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NEUTRON AND X-RAY SCATTERING STUDIES OF PREMARTENSITIC PHENOMENA

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1. Introduction

Competing interactions play an essential role in all types of phase transitions. In the much studied spin glasses it is well known that the competing ferro- and antiferromagnetic interactions lead to a spin's frustration resulting in the frozen spin glass state at low temperatures /1/. In ferroelectrics, the competition is between short range interatomic forces and longer range electric dipolar forces which leads to the structural instability associated with ferroelectric ordering /2/. In metals, where martensitic phase transitions occur, the competing forces are not as well defined, but are likely due to the interatomic forces and the longer range electronic interactions. Depending upon the electronic band structure and the phonon dispersion curves of the solid a variety of structures and microstructures can appear over a wide range of temperatures and compositions.

In this paper I shall discuss neutron and X-ray investigations of some metallic alloys which are known to exhibit martensitic transformations. It will be shown that precursor effects are usually present in the diffuse scattering and in the phonon dispersion curves, but the transition cannot be described in terms of the soft mode picture used in the Landau and Devonshire theory to describe structural phase transitions /2,3/. In addition, it will be seen that it is inappropriate to look at these microstructures as incommensurate systems, but more correctly as a coherent coexistence of two phases.

Martensitic transitions have been studied by metallurgists for nearly one hundred years /4/. The term martensitic was first used to describe the plate like structure observed in quenched hardened steels. Nowadays, the term martensitic is also used to describe transitions in non-ferrous metals and even oxides. In a martensitic transformation the atoms exhibit an anomalous shear like displacive motion. In the low temperature phase the atoms are only slightly displaced from their more symmetric positions of the high temperature phase. This contrast with order disorder transitions where atoms must shift by unit cell lengths in order to achieve the ordered state. Martensitic transitions are usually first order, exhibit hysteresis, but frequently look continuous with temperature. Defects, nucleation, and growth play an important role in the transitions /5/.

In order to obtain microscopic information about the nature of the martensitic transitions, metallurgists have performed extensive electron and X-ray studies on many systems /6/. Usually observed in the diffraction photographs are diffuse spots, rods or planes of scattering (referred as REL spots, rods or walls ; REL = REciprocal Lattice) corresponding to 3, 2 or 1 dimensional correlations. The real space image of this diffuse scattering provides important information about its origin. Ultrasonic studies are usually performed to probe the elastic behavior of the solid particularly the expected shear anomaly. Although these measurements have great sensitivity to small changes, they are restricted to the long wavelength or small momentum response of the system. The diffraction effects observed suggest that anomalies extend out into the Brillouin zone, away from the zone center.

The electron and X-ray observations cannot establish whether the features observed are dynamic or static in origin since no energy analysis of the diffuse scattering is possible. This is because the energy resolution required to separate phonon effects is $\delta E/E_i \sim 10^{-8}$, since the incident energy (E_i) of the photon is of the order of keV and phonon energies are in the range of 10 meV. Presently this resolution is impossible to achieve using X-ray generators, but new instruments situated at synchrotron radiation sources are approaching the required resolution /7/. Inelastic neutron scattering, because of the much lower incident energy, requires a modest resolution of $\delta E/E \sim 0.1$, which is easily achievable with existing triple axis neutron instruments situated at the various reactors in the world. Thus neutron scattering studies of martensitic materials are indispensable in probing the dynamical behavior of the phase transformation.

Most of the earlier neutron studies of structural phase transitions have been performed on perfect or nearly perfect solids /2,3/. In these systems soft modes, i.e. lattice vibrational modes whose frequencies go to zero, or nearly zero, as the transition is approached, are present. Only relatively few systems exhibiting martensitic phase transitions have been studied and some of them are listed in Table I. These are classified by a qualitative estimate of the amount of mode softening which is present. Only few systems exhibit nearly complete softening. The superconducting Al5 materials Nb₃Sn and V₃Si exhibit almost complete softening in the $C' = 1/2(C_{11}-C_{12})$ elastic constant /8/ and nearly the entire [110]-TA₂ branch shows a large decrease in energy as the martensitic transition is approached /9/. The alloy In-Tl also exhibits complete softening of the elastic constant C' as measured by ultrasonic techniques /10/. Neutron scattering studies, on the other hand, show no anomalous temperature dependence of any acoustic modes /11/ implying that the lattice softening occurs only for long wavelength excitations ($\lambda > 250$ Å). The omega (ω) phase alloy is also listed to emphasize the similarity between martensitic systems and those BCC based systems exhibiting ω phases. In the latter, the mode expected to be responsible for the ω transition is the $[\zeta\zeta\zeta]$ -LA, $\zeta = 2/3 \zeta_{ZB}$ where ζ_{ZB} is the zone boundary wavevector. Earlier studies revealed a very broad inelastic response which was temperature dependent, but no clear soft mode was observed /12/. Studies on ω phase materials are limited largely because no known alloy exhibits a reversible ω transition. Most of the systems listed exhibit only a partial softening where the fractional change of phonon energy is $\Delta E/E \sim 10-20\%$. In addition, this anomalous behaviour is not restricted to one q value as seen in many structural phase transitions (either commensurate or incommensurate), but occurs over a broad region of q space.

In the remainder of this paper, I shall review the neutron and X-ray studies of 2 compounds that have recently been studied : Ni-Ti(Fe) /13,14/ and Ni-Al /15/ alloys. I believe the behavior exhibited in these systems is typical of many of the compounds listed in Table I.

2. Ni_xTi_{1-x}(Fe) alloy

The Ni_xTi_{1-x} alloy exhibits the phenomenal property of shape memory /16/. For $x = 50$, it is an ordered alloy with a simple cubic, CsCl or β -phase structure. The martensitic phase transition occurs near room temperature with considerable hysteresis upon heating and cooling. It was realized that premartensitic (PM) effects were present but the structure of the PM and martensite phase remained unresolved for many years. A breakthrough came when it was realized that by alloying with Fe one can depress the martensitic transition temperature revealing more clearly the PM phase /17/. For the composition Ni_{46.8}Ti₅₀Fe_{3.2} the martensite phase is completely suppressed and two well defined phase transitions occur /14,18/. Below $T_I = 232$ K, superlattice reflections appear and at $T_{II} = 224$ K a first order rhombohedral distortion occurs.

Ultrasonic studies in the high temperature cubic phase revealed a small softening of the elastic constant C' with decreasing temperature /19/. Inelastic neutron scattering measurements showed that the major softening occurs, not at

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Table I

Martensitic Systems Exhibiting Phonon Anomalies

Alloy	Transition	References
<u>No Mode Softening :</u>		
Zr ₈₀ Nb ₂₀	BCC	/12/
<u>Nearly complete Softening</u>		
Nb ₃ Sn	SC + Tet	/9/
Ni-Tl(Fe)	SC + Rhombo + Mono	/13/, /14/
InTl	FCC + FCT	/10/, /11/
<u>Partial Mode Softening :</u>		
Li	BCC → 9R	/27/
Na	BCC → HCP	O. Blaschko et al: Phys. Rev. B 30, 1667 (1984)
Au-Cu-Zn	BCC → Rhombo	M. Mori et al: Solid St. Commun. 17, 127 (1975)
Cu-Al-Ni	FCC → Rhombo	S. Hoshino et al: Jpn J. Appl. Phys. 14, 1233 (1975)
Cu-Al-Zn	FCC → 2H FCC → 9R	G. Guenin et al: J. Physique C4, C4-597 (1982)
Fe-Pd	FCC → FCT	M. Sato et al: Phys. Rev. Lett. 12, 2117 (1982).
Fe-Pt	FCC → BCC	K. Tajima et al: Phys. Rev. Lett. 37, 519 (1976)
Fe-Ni	FCC → BCC	Y. Endoh : unpublished
Tl	BCC → HCP	M. Iizumi: J. Phys. Soc. Jpn 52, 549 (1983)
Ni-Al	SC → 7R	/15/

$q=0$, in the elastic regime, but near $q = 1/3[110]$ /13/. This is shown in Fig.1 where neutron intensity contours of the $[\zeta\zeta 0]$ -TA₂ phonon branch are plotted at two different temperatures. The atomic displacements associated with this branch are along the $\zeta\zeta 0$ direction and the limiting slope for $q \rightarrow 0$ corresponds to the elastic constant $C' = 1/2(C_{11}-C_{12})$. At high temperatures $T_1 < T = 350$ K, the phonon energy widths for $\zeta > 0.2$ become very broad but a clear minimum is seen near $\zeta = 1/3$. As the temperature is lowered to $T = 240$ K, there is a dramatic build up of inelastic scattering localized near $\zeta = 1/3$ as shown in the bottom portion of Fig.1. This is consistent with a major softening of the branch near $\zeta = 1/3$. Anomalous inelastic scattering at low energies is also observed in the $[\zeta\zeta\zeta]$ -LA branch near $\zeta = 1/3$, but this is temperature independent.

Elastic neutron and X-ray diffraction scans along the $[\zeta\zeta 0]$ direction revealed critical scattering about $q_1 = 1/3(1,1,0)$ which develops into a sharp peak at T_1 . Additional satellites, with the same temperature dependence, also develop near $q_{11} = \frac{1}{3}(1,1,1)$. The intensity of the satellite increase smoothly with

Figure 1. Inelastic intensity contours for the $[\xi\xi 0]$ -TA₂ phonon branch in Ni-Ti(Fe). The background is 55 cts/12 min. (from ref.13)

Left : T = 350 K

Right : T = 240 K.

decreasing temperature without being affected by the rhombohedral distortion of the cubic lattice which occurs at $T_{II} = 224$ K /18/.

An X-ray examination of the q_I and q_{II} type satellites measured in many different Brillouin zones revealed an intensity pattern that could be explained by displacements arising from a linear combination of three phonon modes with wavevectors $q^{(1)} = 1/3(1,1,0)$, $q^{(2)} = 1/3(0,1,1)$ and $q^{(3)} = 1/3(1,0,1)$ with atomic displacements along $[1\bar{1}0]$, $[01\bar{1}]$ and $[\bar{1}01]$, respectively.

A closer inspection of the satellites show that that they are not located precisely at the commensurate $1/3$ positions. Because of the metallic nature of the system it is tempting to describe the system as being a charge density wave (CDW) transition with the incommensurability related to the Fermi wavevector. Figure 2 shows that this cannot be a correct interpretation. In Fig.2, the intensity contours of two q_{II} type satellites measured at $T = 226$ K are shown.

The left portion shows that the satellite measured in the $(1,1,1)$ Brillouin zone is slightly incommensurate with the cubic phase lattice and the incommensurate wavevector, δ , is directed along the 111 direction. The satellite shown on the right was measured in the $(1,1,2)$ Brillouin zone and the incommensurability is seen to be larger and oriented in a different direction. Similar effects were observed for other q_{II} satellites as well as the $q_I = 1/3(1,1,0)$ type satellites. A schematic representation of these measurements is shown in Fig.3 for the (001) and (011) scattering planes. In this figure, the lengths of the arrows is not significant but the directions indicate the

Figure 2. X-ray equi-intensity contours for two Q_{II} type satellites. The parallel lines corresponds to different settings of the position sensitive detector. The dashed lines represent half the maximum intensity (from ref. 14).

orientation of $\vec{\delta}$. In general the further from the origin the larger the quantity $|\delta|$. Also there is a distinct "swirl" like pattern for the q_I satellites.

The scattering vector for each satellite can be defined as

$$\vec{Q} = \vec{\tau} + \vec{q}_c + \vec{\delta}$$

where $\vec{\tau}$ is a reciprocal lattice vector and $\vec{q}_c$ is a reduced wave vector measured from $\vec{\tau}$ to the $1/3$ position. We demonstrated above that the incommensurate wave vector $\vec{\delta}$ depended upon $\vec{\tau}$. If one had a CDW or a mass density wave, δ would be a constant, independent of which Brillouin zone it is being measured. This is clearly not the case in Ni-Ti and an alternative explanation of the origin of the satellite is needed. Before discussing this, let us look at another martensitic system exhibiting some similar features.

3. Ni_xAl_{1-x} alloy

In the Ni_xAl_{1-x} alloy, the CsCl structure can be maintained at room temperature for $45\% < x < 63\%$ /20/. Below room temperature a martensitic phase transition occurs whose nature and low temperature structure is not fully understood. $Ni_{63}Al_{37}$ has been extensively studied at room temperature by electron and X-ray diffraction /21,22/. Diffuse streaks have been observed in the electron diffraction patterns and their real space image have shown that a "tweed" microstructure is present /23,24,25/. In addition, ultrasonic studies have shown that there is a small softening of the elastic constant C' prior to the phase transition /26/. These observations have revealed the importance of precursor effects in the martensitic phase transformations.

Figure 3. Schematic representation of observed satellites in Ni-Ti(Fe) at $T = 226$ K. The arrows indicate the direction of the incommensurate wavevector, but their length is no significant (from ref. 14).

Top : q_{11} satellites measured in (011) zone

Bottom : q_1 satellites measured in (001) zone.

Figure 4. a) Dispersion curves of $[110]$ - TA_2 (displacements along $[\bar{1}10]$) branch of Ni_xAl_{1-x} for $x = 63, 58, 50$ at T .
b) Deviation of measured phonon frequency E from that determined using a sine wave dispersion, E_S .
c) Variation of the maxima of $E - E_S$ with concentration X (From ref.15)

Neutron scattering experiments have shown that the major anomaly in the phonon dispersion curve is not in the long wavelength regime probed by ultrasonic studies but occurs at finite q values as shown in Fig.4 /15/. Here is shown the dispersion curve of the $[\zeta\zeta0]$ - TA_2 phonon branch (atomic displacements parallel to $[\bar{1}10]$) measured on $\text{Ni}_x\text{Al}_{1-x}$ for $x = 63, 58$ and 50 atomic percent. The composition dependence of the anomalous region is shown in Fig.4b by subtracting the measured phonon energy E from that determined by a harmonic sine wave dispersion: $E_s \sim v_s \sin \pi\zeta$ where v_s is the velocity of sound. $E_s - E$ is plotted for each x and the maximum corresponds to the largest deviation. It is seen in Fig.4c that the position of the maximum anomaly varies linearly with x .

The temperature dependence of the dispersion curve was measured in the $x = 58$ and 63 atomic per cent samples and showed similar behavior. There is a modest amount of softening (10% - 20%) of this branch with decreasing temperature but restricted mostly to the q region where the anomalous behavior occurs. This amount of softening is typical of most martensitic phase transformations /27/.

All three samples studied exhibit diffuse elastic scattering measured along the same $[\zeta\zeta0]$ direction, but the temperature dependence is very different. For $x = 58$ no phase transition occurs and the diffuse scattering is nearly structureless and only weakly temperature dependent. In $x = 63$, however, there

Figure 5. a) Elastic neutron scattering spectrum measured along $[\zeta\zeta0]$ direction about 200 Bragg peak. b) Temperature dependence of the intensity measured at $Q = (2.11 - 0.11, 0)$ measured on heating and cooling (From ref. /15/)

Figure 6. a) Same as Fig.5a only at $T = 150 \text{ K}$
 b) Same as Fig.6a only about (100) Bragg peak
 Top: Representation of observed features in reciprocal space

is structure in the diffuse scattering and it is strongly temperature dependent as shown as Fig.5. At high temperature broad satellites are present on either side of the (200) Bragg peaks at $z = 0.13$. These are localized along the $[110]$ ridge of diffuse scattering. The intensity of this peak increases continuously on cooling, but shows a distinct thermal hysteresis (Fig.5b) indicating a first order phase transition. The peak also sharpens on cooling to low temperatures.

As in NiTi, the phonon softening appears to induce the elastic diffuse scattering since they both occur in the same wavevector region. Examination of different Brillouin zones show that the satellites cannot be described by a simple density wave since the satellite positions vary from zone to zone as shown in Fig.6. Figure 6a is a scan along $[550]$, through the (2,0,0) Bragg peak; the same scan as in Fig.5a only at lower temperature. It is seen that the intensity of the satellites on either side of the Bragg peak is equal or greater than the cubic Bragg peak intensity. Figure 6b, is a parallel scan only through the (1,0,0) Bragg peak. It is clearly seen that the satellite position, δ depends strongly upon the Brillouin Zone being measured. In this case, δ appears to be proportional to Q .

A clearer picture of what is occurring is obtained by looking at the superposition of the cubic reciprocal lattice and those of the measured satellites as shown on the top of Fig.6. It appears that we have a coexistence of the cubic phase with two variants or twins of the low temperature orthorhombic phase. Thus, it is improper to view the peaks appearing in Fig.5 as satellites generated by a density wave. A more correct description is that the new low temperature, the product phase, is growing coherently within the high temperature parent phase.

4. Discussion

In the traditional soft mode picture of structural phase transitions the displacements associated with a particular phonon are just those required to generate the low temperature structure. As the transition temperature is approached, the frequency of the mode decreases and the system becomes unstable and distorts into the new low temperature phase. New Bragg peaks develop and the symmetry of the low temperature phase is a subgroup of the symmetry of the high temperature phase. There is a direct symmetry relationship between the soft mode and the new structure.

In the martensitic transformations, the relationship between the phonon softening and the low temperature structure is not clear. Most of the systems listed in Table I show only a small (<20%) softening, compared to nearly complete softening in "traditional" structural phase transitions occurring in SrTiO_3 and KH_2PO_4 (KDP) /2,3/. Recently LINDGARD and MOURITSAN /28/ showed that it is possible to have a martensitic transformation with only a small change in a mode frequency due to the anharmonic coupling of two modes. The phonon anomalies and their small temperature dependence observed are consistent with their ideas, but the origin of the anomalies is not clear. Since these are good metals it is reasonable to expect that the electronic structure will play an important role via the electron phonon coupling /29,30/.

The new Bragg peaks appearing at low temperatures cannot be described as a simple condensation of a density wave because their wavevector δ varies with Q . Several explanations have been proposed. YAMADA et al /31/ proposed a "Modulation Lattice Relaxation" model which is based on the cubic parent phase having a particular type of phonon dispersion curve plus embryos of the low temperature product phase. Due to the interactions between the product and the parent phase, modulated lattice relaxations occur in the parent phase. This model was successful to explain the "swirl" pattern of δ observed in NiTi and given in Fig.3b. KRUMHANSL /32/ used a model based on stacking solitons proposed by HOROVITZ et al /33/ to explain the similar peak shifts observed in ω phase Zr-Nb alloys, a system which has much in common with the martensitic systems described

here. Finally SALAMON et al /18/ proposed that for NiTi the peaks can be indexed as commensurate reflections on a rhombohedral "ghost" lattice, but with the main Bragg peaks at the original cubic position. This picture is similar to that indicated in NiAl on the top of Fig.6.

Features presented above may occur in many of the systems mentioned in Table I but the studies of the elastic scattering in most experiments is incomplete. It is important to measure the diffuse scattering and new peaks in several Brillouin zones. Most diffraction studies are performed only in one or two Brillouin zones. A recent X-ray diffraction study on the Au-Cd alloy covering many Brillouin zones revealed behavior very similar to Fig.3 observed in NiTi /34/.

The picture of the martensitic systems emerging from these studies is that at high temperatures there exist small regions of the product phase distributed throughout the parent phase. These embryonic regions can grow in size and become more numerous as the temperature is lowered. Thus, above any transition temperature there is a premartensitic phase where there is a coexistence of the parent and product phase. Diffuse scattering may appear when the product embryos are very small. Structure in the diffuse scattering will develop as the embryos grow in size. This nucleation process must depend upon the microscopic forces of the parent phase since phonon anomalies are present in the systems mentioned in Table I. The relationship between the phonon anomalies and low temperature structure needs more clarification.

Indeed, more work needs to be done with the microscopic techniques discussed here to characterize other martensitic transitions before a complete picture of martensitic phase transitions emerges.

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