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Phonon softening in $Ni_{46.8}Ti_{50}Fe_{3.2}$

S. K. Satija* and S. M. Shapiro
Brookhaven National Laboratory, Upton, New York 11973

M. B. Salamon and C. M. Wayman
Materials Research Laboratory, University of Illinois at Urbana—Champaign, Urbana, Illinois 61801
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Inelastic neutron scattering has been used to study the premartensitic phase transition in NiTi:Fe. A phonon softening of the [110]-TA_2 branch near $q_I=(\frac{1}{3},\frac{1}{3},0)$ has been observed. This is near the wave vector where incommensurate superlattice peaks appear below the premartensitic-phase-transition temperature of 232 K. This phonon softening can be understood in terms of a Fermi-surface-driven electron-phonon anomaly.

I. INTRODUCTION

There are now several known cases of structural phase transitions in transition-metal alloys and compounds.[1–4] Typical of these transitions is the presence of pronounced resistivity and specific-heat anomalies as well as various anomalies in the phonon dispersion along certain symmetry directions. Several models have been proposed to explain the phonon anomalies, all based on the electron-phonon interaction, but differing in details.[1] The best known group of compounds exhibiting such anomalies is the layered transition-metal dichalcogenides. These compounds exhibit diffraction satellites whose periodicity is incommensurate with the lattice periodicity.[5] Phonon dispersion curves in these materials also show a dip in the LA branch near the incommensurate superlattice positions.[5] This transition is attributed to Fermi-surface instabilities and charge-density-wave (CDW) formation. These low-dimensional systems are particularly amenable to CDW formation because of their favorable Fermi surfaces. Several years ago Overhauser predicted the presence of a CDW in a simple three-dimensional (3D) system such as potassium.[6] However, no diffraction peaks have been observed in K which can be attributed to a CDW.[7] Other more complicated 3D metals undergo phase transitions where incommensurate superlattice peaks are present,[4,8] but it has not been uniquely established that the transitions are the result of Fermi-surface instabilities.

The subject of the present paper is the premartensitic phase transition in the intermetallic compound $Ni_{46.8}Ti_{50}Fe_{3.2}$. Pure NiTi has long been known to undergo a martensitic transition near 300 K.[9] Above the martensitic phase, however, one observes resistivity and structural anomalies which are attributed to a premartensitic (PM) phase transition.[9] The relationship between the PM phase and the martensitic phase is not clear. The addition of up to 3 at. % Fe for Ni lowers the martensitic transition temperature (T_M) more strongly than the premartensitic phase,[10] thus giving one the opportunity to study the PM phase over a wide range of temperatures. Preliminary neutron scattering results in the PM phase of NiTi:Fe were reported by Salamon *et al.*[2] The appearance of superlattice peaks below the premartensitic-phase-transition temperature $T_I=232$ K near $q_I=(\frac{1}{3},\frac{1}{3},0)$ was attributed to the formation of a CDW analogous to the layered compounds mentioned above. In addition, satellites were also observed near $q_{II}=(\frac{2}{3},\frac{2}{3},\frac{2}{3})$. A study of these effects by means of x-ray and electron diffraction has been performed[2,3] and a more detailed x-ray study is currently underway.[11]

Simple theories predict that CDW phase transitions are accompanied by a soft LA phonon mode whose frequency may go to zero due to a "giant" Kohn anomaly. Experimentally, these anomalies have been observed for layered dichalcogenides as mentioned above,[5] and for the quasi-one-dimensional (1D) conductor $[K_2Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ (KCP).[12] In the 1D organic salt tetrathiafulvalenium tetracyanoquinodimethane (TTF-TCNQ), an anomaly is also observed in a TA branch.[12] In this paper we report inelastic neutron scattering measurements on NiTi:Fe. Phonon softening near the superlattice vector q_I associated with [110]-TA_2 is observed. No strong temperature-dependent dynamical effects were observed near the superlattice peaks at q_{II}. Along both directions the linewidths of the phonons are unusually large. Experimental and sample preparation details are included in Sec. II. Inelastic neutron scattering results are contained in Sec. III, and a comparison with a recent theoretical calcu-

lation of phonon dispersion in NiTi by Bruinsma,[13] based on the theory of Varma and Weber,[14] is discussed in Sec. IV.

II. EXPERIMENTAL

A single crystal of NiTi:Fe was obtained from Raychem Corporation, the composition of which was determined to be $Ni_{46.8}Ti_{50}Fe_{3.2}$ by microprobe analysis. The sample consisted of several grains, the largest of which (≈ 0.1 cm^3) was used for the scattering experiments. The intensity of Bragg scattering from this grain was at least a factor of 20 larger than any other grain observed. The mosaic of this crystallite was better than 0.25°. The sample was wrapped in thin aluminum foil and then mounted in an Air Products Displex refrigerator for temperature control. The room-temperature structure of NiTi:Fe is an ordered CsCl structure with a lattice constant of 3.014 Å. Neutron scattering experiments were performed with a fixed final energy $E_f = 14.7$ meV. Collimations of 40′ were used throughout the spectrometer yielding an energy resolution of $\delta E = 0.85$ meV full width at half maximum at $\hbar\omega = 0$. Higher-order neutrons were filtered by a tuned pyrolytic graphite filter. Both constant E- and constant Q-type scans were employed. Because of large incoherent scattering cross section of Ni and Ti (4.8 and 2.8 b, respectively) the background was unusually high and sometimes energy dependent.

III. INELASTIC SCATTERING RESULTS

The $(h/3,k/3,0)$ superlattice intensities are maximized in a pattern which indicates that atomic displacements are predominantly transverse.[2,3] This is surprising since a usual CDW, being a density wave, should be longitudinal. It is reasonable, therefore, to expect superlattice formation to be accompanied by temperature-dependent inelastic scattering in the TA phonon branch along the $[\zeta\zeta 0]$ direction with displacements along $[\zeta\bar{\zeta}0]$. This [110]-TA_2 branch corresponds to the elastic constants $\frac{1}{2}(C_{11}-C_{12})$ in the limit $\zeta \to 0$. We have studied the temperature dependence of this phonon branch in detail. Limited data were also obtained for phonons propagating in $[\zeta 00]$ and $[\zeta\zeta\zeta]$ directions.

Phonon dispersion curves along $[\zeta\zeta 0]$ direction at $T = 350$ K, which is well above the PM transition temperature $T_I = 232$ K, are shown in Fig. 1. The elastic constants calculated from the initial slope of these curves agree well with both the ultrasonic results[15] and recently measured dispersion curves in pure NiTi by Mercier *et al.*[16] For small ζ the peaks are well defined, but as ζ approaches 0.3, the linewidth increases, and for $\zeta > 0.3$ they are so broad that it is difficult to determine a peak position. The dotted line in Fig. 1 corresponds to the very broad maxima observed in the constant Q-type scans. This feature of extremely broad phonon widths at higher wave vectors is present in all the principal symmetry directions in NiTi:Fe. The anomalous feature in the TA phonon curve is the dip in the phonon frequency near $\zeta = \frac{1}{3}$, where the superlattice peaks appear at lower temperature. This phonon branch seems to be of key importance in the formation of the superlattice and PM phase

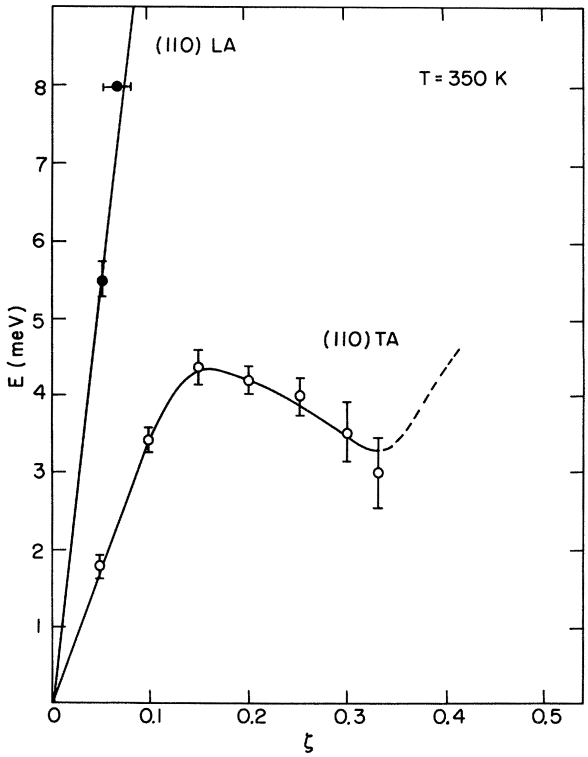

FIG. 1. Phonon dispersion curves along the $[\zeta\zeta 0]$ direction at $T = 350$ K.

at T_I. Because the linewidths become broad as ζ increases, the best way to display the data is by intensity contours as shown in Fig. 2 for $T = 350$ K. An anomaly is clearly present at $\zeta \approx \frac{1}{3}$ although it is not nearly as sharp as that present in the 1D systems such as KCP, but similar to that observed in TTF-TCNQ.[12]

This anomaly is strongly temperature dependent as seen from a similar intensity contour plot along $[\zeta\zeta 0]$ direction at $T = 240$ K shown in Fig. 3. There is only a slight decrease (about 10% from room temperature) in the elastic constant $\frac{1}{2}(C_{11}-C_{12})$, in accord with ultrasonic measurements. More dramatic, however, is the buildup of a rather sharp feature near the point $\zeta = 0.33$ as evidenced by an increase in inelastic intensity at energy transfer between 1 and 2 meV. Scans performed at this temperature reveal well-defined phonons for $\zeta < 0.20$ and only broad scattering for $\zeta > 0.25$.

Figure 4 shows a series of constant Q scans at $\zeta = 0.25$ for several temperatures. A well-defined excitation is observed at $T = 400$ and 350 K. As T decreases, the position shifts to lower energies and the linewidth increases. At $T = 240$ K, only a broad feature remains. This decrease in energy with decreasing T is interpreted as the deepening of the anomaly already present near $\zeta = \frac{1}{3}$ at high temperatures.

A series of constant E scans about $\zeta = \frac{1}{3}$ were performed at several temperatures with $\Delta E = 1.25$ meV and are shown in Fig. 5. At $T = 350$ K, little scattering is present above background near $\zeta = \frac{1}{3}$. As T is decreased, the scattered intensity increases and a well-defined peak appears. For $T = 200$ K $< T_I$, the peak has disappeared

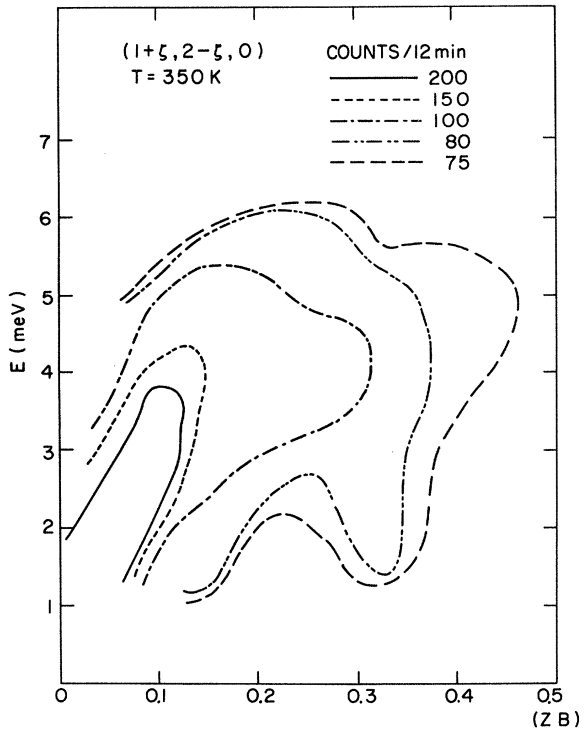

FIG. 2. Inelastic intensity contours for the [ζζ0]-TA_2 branch at $T=350$ K. The background is 55 counts/12 min. ZB denotes zone boundary.

and the spectrum is flat. Since the energy resolution is $\delta E=0.42$ meV half width at half maximum, it could be argued that we are observing the elastic scattering being intercepted by the tails of the resolution function when the spectrometer is set for energy transfer $\Delta E=1.25$ meV.

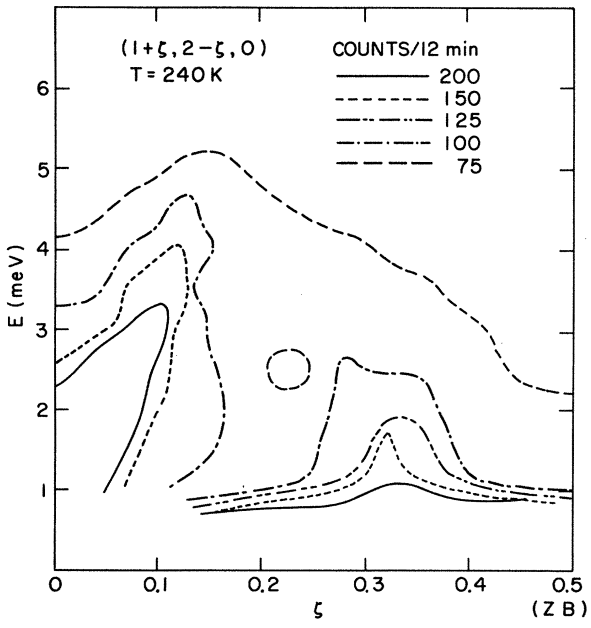

FIG. 3. Inelastic intensity contours for the [ζζ0]-TA_2 branch at $T=240$ K. The background is 55 counts/12 min. ZB denotes zone boundary.

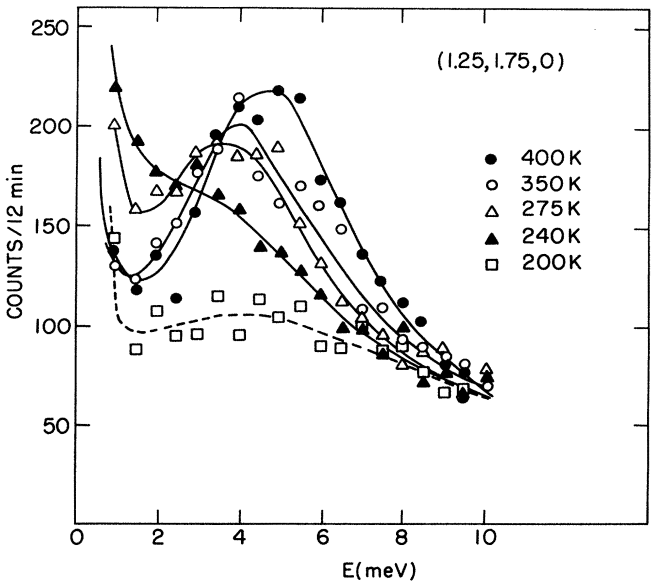

FIG. 4. Constant Q scans at $\zeta=0.25$ in the [110] direction at several temperatures above and below the premartensitic transition temperature T_I.

This is ruled out by the temperature dependence of the scattering as shown in Figs. 5 and 6. Below T_I, an intense superlattice Bragg peak appears at $\Delta E=0$ and $\zeta\approx\frac{1}{3}$, which is several orders of magnitude more intense than the initial scattering observed above T_I at $T=240$ K. If the resolution function were intercepting the zero energy intensity, it would be most intense at the lower tempera-

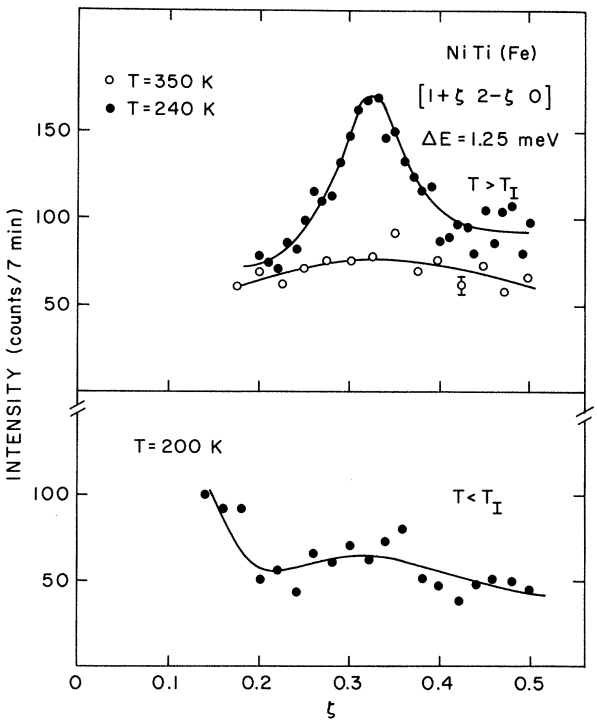

FIG. 5. Constant E scans along the [110] direction at $\Delta E=1.25$ meV.

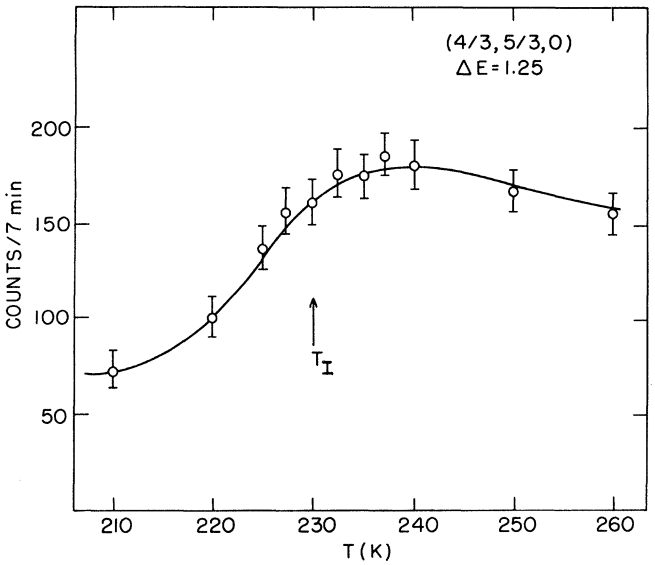

FIG. 6. Temperature dependence of the inelastic intensity to $\Delta E=1.25$ meV at $(\frac{4}{3},\frac{5}{3},0)$.

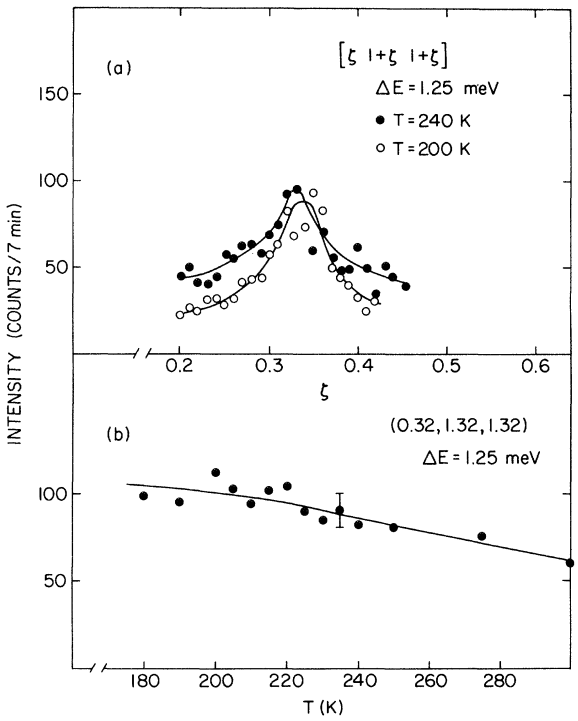

FIG. 7. (a) Constant E scan along the [111] direction at $\Delta E=1.25$ meV. (b) Temperature dependence of the inelastic intensity at $\Delta E=1.25$ meV at $\vec{Q}=(0.32,1.32,1.32)$.

tures. Such is not the case. The temperature dependence of the inelastic intensity at $\zeta=\frac{1}{3}$ is shown in Fig. 6 and shows a gradual increase upon cooling and then a decrease below. This is interpreted as a phonon softening with decreasing temperature until the phase transition at T_I and then an increase in phonon energy below T_I. The phonon branch enters and leaves the energy window of the spectrometer. Unfortunately, due to large inherent width of the phonons, it is not possible to present a detailed analysis of this phonon anomaly.

Mercier *et al.*[16] have recently observed a similar anomaly above T_I in pure NiTi but they have not made a detailed study as a function of temperature. The addition of Fe thus does not seem to change the basic character of the PM phase transition except for a shift in the transition temperature. However, the addition of Fe severely suppresses the martensitic phase transformation. In fact, in our sample no martensitic phase was observed down to 24 K.

The study of the elastic scattering[2,3] in NiTi:Fe revealed superlattice peaks near the $q_{II}=(\frac{1}{3},\frac{1}{3},\frac{1}{3})$ positions. The temperature dependence of the intensity of the satellites at q_I and q_{II} is similar and the relationship between them is not clear. Inelastic neutron scattering measurements were performed with q along the $[\zeta\zeta\zeta]$ direction to determine if phonon softening was present. TA and LA modes were measured out to $\zeta=0.2$; beyond, the linewidths were so broad that phonon frequencies could not be determined. Similar constant E scans to those described above were performed around the $(\frac{1}{3},\frac{1}{3},\frac{1}{3})$ position. Figure 7(a) shows constant $\Delta E=1.25$ meV scans along the $[\zeta\zeta\zeta]$ direction near $\zeta=\frac{1}{3}$. A peak is seen at $T=240$ K but does not change as the sample is cooled through T_I. Figure 7(b) shows the temperature dependence between 180 and 300 K. There is no discernible anomaly at $T_I=232$ K. The peak in the constant E scans is due to an anomalous phonon broadening near $\zeta=\frac{1}{3}$ due to the strong electron-phonon coupling as discussed by Bruinsma.[13] However, the absence of any appreciable temperature dependence rules out any soft phonon at this wave vector. We conclude, therefore, that the primary phonon softening occurs in the [110]-TA_2 branch near wave vector $q_I=(\frac{1}{3},\frac{1}{3},0)$.

IV. DISCUSSION

Our experiments have thus confirmed the precursor phonon softening near the critical wave vector $q_I=(\frac{1}{3},\frac{1}{3},0)$ in NiTi:Fe. As mentioned in Sec. I, an understanding of such a phenomenon in metals and alloys has generally been advanced in terms of electron-phonon interactions. Theoretically, the problem is to obtain phonon frequencies by calculating the dynamical matrix given by

$$D_{\alpha\beta}(\vec{q})=M^{-1}\sum_l \phi_{\alpha\beta}(0,l)e^{-i\vec{q}\cdot\vec{r}_l}, \quad (1)$$

where $\phi_{\alpha\beta}(0,l)$ is the interatomic force constant tensor between the atoms at positions 0 and r_l. For metals, the two major contributions to the dynamical matrix are from (a) Coulomb-coupling coefficients between the ion cores, and (b) the second-order change in the total energy of the valence electrons caused by ionic displacements. The latter contribution, in effect, represents the ion-ion interaction transmitted through the valence electrons and contains the so-called electron-phonon interaction. Several attempts made to calculate these dynamical ma-

trices can be separated into two different approaches. Both involve the fact that large cancellations can be realized between two major contributions to the dynamical matrix, thus reducing the size of the matrix which must be inverted. The first approach is the so-called "charge fluctuation model" used by Sinha *et al.*[1] which employs the rigid muffin-tin spheres coupled rigidly with the ion. This resembles a pseudoatom which has a much reduced charge compared with the bare ion core. The remainder of the charge can then be described in terms of a reduced number of charge fluctuation components. The second approach, mainly used by Varma and Weber,[14] takes into account the tight-binding nature of the *d*-electron wave functions. Varma and Weber have calculated the dynamical matrix in transition metals by using electron-phonon matrix elements calculated in a nonorthogonal tight-binding representation for the *d* electrons. The latter method takes into account the strong dependence of the electron-phonon matrix element on the difference in group velocity of the initial and final electronic states. Such considerations predict Fermi-surface-driven anomalies in the TA as well as LA modes.

With the use of the results of band-structure calculations of Papaconstantopoulos,[17] Bruinsma recently[13] calculated the anomalous electron-phonon contribution to the phonon dispersion curves in NiTi. These calculations show an anomaly, due to the electron-phonon interaction, in the [110]-TA_2 phonon branch at q_I. The magnitude of this effect agrees well with the phonon dispersion curves measured in pure TiNi by Mercier *et al.* at room temperature.[16] The calculations also show an anomaly at q_{II}, however, this anomaly is due to short-range interactions with only a small contribution from electron-phonon interaction matrix elements.

TiNi:Fe is, therefore, the first example of a premartensitic phase transition which is driven by a dramatic softening of a phonon. It lends support for the model of Varma and Weber, and illustrates that anomalies in the electronic group velocity can be as effective as Fermi-surface nesting in stabilizing an incommensurate lattice distortion. The soft mode is located near the $q_I=\frac{1}{3}(1,1,0)$ which is $\frac{2}{3}$ of the way to the zone boundary. This [110]-TA_2 branch contains many of the displacements necessary to drive the cubic CsCl lattice into lower symmetry structures. The role of the [111]-LA phonon remains a mystery. The lack of temperature dependence appears to rule out a soft mode associated with this branch, yet there clearly is an anomaly in the phonon branch near $q=(\frac{1}{3},\frac{1}{3},\frac{1}{3})$. This mode is responsible for the ω-phase distortions in other bcc metals, and it is likely that the tendency for ω-phase formation derives from the soft-mode behavior in the [110]-TA_2 branch. Clearly, further work is needed on this unique, three-dimensional soft-mode transition.

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*Present address: Physics Department, University of Delaware, Newark, Delaware 19711.

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