Analysis of Phonon Modes Strongly Coupled to Electrons in High \( T_c \) Superconducting Phases of Calcium

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Abstract. For a zigzag crystal structure of calcium in the phase V, we estimated the superconducting transition temperature \( T_c \) by the use of the Allen-Dynes formula. If we set the effective screened Coulomb repulsion constant \( \mu^* \) at 0.1, we obtain \( T_c = 16.37 \) K at 120 GPa and \( T_c = 17.15 \) K at 140 GPa. In order to clarify the origin of such high values of \( T_c \), we analyzed a partial electron-phonon coupling constant at each phonon mode. As the result we found that an optical mode at the \( \Gamma \) point strongly interacts with electrons and it induces the high \( T_c \) in the phase V. The phonon mode can exist only in the particular structure like the zigzag structure.

1. Introduction

Calcium shows the pressure-induced superconducting transition in the phase III (Ca-III) of the simple cubic structure. The transition temperature \( T_c \) increases with pressure and it dramatically increases through the transition from Ca-III to Ca-V (139 GPa < \( P \) < Ca-IV (113 GPa < \( P \) < 139 GPa). The value of \( T_c \) reaches to 25 K at 161 GPa in Ca-V, which is the highest record in elements [1]. The structures of Ca-IV and Ca-V are complex crystal structures [2], which we theoretically identified very recently [3]. The structure of Ca-IV has a helical modulation and that of Ca-V a zigzag modulation.

In the theory of superconductivity by Bardeen, Cooper and Schrieffer (BCS), important parameters of the BCS model are the electron density of states (DOS) and the electron-phonon coupling constant at the Fermi level [4]. We can determine these quantities using the first-principles calculation. Actually, in the Kohn-Sham theory [5], we can have an estimation of DOS within a reasonable approximation. Using the first-principles lattice dynamics simulation, we can also determine the electron-phonon coupling constants.

In this study, We estimated the superconducting transition temperature \( T_c \) for the zigzag structure of Ca-V in the framework of the strong coupling theory of the superconductivity. We also analyzed a partial electron-phonon coupling constant at each phonon mode in order to clarify the origin of high \( T_c \) in Ca-V.
2. Computational details
We employed density functional theory in a generalized gradient approximation (GGA) which is the expression by Perdew and Wang [6] and used an ultrasoft pseudopotential. The primitive unit cell of the zigzag structure in Ca-V has the dimensions of \( a = 3.16 \text{ Å}, b/a = 1.00, c/a = 1.39, \alpha = \beta = 90.00^\circ, \gamma = 92.66^\circ \) at 120 GPa. The dimensions at 140 GPa are \( a = 3.10 \text{ Å}, b/a = 1.00, c/a = 1.39, \alpha = \beta = 90.00^\circ, \gamma = 91.94^\circ \). The primitive cell consists of two zigzag chains along c axis (Fig.1): The atomic positions on one zigzag chain are Ca(1)=\((-0.10, 0.10, -0.06)\), Ca(2)=\((0.10, -0.10, 0.44)\) in fractional coordinates, and the other ones are Ca(1')=\((0.40, 0.60, 0.06)\) and Ca(2')=\((0.60, 0.40, 0.56)\) [3].

In this study, assuming the phonon-mediated superconductivity, we estimated \( T_c \) for the zigzag structure by the use of the Allen-Dynes formula. For simple elements the values of \( T_c \) have been reported and they are in good agreement with experimental values [7–10]. In the calculation of the phonon frequency, we employed the linear response method in which the first order corrections are calculated by means of the density functional perturbation theory [11, 12]. The k-space integration for the calculation of the dynamical matrix at each \( \mathbf{q} \) is performed over the \( 8 \times 8 \times 8 \) grid. The electron-phonon matrix element was calculated using the \( 32 \times 32 \times 32 \) k-point grid. For calculations of the electron-phonon coupling constant \( \lambda \) and the logarithmic-averaged phonon frequency \( \omega_{\log} \) we used \( 4 \times 4 \times 4 \) \( \mathbf{q} \)-point grid. We assumed the screened Coulomb interaction constant \( \mu^* \) to be 0.1 in the case of calcium. We set the energy cut-off of the plane wave basis at 24 Ry and performed the calculation by the PWscf code [13].

3. Results
We calculated the electron-phonon coupling constant \( \lambda \), the logarithmic-averaged phonon frequency \( \omega_{\log} \) and the superconducting transition temperature \( T_c \) for the zigzag structure of Ca-V at 120 GPa and those at 140 GPa. As the results, \( T_c, \lambda \) and \( \omega_{\log} \) are 16.37 K, 0.85 and 310.48 K at 120 GPa, respectively. At 140 GPa, we obtain \( T_c = 17.15 \text{ K}, \lambda \) and \( \omega_{\log} \) become 0.83 and 343.17 K, respectively.

Since the calculated \( T_c \)’s show such high values, we explored the phonon modes which enhance the electron-phonon coupling by investigating the partial electron-phonon coupling constant. The partial electron-phonon coupling constant \( \lambda_{\mathbf{q} \nu} \) is defined as the following:

\[
\lambda_{\mathbf{q} \nu} = \frac{1}{\pi N(E_F)} \frac{\gamma_{\mathbf{q} \nu}}{\omega_{\mathbf{q} \nu}^2}
\]

(1)

where \( \gamma_{\mathbf{q} \nu} \) and \( \omega_{\mathbf{q} \nu} \) are the line width and the frequency with respect to the \( \nu \)-th phonon mode from the bottom at \( \mathbf{q} \), respectively. The DOS at the Fermi level is represented as \( N(E_F) \).
Figure 2 and 3 show $\omega_{q\nu}$ and $\lambda_{q\nu}$ at each of 21 symmetry q-points at 120 GPa and those at 140 GPa, respectively. The strength of $\lambda_{q\nu}$ is proportional to radius of circle at each phonon mode. The 5th mode from the bottom at $q_1$, which is an optical mode at the $\Gamma$ point, has the largest electron-phonon coupling at each pressure. Therefore, we strongly believed that the phonon mode is the major factor of the enhancement of $T_c$ in the zigzag structure.

The structure of Ca-V has the zigzag chain along c axis and, in addition, adjacent zigzag chains are slightly translated in the opposite direction along c axis (Fig.1). This means that Ca-V has two mutually independent modulations: An intra-chain modulation and an inter-chain modulation. The 5th phonon mode at $q_1$, which has the strongest $\lambda_{q\nu}$, is the mode that either the intra-chain modulation amplitude or the inter-chain one decreases and the other modulation amplitude increases.

4. Conclusion
Assuming that calcium has the phonon-mediated superconductivity, we calculated $T_c$ for the zigzag structure by the Allen-Dynes formula. As the result the calculated $T_c$ shows the values of approximately 17 K. Investigating the phonon modes which enhance the electron-phonon coupling, we found that the large $T_c$ is due to the phonon mode that the modulation amplitude is transferred between the intra-chain modulation and the inter-chain modulation in the zigzag structure. This phonon mode appears only in the crystal structure with two independent
modulation patterns. Thus, this prediction may be applied to the case of the enhancement of $T_c$ in the complex crystal structure phases of barium and strontium.

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