Observation of a strongly nested Fermi surface in the shape-memory alloy Ni_{0.62}Al_{0.38}

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The Fermi surface topology of the shape-memory alloy Ni_{0.62}Al_{0.38} has been determined using Compton scattering. A large area of this Fermi surface can be made to nest with other areas by translation through a vector of \( \approx 0.18 [1,1,0] (2\pi/a) \), which corresponds to the wavevector associated with martensitic precursor phenomena such as phonon softening and diffuse streaking in electron diffraction patterns. This observation is compelling evidence that these phenomena are driven by the enhanced electron-lattice coupling due to the Fermi surface nesting.

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Smart alloys which exhibit shape-memory and superelastic phenomena have been deployed in a wide variety of applications ranging from actuators in aircraft wings to surgical instruments. However, an atomic-scale understanding of the origin of the martensitic transformation (MT), the structural transformation at the heart of these phenomena, is still lacking. It has been hypothesised that lattice vibrations are the key, an idea supported by first-principles calculations indicating that strong coupling of certain phonons to the electrons (phonon softening), due to particular features in the Fermi surface, plays a crucial role [1, 2, 3, 4, 5, 6]. Owing principally to the compositional disorder inherent to many of these alloys, a Fermi surface determination in these materials is experimentally challenging, with traditional quantum oscillatory techniques suffering due to their reliance on a long electronic mean free path. Recent de Haas-van Alphen experiments in the austenitic phase of the low-temperature shape-memory alloy AuZn have reported an orbit whose cross-sectional area is in excellent agreement with first principles calculations which predict the presence of a strongly nested sheet of Fermi surface [7]. In this Letter we provide experimental evidence in support of the intimate relationship between the phonon softening and the Fermi surface through a Compton scattering study of the shape memory alloy Ni_{0.62}Al_{0.38}.

It is more than a century since Martens’ exploration of the microstructure of steels gave the first insight into the origin of their macroscopic properties, and subsequently led to his name being associated with a more general solid-state phase transformation [8]. While metallurgists have a precise, albeit phenomenological, definition of a MT, and physicists use the term more loosely to define many first-order transitions with acoustic anomalies, both disciplines generally agree that they are purely structural, diffusionless (meaning no atom-by-atom jumping within the unit cell), displacive (meaning a coordinated displacement of the atoms over distances much less than the atomic spacing) solid-solid phase transitions [9]. However, MTs have continued to fascinate generations of scientists. Ni_{x}Al_{1-x} alloys are well known to exhibit a MT for \( x \sim 0.62 \) [1], and represent a prototypical compound for the transformation which is intermediate between weakly (almost second order) and strongly first order.

Early attempts to understand these transformations suggested that a phonon would become unstable at a particular temperature, at which point the lattice would displace spontaneously to a finite amplitude [10, 11]. This ‘soft-mode’ theory, however, is found to be lacking in several key aspects [12] which include (i) the observation that the phonon frequencies only soften slightly, and do not indicate harmonic instability, (ii) the prediction of a second-order transition whereas in practice there is a finite, albeit small discontinuity in the microscopic order parameter (the static amplitude of the frozen-in soft mode), (iii) the empirical absence of critical fluctuations, and finally (iv) the presence of strong precursors of the new phase, or a distorted form of it, which persist well above the transition temperatures; examples of these precursors in the case of Ni_{x}Al_{1-x} include diffuse streaking in electron diffraction patterns and the corresponding ‘tweed’ strain-contrast patterns in transmission electron microscope images, and anomalous softening of the transverse acoustic (TA) phonon branch along [ξξ0] at temperatures well above the MT [2, 3]. These pre-
martensitic phenomena have been associated with local deviations from the perfect cubic structure at temperatures well above the MT, the regions being formed as a result of the coupling of defect-induced strain fields and anomalous phonon softening.

It is well-known that when parallel pieces of Fermi surface exist in a metal, there will be a strong electronic response at the wavevector which translates, or nests, one parallel piece onto the other. This role of the Fermi surface in influencing the electron-phonon coupling, was extensively investigated during the last two decades (see, for example, [14–16]), where premartensitic phenomena [9, 13] were explicable in terms of Fermi surface nesting.

While anharmonic effects are thought to be responsible for the MT [17], it is Kohn anomalies [18] driven by nestable regions on the Fermi surface impacting on the electronic screening (and hence on the electron-phonon coupling), that were initially suggested as the origin of the premartensitic phenomena [1]. Given the disordered nature of the Ni$_{x}$Al$_{1-x}$ alloys, the degree to which the Fermi surface remains a well-defined, sharp entity is an important consideration. Stocks et al. [19] tackled this issue by calculating the effect of disorder within the framework of the coherent potential approximation (CPA). They were able to show that although there is significant smearing of the Fermi surface in many areas of the Brillouin zone, the region of Fermi surface first identified by Zhao and Harmon [1] as exhibiting nesting (surprisingly, perhaps) remains rather sharp.

The key questions addressed here, however, are whether the actual Fermi surface of Ni$_{0.62}$Al$_{0.38}$ resembles that predicted by ab initio calculation [1, 19], and whether any nesting vector matches that of the strongly softened phonons. A previous attempt (also using Compton scattering) to establish a connection between the Fermi surface topology and any shape-memory behavior [21] was unsuccessful, principally due to the complexity of the Fermi surface of their Ti$_{48.5}$Ni$_{51.5}$ alloy. Here, we present our measurement of the Fermi surface of Ni$_{0.62}$Al$_{0.38}$ using the technique of Compton scattering [21].

In order to make a direct comparison with the Fermi surface predicted by band theory, we performed ab initio electronic structure calculations to reproduce the earlier work of Stocks et al. [19] for the disordered Ni$_{0.62}$Al$_{0.38}$ alloy. We employed the fully relativistic Korringa-Kohn-Rostoker (KKR) method within the atomic sphere approximation, and the disorder was taken into account by the coherent potential approximation [22]. The lattice constant was taken to be 2.82 Å and convergence was achieved at 816 k-points within the irreducible Brillouin zone. The Fermi surface was identified by the locus of the peaks in the Bloch spectral function, $A(k, \epsilon)$. The sheet of (nestable) Fermi surface identified by Zhao and Harmon [1] is presented in Fig. 1a alongside the three dimensional Fermi surface.

Our single crystal sample was cut by spark erosion from a single grain of a large ingot of Ni$_{0.62}$Al$_{0.38}$ grown using the Bridgman method. It was subsequently annealed under argon at temperatures between 1230K and 1270K for a total of 30 hours, followed by a vacuum degas at 900K.

A total of twenty-four Compton profiles along different crystallographic directions were measured at room temperature on the high-resolution Compton spectrometer of beamline BL08W at the SPring-8 synchrotron [23, 24]. This spectrometer is a Cauchois-type spectrometer, consisting of a Cauchois-type crystal analyser and a position-sensitive detector, with a resolution FWHM at the Compton peak of 0.155 a.u (1 a.u. of momentum = 1.99 ×10$^{-24}$ kg m s$^{-1}$) [23, 24]. Whereas other Fermi surface techniques rely on a long mean-free-path of the electron or relatively defect-free crystal, Compton

![FIG. 1: (color online) (a) The Fermi surface of Ni$_{0.62}$Al$_{0.38}$, determined via the KKR calculation (shown alongside are the location of some relevant symmetry points within the Brillouin zone), and (b) the intensity of the Bloch spectral function, where dark shades represent high intensity, of the sheet of Fermi surface proposed to accommodate the nesting in Ni$_{0.62}$Al$_{0.32}$, shown on the $k_\perp$ ≈ 0.48 ($\pi/a$) plane. The Fermi surface can be identified as the strong oval features located on the edges of the Brillouin zone (the fainter lines being spectral weight from a band close to the Fermi energy). The arrow indicates the proposed nesting vector (along the [110] direction) and the edge of the first Brillouin zone is marked. Note that this sheet remains relatively sharp throughout the Brillouin zone, despite the disorder inherent to the system.](image-url)
scattering is a robust technique insensitive to defects or disorder, providing a one-dimensional projection (double integral) of the underlying bulk electron momentum distribution. For each Compton profile $\sim 300,000$ counts in the peak data channel were accumulated. Of the twenty-four Compton profiles that were collected, three were of high-symmetry directions, namely [100], [110] and [111], and ten were the ‘special directions’ outlined by Kontrym-Sznajd et al. 28: the remaining eleven Compton profiles were chosen in such a way so as to be equally spaced throughout the Brillouin zone. Each Compton profile was corrected for possible multiple-scattering contributions using a Monte Carlo method 29.

A three-dimensional momentum density was reconstructed 25 from this set of 24 profiles and then folded back into the first Brillouin zone using the Lock-Crisp-West procedure 26 to obtain the occupation density. The experimental Fermi surface (shown in Fig. 2) was extracted by contouring this density at a level fixed by an extremum in the first derivative along a direction where our calculations indicated the Fermi surface was likely to be well-defined 27. To illustrate that the reconstruction procedure does not introduce artefacts, the Fermi surface reconstructed from the Compton profiles calculated by the KKR method along the same 24 directions is shown in Fig. 3.

Before addressing the issue of how faithfully the $ab\ initio$ calculations have described the observed Fermi surface, it is important to investigate the nesting properties of the experimentally determined one. A plane-by-plane inspection of the Fermi surface throughout the Brillouin zone revealed that a vector $\approx 0.18[1, 1, 0](2\pi/a)$ connects a large area in the manner predicted by Zhao and Har-
of Fermi surface responsible for the nesting are observed experimentally to be relatively flat. This, in conjunction with the large density of states (predicted by the calculations) spanning these wavevectors, provides a large propensity for nesting. There is, however, some noteworthy discrepancy between the calculated and experimental Fermi surfaces. Experimentally, a neck is observed to open around the X-point of the Brillouin zone whereas according to the calculations this sheet remains closed. The calculated bandstructure reveals flat (almost dispersionless) bands along X – M and M – R, lying just below the Fermi level, leading to a van Hove singularity in the density of states at that energy. The opening up of a Fermi surface neck along Γ – X implies that the Fermi level has crossed below this van Hove singularity and may be indicative of the impending lattice instability at the martensitic transformation (where the Fermi surface would undergo more substantial rearrangement).

In conclusion, we have presented the experimental Fermi surface of the disordered alloy Ni$_{0.62}$Al$_{0.38}$ from the results of Compton scattering experiments, providing evidence in support of the intimate link between the electronic structure and the observed phonon softening. The Fermi surface obtained from ab initio calculations within the KKR-CPA framework has been shown to be in good agreement with the experimentally determined Fermi surface, with the exception of the opening of a neck along the X direction of the Brillouin zone. It is tentatively suggested that this topological disagreement may be explained by the proximity of the Fermi level to a van Hove singularity in the density of states.

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[1] G. L. Zhao & B. N. Harmon, Phys. Rev. B 45, 2818 (1992).
[2] E. I. Isaev et al., Solid State Commun. 129, 809 (2004).
[3] X. Huang, G. J. Ackland & K. M. Rabe, Nature Materials 2, 307 (2003).
[4] I. I. Naumov & O. I. Velikokhatniy, J. Phys.:Condens. Matter 9, 10339 (1997).
[5] X. Y. Huang, I. I. Naumov & K. M. Rabe, Phys. Rev. B 70, 064301 (2004).
[6] C. Bungaro, K. M. Rabe & A. DalCorso, Phys. Rev. B 68, 134104 (2003).
[7] R. D. McDonald et al., J. Phys.:Condens. Matter 17, L69 (2005); P. A. Goddard et al., Phys. Rev. Lett. 94, 116401 (2005).
[8] Z. Nishiyama, Martensitic Transformation (Academic Press, New York, 1978).
[9] S. M. Shapiro, B. X. Yang, Y. Noda, L. E. Tanner & D. Schryvers, Phys. Rev. B 44, 9301 (1991).
[10] W. Cochran, Adv. Phys. 9, 387 (1960).
[11] P. W. Anderson, Fizika Dielectrikov, edited by G.I. Skanavi (Acad. Nauk. SSR, Moscow, 1960).
[12] J. A. Krumhansl & R. J. Gooding, Phys. Rev. B 39, 3047 (1989).
[13] S. M. Shapiro, J. Z. Larese, Y. Noda, S. C. Moss & L. E. Tanner, Phys. Rev. Lett. 57, 3199 (1986).
[14] R. Bruinsma, Phys. Rev. B 25, R2951 (1982).
[15] G. L. Zhao et al., Phys. Rev. B 40, 7999 (1989).
[16] G. L. Zhao and B. N. Harmon, Phys. Rev. B 48, 2031 (1993).
[17] Y.-Y. Ye, Y. Chen, K.-M. Ho, B. N. Harmon & P. A. Lindgard, Phys. Rev. Lett. 58, 1769 (1987).
[18] W. Kohn, Phys. Rev. Lett. 2, 393 (1959).
[19] G. M. Stocks et al., in Ordered Intermetallics - Physical Metallurgy and Mechanical Behaviour, edited by C. T. Liu et al., (Kluwer Academic Publisher, Dordrecht, 1992), pp. 15–36.
[20] N. Shiotani, et al., J. Phys. Soc. Japan 73, 1627 (2004).
[21] M. J. Cooper, Rep. Prog. Phys. 48, 415 (1985).
[22] H. Ebert, in Electronic Structure and Physical Properties of Solids, edited by H. Dreyssé, Lecture Notes in Physics Vol. 535, (Springer, Berlin, 1998), p. 191; http://olymp.cup.uni-muenchen.de/ak/ebert/SPRKKR/
[23] N. Hiraoka, M. Itou, T. Ohata, M. Mizumaki, Y. Sakurai & N. Sakai, J. Synchrotron Rad. 8, 26 (2001).
[24] Y. Sakurai & M. Itou, J. Phys. Chem. Solids 65, 2061 (2004).
[25] G. Kontrym-Sznajd & M. Samsel-Czekala, Applied Physics A - Materials Science & Processing 70, 89 (2000).
[26] D. G. Lock, V. H. C. Crisp & R. N. West, J. Phys. F : Metal Physics 3, 561 (1973).
[27] Zs. Major et al., Phys. Rev. Lett. 92, 107003 (2004).
[28] G. Kontrym-Sznajd, A. Jura & M. Samsel-Czekala, Appl. Phys. A 74, 605 (2002).
[29] N. Sakai, J. Phys. Soc. Japan 56, 2477 (1987).