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RESEARCH ARTICLE

Influence of Magnetic Fields on Structural Martensitic Transitions

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We show evidence that a structural martensitic transition is related to significant changes in the electronic structure, as revealed in thermodynamic measurements made in high magnetic fields. The effect of magnetic field is considered unusual as many influential investigations of martensitic transitions have emphasized that the structural transitions are primarily lattice dynamical and are driven by the entropy due to the phonons. We provide a theoretical framework which can be used to describe the effect of magnetic field on the lattice dynamics in which the field dependence originates from the dielectric constant.

Keywords: martensitic transition, shape-memory alloy, Fermi surface, dielectric function, phonon softening.

1. Introduction

Martensitic transitions are often defined as diffusionless structural transitions that lower the symmetry, and in which the order parameter has a discontinuity. This definition is generic and is compatible with a group theoretical analysis performed by Anderson and Blount [1] which showed that the transition is usually first-order and could only be second-order at an isolated point in the phase diagram. Similarly, Wang *et al.* have shown similar second-order behaviour in a strain-glass region of the phase diagram of the AuCd system [2, 3]. Recently, Lashley *et al.* performed inelastic neutron scattering measurements on the Hume-Rothery alloy, AuZn [4], which showed that although the transition was strongly first-order in the non-stoichiometric compounds, the hysteresis was greatly reduced and the order parameter extracted from the satellite intensity was a continuous function of temperature for stoichiometric AuZn.

Although there is a large body of work on ferromagnetic Heuslers, in which a large magneto-elastic coupling exists [5–7], we shall restrict our focus to nonmagnetic systems. In particular we consider AuZn in which the lattice dynamics and structural transition are strongly affected by an applied magnetic field, although the transition temperature is at most only weakly field dependent. The field dependence is considered unusual as many influential investigations of martensitic

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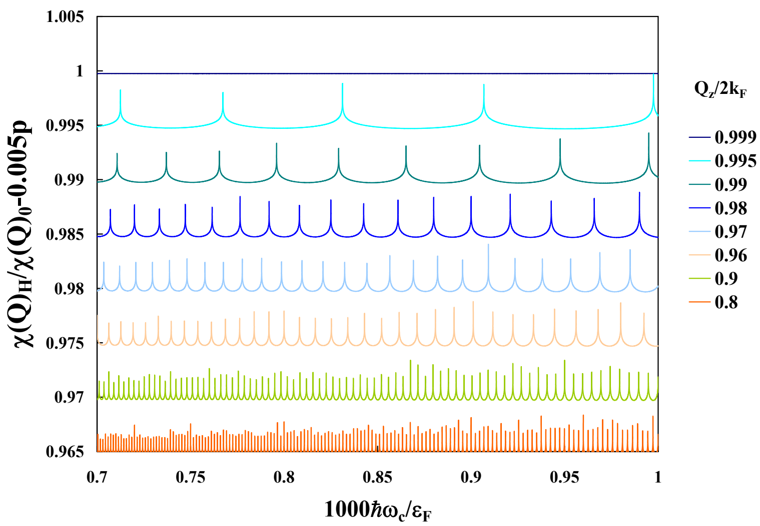

Figure 1. The oscillations of the normalized Lindhard function $\chi_H(Q_z)/\chi_0(Q_z)$ with the magnetic field directed parallel to $\underline{Q}$. For clarity, the response is normalized to the $H = 0$ value and then is lowered by a multiple (p) of 0.005 for successively lower values of $Q_z/2k_F$. The curves are limited by the resolution of the plotting program.

transitions have emphasized that the structural transitions are primarily lattice dynamical [8] and are driven by the entropy due to the phonons [9, 10]. We shall provide a theoretical framework which can be used to describe the effect of the field on the lattice dynamics in which the field dependence originates from the dielectric constant. The weak field dependence of the martensitic transition temperature in AuZn is contrasted with the strong field dependence in V_3Si and the difference is related to the difference in the dimensionality of these two materials.

2. Model

For a first-order martensitic transition where the phonons only partially soften [11, 12], the martensitic transition temperature, T_M, can be found by considering the balance between the difference in the structural energy [9, 10] of the two phases, ΔE_s, and the difference in the phonon entropies, ΔS,

$$\Delta E_s \; = \; T_M \, \Delta S \tag{1}$$

A rough approximation for the structural energy, E_s, of a metal with a monatomic basis is given [13] as a sum, over reciprocal lattice vectors, of the squared modulus of the structure factor, $S(\underline{Q})$, and the screened atomic pseudo-potential, $V_0(\underline{Q})$,

$$E_s \; = \; \frac{1}{2} \, \frac{N^2}{V} \sum_{\underline{Q} \neq 0} \mid S(\underline{Q}) \mid^2 \mid V_0(\underline{Q}) \mid^2 \chi(\underline{Q}) \; \varepsilon(\underline{Q}) \tag{2}$$

in which $\chi(\underline{Q})$ is the Lindhard function and $\varepsilon(\underline{Q})$ is the dielectric constant. It is expected that the main field dependence of the transition temperature will be governed by the field-dependence of the Lindhard function at the reciprocal lattice vectors ($Q <$ or $\sim 2k_F$) which are appreciably different between the two structures.

The Lindhard function can be expressed as a sum over the occupied Landau levels, n

$$\chi(\underline{Q})_H \;=\; -\,\frac{1}{2\pi^2\hbar\omega_c Q_z r_c^4}\sum_{n,m,\sigma} \mid F_{n,m}(Q_\perp)\mid^2 \,\ln\left|\frac{2m_e(n-m)\omega_c/\hbar - Q_z^2 - 2Q_z k_{F,n\sigma}}{2m_e(n-m)\omega_c/\hbar - Q_z^2 + 2Q_z k_{F,n\sigma}}\right|; \tag{3}$$

where $k_{F,n\sigma}$ is the Fermi wave vector of the n-th spin split occupied Landau level

$$k_{F,n\sigma} \;=\; \sqrt{\frac{2m_e}{\hbar^2}\left[\,\epsilon_F - \left(n + \frac{1-\sigma}{2}\right)\hbar\omega_c\,\right]}, \tag{4}$$

and the Larmour frequency is given by

$$\omega_c = \frac{|e|\ H_z}{m_e\ c}. \tag{5}$$

The Fourier Transform of the matrix elements of the density operator between the various Landau levels is given by

$$F_{n,m}(Q_\perp) \;=\; \left(\frac{n!}{m!}\right)^{\frac{1}{2}}\left(\frac{r_c\ (\ i\ Q_x\ -\ Q_y\ )}{\sqrt{2}}\right)^{m-n}\ \exp\left[\,-\,\frac{r_c^2\ Q_\perp^2}{4}\,\right] L_n^{m-n}\left(\frac{r_c^2\ Q_\perp^2}{2}\right) \tag{6}$$

for $m > n$ and where the radii of the Landau orbits, r_c, are given by:

$$r_c \;=\; \sqrt{\frac{\hbar\ c}{|e|\ H_z}} \tag{7}$$

and where $L_m^n(x)$ represents the associated Laguerre functions. The k_y dependence of the matrix elements occurs in the form of a trivial phase factor, which we have omitted since it drops out of the Lindhard function. To obtain an estimate of the relative contributions to the field dependence from the Landau quantization and the spin splitting, we shall set $Q_\perp = 0$. Since $F_{n,m}(0) = \ \delta_{n,m}$, only one summation remains and the resulting expression

$$\chi(Q_z)_H \;=\; -\,\frac{1}{2\pi^2\hbar\omega_c Q_z r_c^4}\sum_{n,\sigma}\ln\left|\frac{Q_z + 2k_{F,n\sigma}}{Q_z - 2k_{F,n\sigma}}\right|. \tag{8}$$

The summation includes a term which is logarithmically divergent when $Q = 2k_{F,n\sigma}$. The above expressions reduce to the usual expression when $H = 0$, as can be seen from the following analysis. The summation can be evaluated with the aid of the Euler-MacLaurin summation formulae. The integral expression yields the usual zero-field expression for the Lindhard function, except that the Fermi wave vector k_F is spin-dependent

$$\chi(Q_z)_H \;=\; -\,\frac{1}{2\ \pi^2}\left(\frac{m_e}{\hbar^2}\right)\sum_{\sigma=\pm 1}\left[\,\frac{k_\sigma}{2} + \left(\frac{4k_\sigma^2 - Q_z^2}{8\ Q_z}\right)\ln\left|\frac{Q_z + 2k_\sigma}{Q_z - 2k_\sigma}\right|\,\right]\Bigg|_{k_{min,\sigma}}^{k_{F,\sigma}} \tag{9}$$

where the maximum and minimum values of k_σ are given by

$$k_{F,\sigma} \;=\; \sqrt{\frac{2\ m_e}{\hbar^2}\left[\,\epsilon_F - \hbar\omega_c\left(\frac{1-\sigma}{2}\right)\,\right]} \tag{10}$$

and

$$k_{min,\sigma} \;=\; \sqrt{\frac{2\,m_e}{\hbar^2}\left[\;\epsilon_F - \hbar\omega_c\left(n_{max,\sigma} + \frac{1-\sigma}{2}\right)\;\right]}. \tag{11}$$

The discrete end-point corrections represent the effects of the Landau level quantization. The Lindhard function is a periodic function of

$$\left[\,1 - \left(\frac{Q_z}{2k_F}\right)^2\,\right]\left(\frac{\epsilon_F}{\hbar\omega_c}\right) \tag{12}$$

for $1 > \frac{Q_z}{2k_F}$. The oscillations in $\chi_H(Q_z)$ are shown in Fig. 1 for various values of $Q_z/2k_F$. It is expected that disorder, temperature and many body effects will smear and diminish the amplitude of the oscillations due to Landau level quantization. However, it is expected that these effects will not alter the field-dependence originating from the spin split Fermi surfaces.

The change in T_M with field can be estimated by considering a spin splitting of $2\,\delta k$ between the up-spin and down-spin Fermi surfaces. In the limit of low magnetic field, the spin splitting is expected to be linear in the field and proportional to $\rho(\epsilon_F)$ the density of states at the Fermi energy

$$\frac{\delta k}{k_F} \;\sim\; \rho(\epsilon_F)\;\mu_B H \tag{13}$$

where $\mu_B \;=\; \frac{|e|\;\hbar}{2\;m\;c}$. The spin splitting results in the change

$$\chi(Q)_H \;=\; \chi(Q)_0 \;+\; \frac{1}{2!}\,\frac{\partial^2\chi(Q)_0}{\partial k_F^2}\;\delta k^2 \;+\;\ldots \tag{14}$$

which can be estimated for a three dimensional nearly free-electron metal as

$$\chi(Q)_H \;\approx\; \chi(Q)_0 \;+\; \frac{k_F^2}{2!}\,\frac{\partial^2\chi(Q)_0}{\partial k_F^2}\left(\frac{\mu_B H}{\epsilon_F}\right)^2 \tag{15}$$

if $k_B T_M \ll \varepsilon_F$. Therefore, one expects that the relative change in T_M should be given by

$$\begin{aligned}\frac{\Delta T_M(H)}{T_M(0)} &\approx \frac{k_F^2}{2!\;\chi(Q)_0}\;\frac{\partial^2\chi(Q)_0}{\partial k_F^2}\;\left(\frac{\mu_B H}{\epsilon_F}\right)^2\\ &\approx -\left[\;\frac{k_F}{2\;Q}\ln\left|\frac{2k_F - Q}{2k_F + Q}\right| \;+\; \frac{2k_F^2}{4k_F^2\;-\;Q^2}\;\right]\left(\frac{\mu_B H}{\epsilon_F}\right)^2\end{aligned} \tag{16}$$

where we have neglected the weak logarithmic dependence of the denominator on Q. Hence, one expects that the relative change in T_M will depend on the field through the factor $(\frac{\mu_B H}{\epsilon_F})^2$, but can be extremely large if Q is extremely close to $2k_F$. The free electron model yields the estimate

$$\left(\frac{k_F a}{2\pi}\right) \;=\; \left(\frac{9}{4\pi}\right)^{\frac{1}{3}} \tag{17}$$

for the Fermi wave vector of AuZn, so for [111] one has $Q/2k_F \approx 0.9680$ which leads to the geometrical factor in eqn(16) having a magnitude of about 8.92. On the other hand, for an applied magnetic field of 9 T one has $\hbar\omega_c \approx 1.04$ meV while $\epsilon_F \approx 11.8$ eV since $a \approx 3.19$ Å, which leads to the estimate for a relative change in T_M of the order of 10^{-7}.

3. Lattice Dynamics

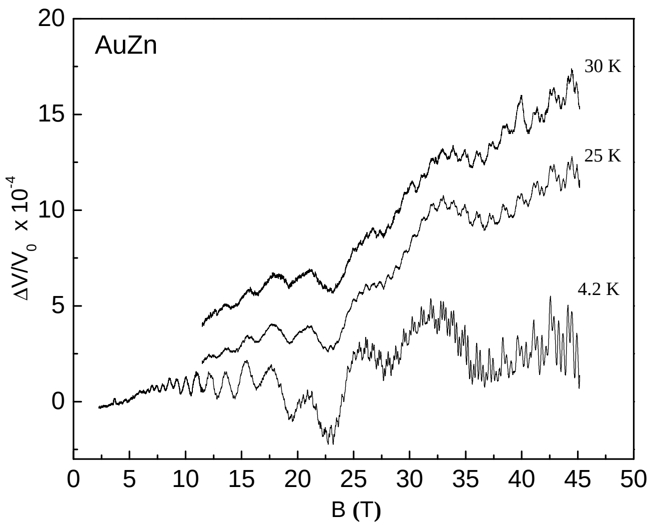

Figure 2. The oscillations of the speed of sound of AuZn measured at several temperatures in the martensitic phase. [After J.C. Lashley *et al.* (2007).]

Alternatively, one can also obtain a similar criterion by considering the softening of the phonon modes as was considered by Dieterich and Fulde [14]. Their analysis can be extended to the case of second order martensitic phase transitions [4] in which the softening occurs at a finite value of q as is the case for AuZn. In particular, the phonon frequencies, $\omega_\alpha(\underline{q})$, and the polarization vectors, $\underline{\epsilon}_\alpha(\underline{q})$ are determined from the eigenvalue equation [15]

$$M\ \omega_\alpha^2(\underline{q})\ \underline{\epsilon}_\alpha(\underline{q}) = N \sum_{\underline{Q}} (\ \underline{q}+\underline{Q}\ )\ \Theta(\underline{q}+\underline{Q})\ (\ \underline{q}+\underline{Q}\ )\ .\ \underline{\epsilon}_\alpha(\underline{q}) - N \sum_{\underline{Q}} \underline{Q}\ \Theta(\underline{Q})\ (\ \underline{Q}\ .\ \underline{\epsilon}_\alpha(\underline{q})\ ) \quad (18)$$

where the sum over $\underline{Q}$ is a sum over reciprocal lattice vectors and where the Fourier Transform of the pair-potential,$\Theta(\underline{k})$, is approximated by the screened Coulomb interaction

$$\Theta(\underline{k}) \ = \ \frac{1}{V} \left(\frac{4\ \pi\ Z^2\ e^2}{k^2\ \epsilon(\underline{k})} \right) \widetilde{V}_0(k)^2 \quad (19)$$

and $\widetilde{V}_0(k)$ is a dimensionless oscillatory function of k that only depends on the core radius. Therefore, we argue that the field dependence of the phonon frequencies originates from the dielectric constant. This conclusion is consistent with the earlier observations of the oscillations of the sound velocity with increasing magnetic field

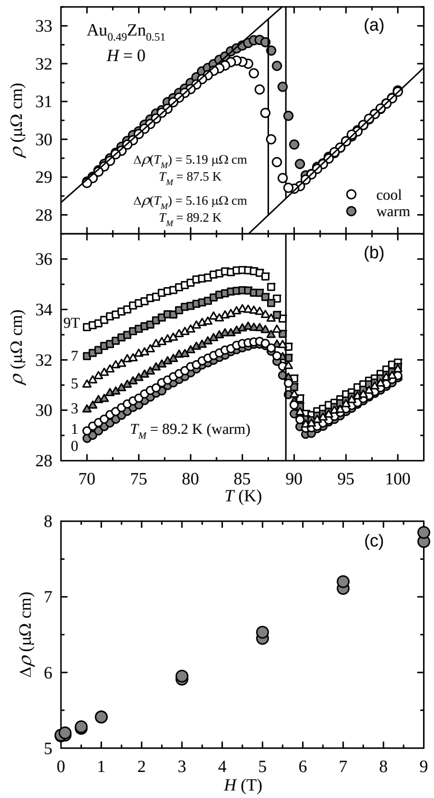

Figure 3. The temperature-dependence of the resistivity anomaly at the martensitic transition of the slightly off-stoichiometric compound $Au_{0.49}Zn_{0.51}$ showing (a) the thermal hysteresis in the vicinity of the transition, and (b) the variation with applied magnetic field. The field-dependence of the resistivity change at the martensitic transition of AuZn, as defined schematically by the full line in (a) is plotted in (c).

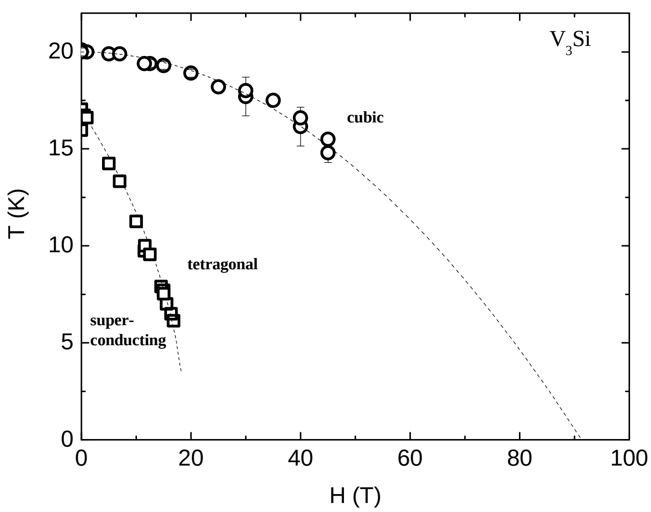

Figure 4. The field-dependence of the martensitic (cubic to tetragonal) phase transition and superconducting temperatures in V_3Si. [After P. A. Goddard *et al.* (2009).]

at temperatures well below the martensitic transition [16]. The oscillatory field-dependence of the speed of sound is shown in Fig. 2. Because the Fourier spectrum of the oscillations of the speed of sound shows peaks at the frequencies obtained from de Haas-van Alphen measurements [17, 18] and the amplitudes follow the Lifschitz-Kosevitch formula [16], it was concluded that these oscillations originate from Landau-level quantization as manifested by the dielectric constant at $Q \to 0$.

Thus, one expects that the end result for $\Delta T_M(H)$ would be a similar expression to that given previously in eqn(16), in which the field-dependence of T_M is related to the field-dependence of the density-density response function. The magnitude of the jump in resistivity ($\Delta\rho$=ρ_R-ρ_{B2}) of AuZn exhibits significant field-dependence, which is shown in Fig. 3 (c). The field-dependence of the resistivity, Fig. 3 (b) and (c), is consistent with a gap opening up on part of the Fermi-surface where the gap is proportional to the order parameter. The specific heat jump (not shown) is also consistent with a linear temperature variation of the square of the order parameter. For small fields, the inferred gaps grow quadratically with increasing fields but deviate for large fields. However for AuZn, which is three-dimensional and has a relatively large Fermi-energy, the field-dependence of T_M, found from the temperatures at which the specific heat jumps or the resistivity anomalies occur, is negligibly small. By contrast, for the case of V_3Si considered by Dieterich and Fulde, the Labbe-Friedel [19] model suggests that the Fermi-energy lies extremely close to the bottom of a quasi-one-dimensional density of states, so that ϵ_F has the extremely small value of 22 K. Hence, for V_3Si one expects a large depression of T_M with increasing field [21] as can be seen in the cubic to tetragonal martensitic transition phase diagram in Fig. 4, but not in AuZn. Depending on the degree of strain present in V_3Si, the upper critical field shown in Fig. 4, is consistent with the earlier work of Testardi [22].

4. Summary

We have indicated that, irrespective of the order of the transition, that structural properties of AuZn are strongly affected by magnetic field. Furthermore, we have proposed a model of the structural properties in which the field-dependence originates through the dielectric constant. The proposed model forms a connection between phonon-entropy stabilization pictures with Jones's description [20] of Hume-Rothery's observations [23]. Jones's explanation was that the structural transitions are purely electronic and driven by the Fermi-surface nesting with the Brillouin Zone boundary. We note that Fermi-surface nesting has been gauged by diffuse electron scattering inV_3Si, [24, 25]. Similarly in the In-Tl system, the pressure dependence of the superconducting transition temperature, T_c, and the variation of T_M with composition, demonstrated the martensite boundary to be the result of Fermi surface-Brillouin Zone boundary interaction [26].

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