Temperature dependence of the phonon frequencies in Nb_3Sn and V_3Si

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The softening of the phonon frequencies, which was observed in [1, 2] for a wide interval of wave vectors, is explained using the model of [3] with two peaks in the state density, under the assumption that the Fermi level is located near one of the peaks. The proximity of the sample to the martensitic transition favors superconductivity, since this proximity reflects the proximity of the chemical potential to the position of one of the peaks.

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In[1,2] they performed neutron measurements of the temperature dependence of the phonon frequency in Nb_3Sn and V_3Si for the directions [110] and [100]. It turned out that there is a noticeable decrease of phonon frequencies when the temperature is lowered, and this decrease covers the entire interval of wave vectors of the phonons, up to the boundaries of the Brillouin zone. We shall show in this article that this phenomenon follows from the theory proposed by one of us,[3] and also discuss its connection with superconductivity.

In[3], the electronic term for chains of transition-element atoms, which is doubly degenerate if the overlap of the orthogonal strings is neglected,[4] splits and shifts when the overlap is taken into account. The spectrum takes the form

$$\epsilon = -T^* a \pm \sqrt{v^2 p_z^2 + T^{*2} c^2}, \tag{1}$$

where

$$a = \cos^2\phi + \cos^2\psi; \quad c = \cos^2\phi - \cos^2\psi + d_1(\epsilon_{xx} - \epsilon_{yy}) \tag{1'}$$

and $(\phi, \psi) = (p_x a/2, p_y a/2)$ for the filaments along z. The quantity T^* characterizes the overlap of the strings. The potential d_1 describes the electron interaction with the lattice deformations. The spectrum (1) leads to a fine structure of the density of states of the band $\nu(\epsilon)$ with two logarithmic peaks at $\epsilon = 0$ and $\epsilon = -2T^*$:

$$\nu(\epsilon) = \nu(0)\frac{2}{\pi^2}\ln\frac{T^*}{|\Delta\epsilon|}, \tag{2}$$

where $\nu(0)$ is the density of states of the isolated strings. According to[3], anomalous properties are

possessed by crystals in which the chemical potential level falls in the vicinity of one of the singularities of (2). According to the estimates, the interval $2T^*$ corresponds to a change in the composition of several percent. A direct indication in the favor of the existence of two peaks in the density of states is the behavior of T_c in Nb_3S doped with elements of group IV or V.[5] The obtained dependence takes the form of a "crater" near the stoichiometric Nb_3Sn.

The interaction with the phonons d_1 in (1′) leads to electronic corrections to the phonon frequencies. The latter are given by the polarization operator $\Pi(q,\omega)$, which can be represented in the form

$$\Pi = \frac{\text{const}}{4\pi i}\int\!\!\int\!\!\int d\phi d\psi dp_z dz \operatorname{th}\frac{z}{2T}\frac{1}{2}\operatorname{Sp}\{\hat{r}_x\hat{G}^R(p_+, z)\hat{r}_x\hat{G}^R(p_-, z) - \text{c.c.}\} \quad (3)$$

$(p_\pm, \phi_\pm, \psi_\pm) = (p_z, \phi \pm q_x a/2, \psi \pm q_y a/2)$. The Green's function of the electrons is a matrix, since the initial term[4] is doubly degenerate, and takes in terms of the Pauli matrices the form

$$\hat{G}(p, z) = [(z+a)\hat{e} + vp_z\hat{r}_y - cr_x][(z+a)^2 - v^2p_z^2 - c^2]^{-1}. \quad (4)$$

Expression (3) is additive in the three orthogonal systems of strings.

The main features of the phonon spectrum, which are connected with the increments (3) due to the electrons, can be qualitatively explained even in the isolated-string approximation [$T^* = 0$ in (1)]. The integration with respect to p in (3) has a logarithmic character and, if the projection of the wave vector of the phonon on the chain direction is small, $q_z v \ll T^*$, the integration is cut off at $vp \sim T$. The corresponding contribution is proportional to $d_1^2\nu(0) \sim \ln(E_F/T)$, causing a softening of the elastic modulus C_s. To the contrary, at $q_z v \gg T^*$, the integration extends to $q_z v$, and the temperature increments from this string are small[4] [$\sim (T/q_z v)^2$]. Consider a phonon with an arbitrary wave vector $q = \{q_x q_y q_z\}$. In this case all the strings are "turned off." At small q_z but at arbitrary q_x and q_y, a nontrivial contribution to (3) is due to the filaments z. Finally, if q is directed along one of the principal axes, then one should expect a noticeable temperature contribution from the two remaining strings. The specific form of the term $d_1(\epsilon_{xx} - \epsilon_{yy})$ in (1), which is due to symmetry requirements, leads to further limitations on the type of lattice oscillations, where the described effects become manifest.

The critical values q_{crit} of the projection of the wave vector on any particular axis, at which "turning off" of the contribution from the corresponding chain takes place, may be indicated quite accurately by using the position of the "ledge" observed in[2] in the spectrum of the transverse phonon:

$$q_{crit} \approx 0.1(2\pi/a). \quad (5)$$

The general situation in V_3Si and Nb_3Sn apparently corresponds to the case $T \ll T^*$. In this limit, Eq. (3) can be expanded in powers of T/T^*, and it is natural that the main contribution comes from the low-lying parts of the energy spectrum. If the chemical potential is close to $\epsilon = 0$, i.e., to the position of one of the singularities of (2), then the temperature increments in (3) are determined mainly by the first of the roots of (1) under conditions when either $\cos\phi$ or $\cos\psi$ is small (i.e., near the edges of the reciprocal-lattice cube). The calculation of (3) is facilitated in this case, since the corresponding denominators in (4) become simpler.

Let us present the results. The dispersion law of the longitudinal phonon ([100] axis) is determined by the dispersion of the modulus

$$C_{11}(q_x, T) = C_{11}^{(0)}(q_x) - d_1^2\nu(0)\frac{4}{3\pi^2}\ln\frac{T^*}{T}\int_{-\pi/2}^{\pi/2}d\phi\frac{|\cos\phi_+|\,|\cos\phi_-|}{|\cos\phi_+| + |\cos\phi_-|}. \quad (6)$$

The integral factor changes from unity at $q_x = 0$ to 0.75 at $q_x = \pi/a$. Thus, the "softening" is large and is of the same order of magnitude as for the shear modulus.[3] On going to the (x,y) plane, the "temperature" contribution from the y axis is "turned off" at the values of q_y from (5). At $q_x, q_y > (\pi/a)\sqrt{T/T^*}$, the temperature increments connected with the z axis are proportional to $(T/T^*)^{3/2}$, and for all values of q_x and q_y they cause the frequencies to decrease with decreasing temperature. It is convenient to express the result as an increment to the energy of the elastic deformation with a wave vector $q = (q_x q_y 0)$:

$$\delta\Omega = d_1^2\nu(0)\frac{2\zeta(3/2)}{3\pi^{3/2}}\left(1 - \frac{1}{\sqrt{2}}\right)|\epsilon_{xx}(q) - \epsilon_{yy}(q)|^2 I_{\alpha\beta}, \quad (7)$$

where $\alpha = \sin\kappa_x$, $\beta = \sin\kappa_y$, and the integral

$$I_{\alpha\beta} = -\left(\frac{\alpha}{\beta} - \frac{\beta}{\alpha}\right)^2\left(\frac{T}{T^*}\right)^{3/2}\int_0^\infty\!\!\int_0^\infty dxdy \times \left\{\frac{1}{\alpha\sqrt{y^2+1} + \beta\sqrt{x^2+1}} - \frac{1}{\alpha y + \beta x}\right\} > 0$$

appears when the singular terms $z^{1/2}$ are eliminated from (3). The case $\alpha = \beta$, i.e., q along [110], calls for further analysis. For the shear modulus $C_s(q)$, which determines the frequencies of the phonons with $q = (2\pi/a)[\xi\xi 0]$ and with a polarization $e \parallel [110]$, we have

$$C_s(q, T) = C_s^{(0)}(q) + d_1^2\nu(0)\frac{8}{9}\frac{T^2}{T^{*2}}\ln^2\sqrt{\frac{T}{T^*}}\frac{1}{\sin^2\zeta\pi}.$$

From the data of[2] we obtain the estimate $T^*_{Nb_3Sn} \sim 600$ °K.

In connection with the results of[1,2], the question was frequently raised of the role played by soft phonon modes in the superconductivity of these compounds. Since in our model even small changes of the position of the chemical potential near the singularity of (2) eliminate the martensitic transition, the first question would concern the extent to which the effective constant g_{eff} of the interelectron attraction changes when T_m changes by an amount equal to its order of magnitude. In the BCS theory, g_{eff} is induced by phonons and is proportional to the average, over the Fermi surface, of the quantity

$$g_{eff} \sim \left\langle \frac{M(p-p')}{\omega^2(p-p')} \right\rangle,$$

where the phonon wave vector $q = p - p'$ corresponds to the distance between two points on the Fermi surface.

For linear strings this surface is a plane in the first-order approximation. Therefore $\delta g/g_{eff} \propto \langle \Delta\omega^2/\omega^2 \rangle$ can be estimated from formulas (5) and (6). According to (6), $\Delta\omega^2/\omega^2$ is large in a narrow band of width $\Delta g \sim \sqrt{T/T^*}$. Therefore the change of $\delta g/g_{eff}$ will have a smallness expressed by $\sqrt{T_m/T^*}$. Of course, the connection between T_c and T_m at small changes of the composition does not reduce to a change of the constant g_{eff}, but includes also effects of the state density.

The second formulation of the problem is connected with the change of the composition at which the level of the chemical potential shifts significantly relative to the singularities of (2) (for example, the stoichiometric composition corresponds to $\mu = -T^*$ and to a minimum in the density of states). Here, generally speaking, there are no soft phonon modes at all, i.e., the phonon frequencies change by an order of magnitude equal to the frequencies themselves. Therefore the proximity to the martensitic transition, insofar as it denotes proximity to one of the singularities of (2), and consequently the "softer" modes [see formulas (5)–(7)], favors the superconductivity. The change of g_{eff} is of the order of unity, but a numerical estimate is difficult to obtain. According to[5], the effect is not too large.

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