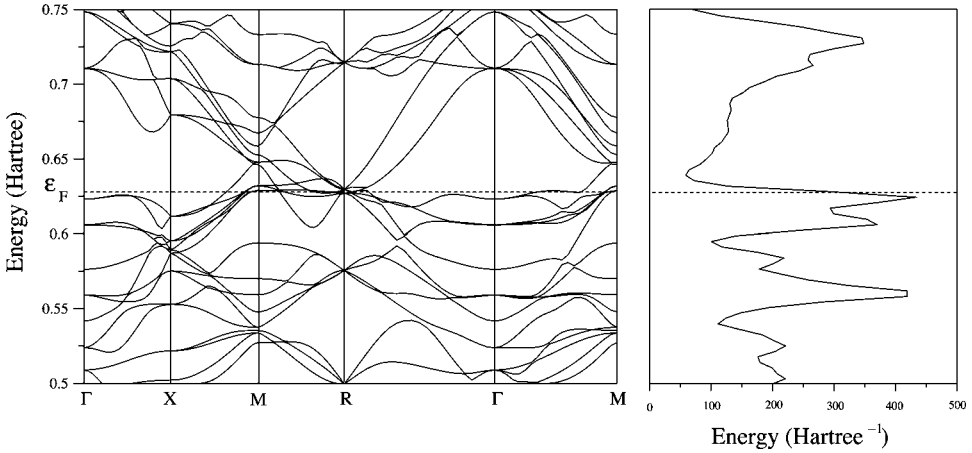


FIG. 1. Electronic band structure and density of states for $Nb_3Sn$.

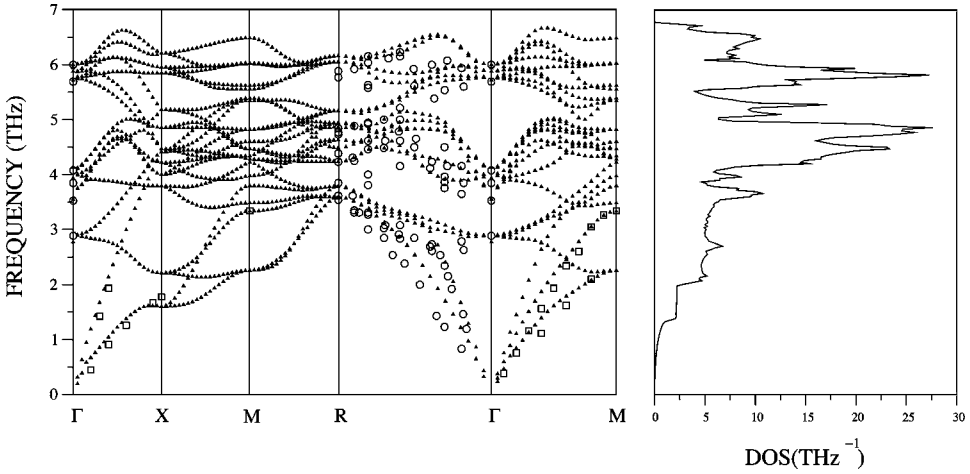


FIG. 2. Phonon dispersion and density of states for $Nb_3Sn$. Open triangles show the calculated results. Open squares and open circles are the experimental data from Refs. 2 and 3 and Ref. 5, respectively.

### B. Phonons and superconductivity

The phonon dispersion curves are presented in Fig. 2. The calculated transverse acoustic (TA) branches show good agreement with experimental measurements.[5] Our work clearly suggests that the degenerate TA branch along $\Gamma$-$X$ becomes flat at $X$. Along $\Gamma$-$M$ the upper TA branch crosses the lowest optical branch. At the $M$ point the lower TA mode becomes degenerate with the lowest optical mode. The (degenerate) TA branch along $\Gamma$-$R$ is further degenerated with the lowest optical branch near and at $R$.

Figure 3 shows the dispersion of the LA and a group of low-lying optical branches. Against the previous theoretical prediction by Weber,[12] our work does not show any clearly defined dip in the dispersion in either the LA branch or any of the low-lying optical branches. Our work does indicate that the dispersion of the LA branch is quite flat in the range $0.37\Gamma R-0.75\Gamma R$. Our work also clearly suggests that there is a strong mixing between the LA and low-lying optical branches, as can be clearly seen in Figs. 2 and 3. There is a good level of agreement between our results and the inelastic neutron scattering measurements by Pintschovius *et al.*[5] Although the theory is valid for $T=0$, we note better agreement between theory and experiment at room temperature.

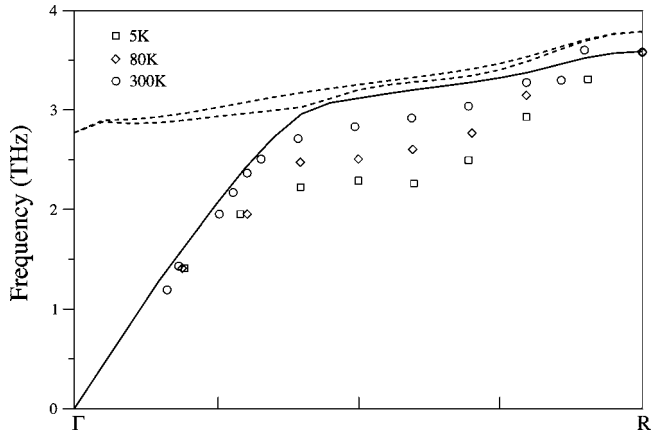


FIG. 3. Dispersion of the LA branch (solid curve) and the lowest three optical branches (dotted curves) along the $\Gamma$-$R$ direction for $Nb_3Sn$. It can be seen that the dispersion of these modes is flat in the range $0.37\Gamma R-0.75\Gamma R$. Also shown, for comparison, are the inelastic neutron scattering data reported in Pintschovius *et al.* (Ref. 5) at 300 K, 80 K, and 5 K.

In another theoretical work, Klein and Lu[16] employed the linearized augmented-plane-wave (LAPW) method and reported the existence of an unstable zone-center optical phonon mode for the cubic phase of the A15 structure for $Nb_3Sn$. They further reported stability of a tetragonally distorted ($c/a<1$) phase. Due to this distortion (see Fig. 1 in Ref. 16), Nb atoms can interact with each other strongly which leads to unstable zone-center phonon modes. We note that Klein and Lu did not present results of their electronic band structure, nor did they make calculations of the full phonon spectrum. Furthermore, they did not present any details of how the dynamical matrix was set up, except to point out that they adopted the "frozen phonon" approach for calculations of zone-center optical modes. In view of these unclear issues we cannot comment much more on their finding, except to remark that this requires further investigation, especially in view of the fact that the cubic A15 phase of $Nb_3Sn$ has been observed to be stable and thus should not possess any unstable optical phonon modes.

Previous works have suggested that the coupling between intrachain Nb $d$ orbitals in $Nb_3Sn$ near the Fermi level leads to strong electron-phonon interaction and thus to the development of superconductivity within the Bardeen-Cooper-Schrieffer (BCS) theory. It is also known that phonons of large $\mathbf{q}$ vectors are important in the BCS theory. We have calculated the electron-phonon coupling parameters $\lambda_{\mathbf{q}j}$ for all polarization modes at the zone edge point $R$. From our calculations we find that six modes at $R$ are involved in the largest contribution to the electron-phonon coupling. These are at the frequencies 4.234 THz (doubly degenerate), 4.486 THz, 4.629 THz (doubly degenerate), and 4.864 THz. These modes result from Nb intrachain atomic vibrations. It is these states that strongly couple with the $p$-$d$ electronic states near the Fermi level. For clarification, we have shown in Fig. 4 the atomic vibrational pattern of one of these modes (other modes have similar pattern) together with the $dd\sigma$ electronic orbitals along a Nb-Nb chain. The electron-phonon coupling parameters corresponding to these modes are 0.282, 0.168, 0.232, and 0.139, respectively. Other modes, and in particular modes involving vibrations of Sn atoms, contribute much less towards $\lambda$.

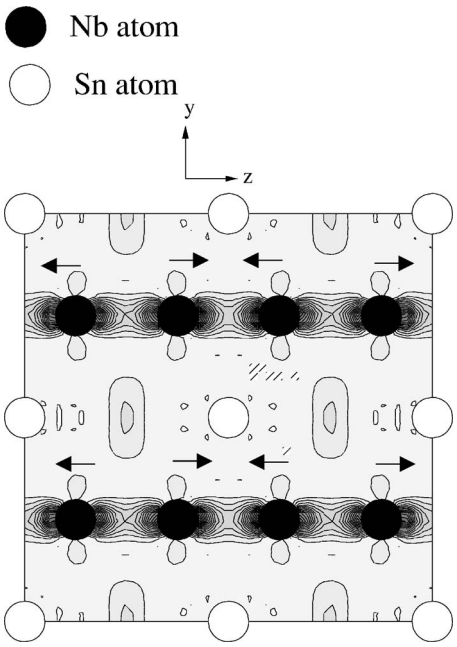


FIG. 4. Plots for $Nb_3Sn$ of the electronic charge density of the $\Gamma_{12}$ band near the Fermi level. Phonon eigenvectors corresponding to optical modes (see text) at the zone boundary point $R$ are indicated with arrows.

Although we have employed the state-of-the-art method in this study, our calculated value of the electron-phonon mass-enhancement coupling parameter $\lambda=1.51$ is rather similar to theoretical value of 1.5 obtained in the tight-binding work of Weber.[12,13] Whereas in Weber's work the largest contribution to $\lambda$ comes from the LA branch due to its anomalous dispersion (i.e., a dip), our work does not predict any anomaly in the LA dispersion. Our work clearly shows that there are large contributions to $\lambda$ from a group of phonon modes with average frequency of 4.5 THz. This observation has been made in the tight-binding work of Weber[12,13] (see Eliashberg function in Ref. 12 and 13).

With the above consideration we have used the McMillian expression to calculate the superconducting transition temperature $T_c$ (Ref. 24),

$$T_c = \frac{\hbar\omega}{1.45k_B}\exp\left(-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right). \quad (3)$$

The normal range for $\mu^*$ is 0.1–0.2.[24] We considered the frequency $\omega$ as the average of the six modes (i.e., 4.51 THz) and obtained $T_c$ values of 20.7 K, 17.7 K, and 14.7 K for $\mu^*$ values of 0.1, 0.15, and 0.2, respectively. These estimates for $T_c$ compare well with the experimental value of 17.8 K (Ref. 8) and provide strong support for the on-set of superconductivity in this material within the BCS theory.

## IV. SUMMARY

In summary, we have presented results of *ab initio* investigations of electronic band structure and phonon dispersion curves of $Nb_3Sn$. It is shown that electronic bands near the Fermi level show a wavy dispersion along $\Gamma$-$R$ and $\Gamma$-$M$. The calculated phonon spectrum for the LA branch, in reasonable agreement with inelastic neutron scattering data obtained by Pintschovius *et al.*, suggests a flattening behavior in the range $0.37\Gamma R$–$0.75\Gamma R$. While the departure from the sinusoidal form of the LA dispersion along [111] can be considered anomalous, our state-of-the-art work disproves the presence of dips in the dispersion curves predicted by Weber in 1984. Also, against the existing theoretical view, we find that the electron-phonon interaction is not only contributed by the (nonanomalous) LA branch but also with a group of phonon modes with average frequency of 4.5 THz. The strong electron-phonon coupling parameter, $\lambda=1.51$, explains the on-set of superconductivity in the A15 material $Nb_3Sn$ with $T_C=17.7$ K within the BCS scheme.

This work was supported by the Scientific and Technical Research Council (TUBİTAK) of Turkey and the Engineering and Physical Sciences Research Council (EPSRC) of the United Kingdom.

[1] W. Rehwald, M. Rayl, R. W. Cohen, and G. D. Cody, Phys. Rev. B **6**, 363 (1972).
[2] J. D. Axe and G. Shirane, Phys. Rev. B **8**, 1965 (1973).
[3] G. Shirane and J. D. Axe, Phys. Rev. B **18**, 3742 (1978).
[4] J. D. Axe and G. Shirane, Phys. Rev. B **28**, 4829 (1983).
[5] L. Pintschovius, H. Takei, and N. Toyota, Phys. Rev. Lett. **54**, 1260 (1985).
[6] L. Y. L. Shen, Phys. Rev. Lett. **29**, 1082 (1972).
[7] G. R. Stewart, B. Cort, and G. W. Webb, Phys. Rev. B **24**, 3841 (1981).
[8] V. Guritanu, W. Goldacker, F. Bouquet, Y. Wang, R. Lortz, G. Goll, and A. Junod, Phys. Rev. B **70**, 184526 (2004).
[9] L. F. Mattheiss, Phys. Rev. B **12**, 2161 (1975).
[10] B. M. Klein, L. L. Boyer, D. A. Papaconstantopoulos, and L. F. Mattheiss, Phys. Rev. B **18**, 6411 (1978).
[11] L. F. Mattheiss and W. Weber, Phys. Rev. B **25**, 2248 (1982).
[12] W. Weber, in *Electronic Structure of Complex Systems*, edited by P. Hariseau and W. M. Temmerman, NATO Advanced Study Institute, Vol. 113 (Plenum, New York, 1984).
[13] W. Weber, Physica B & C **126B**, 217 (1984).
[14] B. Sadigh and V. Ozolins, Phys. Rev. B **57**, 2793 (1998).
[15] Z. W. Lu and B. M. Klein, Phys. Rev. Lett. **79**, 1361 (1997).
[16] N. M. Klein and Z. W. Lu, Physica B **296**, 120 (2001).
[17] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[18] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
[19] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[20] S. Baroni, S. de Gironcoli, A. Dal. Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001).
[21] S. Baroni, A. Dal Corso, S. de Gironcoli, and P. Giannozzi, http://www.pwscf.org
[22] F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **50**, 697 (1944).
[23] M. J. Mehl, B. M. Klein, and D. A. Papaconstantopoulos, in *Intermetallic Compounds*, edited by J. H. Westbrook and R. L. Fleischer (Wiley, New York, 1994), Vol. 1, p. 195.
[24] W. L. McMillian, Phys. Rev. **167**, 331 (1968).