Electron-phonon interaction in Ni-Ti

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The contribution of electron-phonon interaction to the phonon dispersion curve is calculated for Ni-Ti. The anomalies in the dispersion curve are qualitatively reproduced and associated with areas of the Fermi surface having large electron-phonon matrix elements. This provides an understanding of the pre-Martensitic phenomena in Ni-Ti.

The equiatomic transition-metal alloy Ni-Ti has a B_2 structure (CsCl) above room temperature. It undergoes a Martensitic phase transition to what seems, a B_{19} structure at T_m (300 K).[1] Above T_m, x-ray and electron diffraction[2] show diffuse scattering at $\vec{q}_{\rm I}=\frac{1}{3}(1,1,1)$ with polarization along [111] and at $\vec{q}_{\rm II}=\frac{1}{3}(1,1,0)$ with polarization $[\bar{1}10]$, while inelastic neutron scattering[3] finds phonon softening at $\vec{q}_{\rm II}$ and a convex curvature in the dispersion curve of the TA modes. In addition there is anomalous temperature dependence of the C_{44} elastic constant.[4] The relation between the pre-Martensitic phenomena and the Martensitic phase transition is not understood. A 3% addition of Fe, which is substitutional for Ni, suppresses the Martensitic phase transition and a continuous displacive phase transition occurs at 230 K, with a soft phonon at $\vec{q}_{\rm II}$ (but not at $\vec{q}_{\rm I}$) producing an incommensurate superlattice with wave vectors near $\vec{q}_{\rm I}$ and $\vec{q}_{\rm II}$.[5] It seems likely then that the Martensitic phase transition has an origin different from the soft modes. Soft modes of type I have been observed in Zr and Ti alloys (ω phase) and are sometimes attributed to formation of a charge density wave,[6] while soft modes of type II are seen in transition-metal carbides[7] where they are associated with electron-phonon interaction involving p-d hybridized bands.[8] For pure Ni-Ti, infrared absorption[9] indicates the disappearance of large sections of the Fermi surface at the Martensitic phase transition consistent with charge-density wave formation. We will assume then that electron-phonon interaction is responsible for the pre-Martensitic phenomena. A screened Coulomb interaction can be used to understand a *longitudinal* soft mode, but it does not give rise to any transverse anomalies.[8]

A general method for calculating the electron-phonon matrix elements in single basis transition metals was developed by Varma *et al.*[10] Using their method, the anomalous electron-phonon contribution to the phonon dispersion curve may be calculated once the band structure is known. A self-consistent augmented plane wave (APW) calculation was performed by Papaconstantopoulos.[11] His calculation was fitted[12] with an orthogonalized tight-binding Hamiltonian involving s, p, and d orbitals on both Ni and Ti, providing 18 electronic levels $\epsilon_\mu(\vec{k})$ with $\mu=1,18$ (Fig. 1). The fitting parameters are tabulated in Table I. The rms error at Γ,X,M,R and halfway Λ, Σ, and Δ was 0.7×10^{-3} Ry. The result of Varma *et al.* may be generalized to include a multiple basis. Since Ni-Ti has an inversion center at every atom it is convenient to calculate the modified dynamical ma-

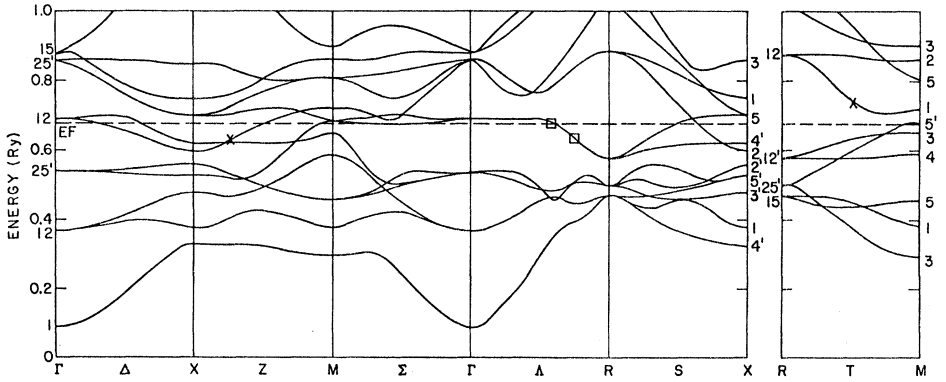

FIG. 1. Band structure produced by a tight-binding fit to Ref. 10. The crosses indicate initial and final points of the dominant scattering contributing to the Σ_4 mode, the squares are initial and final points of scattering contributing to Λ_1.

TABLE I. Slater-Koster fitting parameters for Ni-Ti (in Ry). The parameters not cited here were determined from the rule $(sp\sigma)=(ss\sigma\times pp\sigma)^{1/2}$.

	Ni-Ni	Ti-Ti	Ni-Ti
E_s	0.582 98	2.4009	
E_p	0.926 84	2.7097	
E_{dt}	0.535 65	0.734 12	
E_{de}	0.536 89	0.737 25	
$ss\sigma$	−0.073 48	0.150 73	−0.048 27
$pp\sigma$	0.106 16	−0.143 54	0.062 31
$pp\pi$	−0.062 79	−0.062 77	0.204 07
$dd\sigma$	−0.018 10	−0.044 27	−0.045 62
$dd\pi$	0.006 81	0.028 64	0.031 08
$dd\delta$	0.000 84	−0.004 00	−0.005 00

trix, which is real and symmetric in this case. The modified dynamical matrix is defined as

$$C_{\alpha\beta}(\kappa,\kappa'|\vec{q})=\frac{1}{\sqrt{M_\kappa M_{\kappa'}}}\sum_l \Phi_{\alpha\beta}(0,\kappa|l,\kappa')\times\exp[i\vec{q}\cdot(\vec{R}_l+\vec{x}_{\kappa'}-\vec{x}_\kappa)]\,, \tag{1}$$

where l runs over all unit cells. The matrix $\Phi_{\alpha\beta}$ gives the force constant between atom κ with position $\vec{x}_\kappa$ and mass M_κ and atom κ' with position $\vec{R}_l+\vec{x}_{\kappa'}$ and mass $M_{\kappa'}$.

The second-order electron-phonon contribution to the modified dynamical matrix is

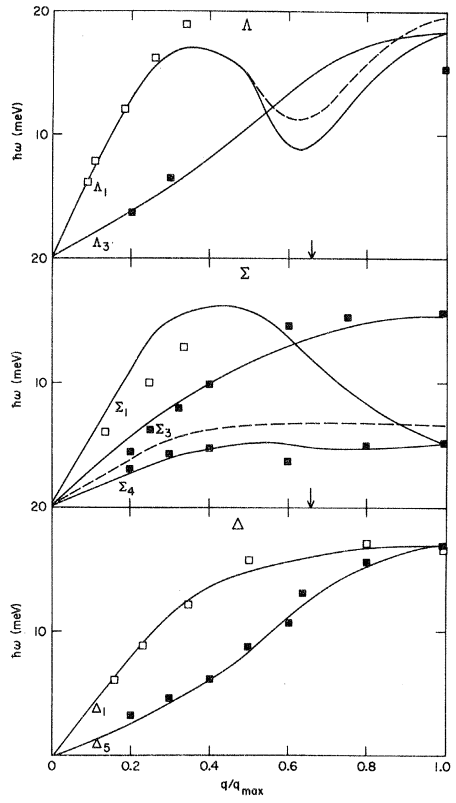

FIG. 2. Phonon dispersion curves along Δ, Σ, and Λ. The experimental points are those of Bührer *et al.* (□ longitudinal mode, ■ transverse mode). The dotted lines indicate the short-range contribution to Λ_1 and Σ_4. The arrows indicate the position of the wave vectors of the superlattice which appears below 230 K in Ni-Ti (Fe).

$$C^{(2)}_{\alpha\beta}(\kappa,\kappa'|\vec{q})=\frac{1}{\sqrt{M_\kappa M_{\kappa'}}}\sum_{\substack{\mu=1,18\\ \mu'=1,18}} g^{\mu,\mu'}_{\alpha,\kappa}(\vec{k},\vec{k}+\vec{q})\,g^{*\mu,\mu'}_{\beta,\kappa'}(\vec{k},\vec{k}+\vec{q})\frac{f_\mu(\vec{k})-f_{\mu'}(\vec{k}+\vec{q})}{\epsilon_\mu(\vec{k})-\epsilon_{\mu'}(\vec{k}+\vec{q})} \tag{2}$$

with $\kappa=1$ for Ni and $\kappa=2$ for Ti and $f_\mu(k)$ is the Fermi distribution function. The electron-phonon matrix element is given as

$$g^{\mu,\mu'}_{\alpha,\kappa}(\vec{k},\vec{k}+\vec{q})=q^2\sum_{n=1,9} A^{+}_{\mu,\kappa n}(\vec{k})A_{n\kappa,\mu'}(\vec{k}+\vec{q})[v^\alpha_\mu(\vec{k})-v^\alpha_{\mu'}(\vec{k}+\vec{q})]\,, \tag{3}$$

where $A_{n\kappa,\mu}(\vec{k})$ is the 18×18 unitary eigenvector matrix of the tight-binding Hamiltonian and $v^\alpha_\mu(\vec{k})$ is $\partial\epsilon_\mu/\partial k_\alpha$. The coefficient q^2 is given by

$$q^2=4/a^2\,, \tag{4}$$

where a is the lattice constant (3 Å). This relation assumes that overlap integrals vary with distance as $1/R^2$. The result of the calculation is shown in Fig.

2. The short-range force constants [1 NN (nearest neighbor) and 2NN] were determined by a least-square fit to the BZ boundary phonon frequencies and the sound velocities. In usual notation, $F^{1NN}_{\alpha\beta}(1,2)=A\,\delta_{\alpha\beta}+B(1-\delta_{\alpha\beta})$; $F^{2NN}_{xx}(\kappa,\kappa)=A_\kappa$; $F^{2NN}_{yy}(\kappa,\kappa)=F^{2NN}_{zz}(\kappa,\kappa)=B_\kappa$; $F^{2NN}_{xy}(\kappa,\kappa)=0$, they were in units of 10^4 dyn/cm: $A=0.78$, $B=1.83$, $A_1=0.35$, $B_1=0.18$, $A_2=6.15$, and $B_2=-0.18$. Along Σ, the modified dynamical matrix has the fol-

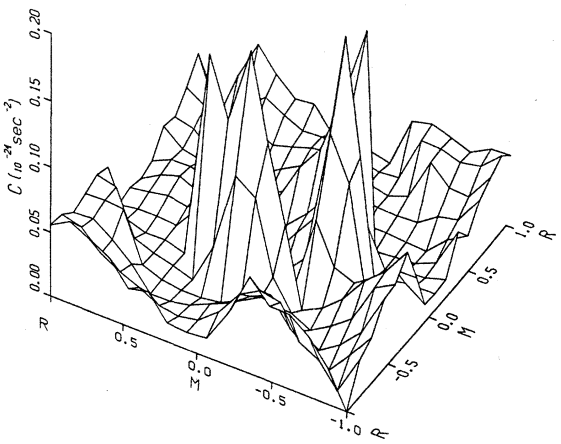

FIG. 3. Electron-phonon contribution to the dynamical matrix $C \equiv C_5^{(2)}(\vec{q}) - C_4^{(2)}(\vec{q})$ with phonon wave vector $\vec{q} = 0.31\ (1,1,0)2\pi/a$ and polarization $[\bar{1}10]$ (Σ_4). The electronic wave vector is restricted to the *RXM* plane.

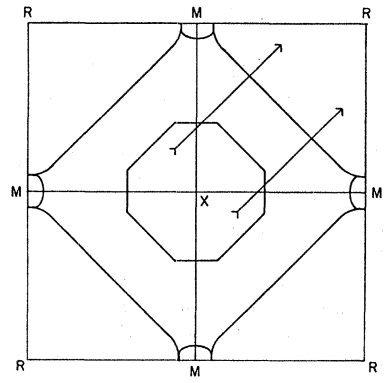

FIG. 4. Fermi surface in the *RXM* plane. Arrows indicate the dominant scattering producing the anomaly in Σ_4.

lowing general form:

$$C_{\alpha\beta}(1,1|\vec{q}) = \begin{bmatrix} C_1(\vec{q}) & C_2(\vec{q}) & 0 \\ C_2(\vec{q}) & C_1(\vec{q}) & 0 \\ 0 & 0 & C_3(\vec{q}) \end{bmatrix} \quad \text{(Ni–Ni)} \ , \tag{5a}$$

$$C_{\alpha\beta}(2,2|\vec{q}) = \begin{bmatrix} C_4(\vec{q}) & C_5(\vec{q}) & 0 \\ C_5(\vec{q}) & C_4(\vec{q}) & 0 \\ 0 & 0 & C_6(\vec{q}) \end{bmatrix} \quad \text{(Ti–Ti)} \ , \tag{5b}$$

$$C_{\alpha\beta}(1,2|\vec{q}) = \begin{bmatrix} C_7(\vec{q}) & C_8(\vec{q}) & 0 \\ C_8(\vec{q}) & C_7(\vec{q}) & 0 \\ 0 & 0 & C_9(\vec{q}) \end{bmatrix} \quad \text{(Ni–Ti)} \ . \tag{5c}$$

The anomaly in Σ_4 is caused by the large electron-phonon contribution to $C_4(\vec{q}) - C_5(\vec{q})$. Note that this only involves interactions between Ti atoms. The electron-phonon contribution $C \equiv C_5^{(2)}(\vec{q}) - C_4^{(2)}(\vec{q})$ has a maximum along Σ at $\vec{q}_M \simeq 0.31 \times (1,1,0)2\pi/a$, close to $\vec{q}_{II}$. The maximum is caused by a large contribution from the region around $\vec{k} = (0.13, -0.06, -0.5)2\pi/a$ to the summation in Eq. (1). In Fig. 3(a) the contributions to C in the $k_z = -\pi/a$ plane are plotted for $\vec{q} = \vec{q}_M$. The peak is caused by a transition from a Z_1 level to a T_1 level, both with large $v_\mu(\vec{k})$ (Fig. 1). Both levels are $d_{x^2-y^2}$ levels localized on Ti, with only little p-wave admixture, contrary to the conclusion of Ref. 8.. The energy transfer is 0.11 Ry.

The anomaly in Λ_1 is caused by a maximum along Λ in $C(\vec{q}) \equiv -[C_7^{(2)}(\vec{q}) + 2C_8^{(2)}(\vec{q})]$ at $\vec{q}_M \simeq 0.25(1,1,1)2\pi/a$ which is, again, close to q_{II}, and again only involving Ti-Ti force constants. The maximum is due to large contributions from the regions around $\vec{k} \simeq 0.27(1,1,1)2\pi/a$ and $\vec{k} \simeq (-0.12, -0.12, 0.4)2\pi/a$.

In the first case the transition is from a Λ_3 level to the same level with an energy transfer of 0.03 Ry. This is a d level involving both Ni and Ti atoms. In the second case the transition is from a S_4 level to a Λ_3 level with an energy transfer of 0.02 Ry. The S_4 level and Λ_3 level are d levels localized on Ti. The pre-Martensitic phenomena in Ni-Ti (Fe) thus seem due to formation of a gap on the electron pocket centered at X (Fig. 4) and the flat Fermi surface along Λ.

As was mentioned, a 3% addition of Fe to pure Ni-Ti causes the phonon anomalies to produce a superlattice at $T \simeq 230$ K. Within the rigid-band model no appreciable effect was found on the phonon anomalies. The Fe impurities possibly cause local strains contributing to the central peak above 230 K observed in neutron scattering.[13]

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