Acoustic-Phonon Softening in the Invar Alloy Fe_3Pt†

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Inelastic neutron scattering experiments on an ordered Invar alloy Fe_3Pt show large softening of the [100]TA and [110]TA_1 acoustic shear modes below the Curie temperature. In addition, a central peak is observed below 100 K, which, however, behaves noncritically. The phonon softening is discussed in terms of the magnetoelastic coupling caused by the electron-phonon interaction.

Iron-platinum alloys near the stoichiometric composition Fe_3Pt are ferromagnetic and exhibit a very small thermal expansion below the Curie temperature[1,2] which is known as the Invar effect. Measurements on forced volume magnetostriction,[3] pressure dependence of the Curie temperature,[3] and high-field susceptibility[4] also show anomalous behavior. Although the correlation between the Invar effect and these magnetic anomalies has been considered, a clear understanding of the "Invar problem" is still beyond reach. A martensitic phase transition from fcc to bcc occurs at lower Pt concentrations.[5] This transformation not only occurs in Fe_3Pt but in other Invar alloys, such as FeNi, as well. Detailed crystallographic studies on this transition have been made,[6] but it is still not clear whether or not the martensitic transformation is correlated with the Invar effect.

Measurements of the elastic constants in Invar alloys would provide rather important information on this problem because in this manner any magnetoelastic interaction might be directly observed. Utilizing an ultrasonic technique, Hausch[7] recently reported that the elastic constants of disordered Fe_3Pt show anomalous behavior, exhibiting a continuous decrease in the shear constants $(C_{11}-C_{12})/2$ and C_{44} with decreasing temperature below the Curie temperature T_C. In particular, $(C_{11}-C_{12})/2$ exhibits a large anomalous effect tending to a very small value at low temperatures. Hausch found that the anomalous part of the elastic constant is proportional to the square of the magnetization. He suggested that the anomalous behavior could be attributed to a magnetoelastic coupling which modifies the bare elastic interaction force constants.

One might expect these elastic anomalies to be reflected in the phonon dispersion observed by inelastic neutron scattering. However, such experiments on FeNi Invar alloy show no apparent anomalies in the phonon dispersion,[8,9] although anomalies in the elastic constants were observed in ultrasonic measurements.[10,11] The discrepancy in the results obtained by these two methods has been interpreted to be due to the difference in the measuring time.[12] For neutron scattering where the sampling frequency ω is larger than the inverse thermal phonon life time τ^{-1}, elastic waves propagate in the collision-free regime (zero sound). In ultrasonic measurements, however, $\omega \ll \tau^{-1}$ and the sound wave propagation is in thermal equilibrium states (first sound).

Among Invar alloys ordered Fe_3Pt is the most promising material for such investigations on this anomalous behavior of elastic properties since the effect is expected to be larger than in FeNi Invar and there is no problem with metallic inhomogeneity as is found in the latter.[13] We report here measurements on the temperature dependence of acoustic phonons in ordered Fe_3Pt by inelastic neutron scattering.

Ordered Fe_3Pt has a structure of the Cu_3Au type[5] and is ferromagnetic below about 500 K.[13] A 2-cm^3 single crystal was grown at Tohoku University by the Bridgman method and annealed at 600°C for one week. Chemical analysis gave the exact composition as $Fe_{72.2}Pt_{27.8}$. The lattice constant of the sample is 3.738 Å at room temperature.

Experiments were carried out on both the IN2 and IN3 triple-axis spectrometers at the high-flux reactor of the Institut Laue-Langevin, Grenoble. Copper (111) and zinc (002) crystals were used for the monochromator and analyzer, respectively, in high-temperature measurements at the IN3 spectrometer, while Pyrolytic graphite (002) crystals were used as analyzer and

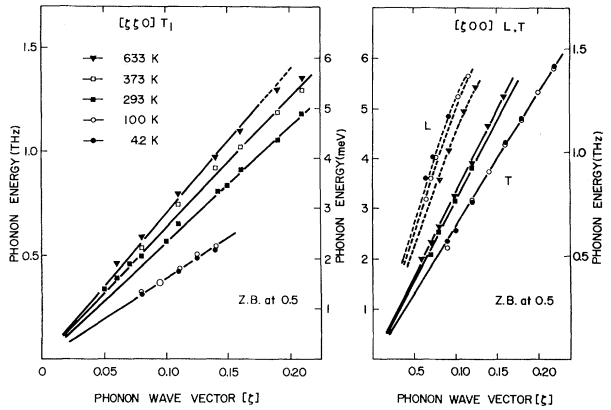

FIG. 1. Temperature variation of [110]TA_1, [100]TA, [100]LA phonon modes.

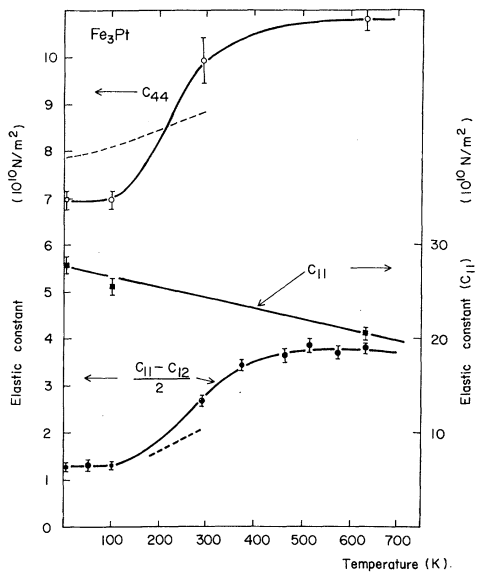

FIG. 2. Temperature dependence of the elastic constants $(C_{11}-C_{12})/2$, C_{44}, and C_{11} calculated from the results of Fig. 1. Dotted lines represent the results for the ordered Fe_3Pt obtained by the ultrasonic technique.

monochromator in low-temperature measurements on the IN2 spectrometer. We concentrated on measurements of the [110]TA_1, [100]TA, and [100]LA phonon branches in the (100) plane; the temperature range studied was from 4.2 to 633 K with a maximum wave vector of $\zeta \sim 0.22$ (where ζ is the reduced wave vector and at the zone boundary $\zeta = 0.5$). Gaussian least-squares fitting was carried out for all the phonon spectra, allowing for the variation in analyzer resolution.[14] No resolution correction has been made, but the error due to this correction is within the error bar shown in Fig. 1. The temperature variations of [110]TA_1, [100]TA, and [100]LA phonon dispersions are shown in Fig. 1. We observed a continuous softening of the phonon frequencies on lowering the temperature from 633 to 100 K for both the TA_1 and TA modes. The softening of the TA_1 mode is especially large. Below 100 K, however, the softening effects are almost negligible. For the LA mode no such anomalous effect was observed. The softening of the TA_1 and TA mode occurs over the entire wave vector region which we studied so that the linear relationship between frequency and wave vector always holds down to the lowest temperature. Softening of the acoustic phonon has previously been observed slightly above the martensitic phase transformation temperature; e.g., in Nb_3Sn.[15] However the softening occurs only over a small wave vector region and then the phonon dispersion curve bends at a certain wave vector. This is not so in the present case.

The elastic constants C_{11}, C_{44}, and $(C_{11}-C_{12})/2$ were determined from phonon velocities of [100]-LA, [100]TA, and [110]TA_1 modes, respectively, using a calculated molecular weight $M = 94.56$ and the lattice parameter observed in this experiment. These are shown as a function of temperature in Fig. 2. Both shear elastic constants continuously decrease below T_c of 500 K, tending to small values at low temperatures, which is very similar to the previous ultrasonic results for disordered Fe_3Pt.[7] On the contrary, the longitudinal one increases with decreasing temperatures as is normal. In this figure we also plot the elastic constants for ordered Fe_3Pt determined recently by Hausch, using an ultrasonic technique.[16] Although the measurements were limited to a small temperature range, reasonable agreement is obtained between the neutron scattering and ultrasonic measurements for $(C_{11}-C_{12})/2$ at low temperatures. However, for C_{44} the neutron scattering measurement gives a smaller value than the latter method at 4 K. Except for this detail, the overall qualitative agreement between the two different measurements contrasts strongly with the results obtained on the FeNi Invar.

An unexpected "central peak" around $\hbar\omega = 0$ was observed at low temperatures, in addition to the soft phonon side peaks. One of the typical data is shown in Fig. 3, which was taken at $\zeta = (0.11, -0.11, 0)$ from the (220) reciprocal lattice point. The intensity of the central peak develops gradually upon reducing the temperature from 100 to

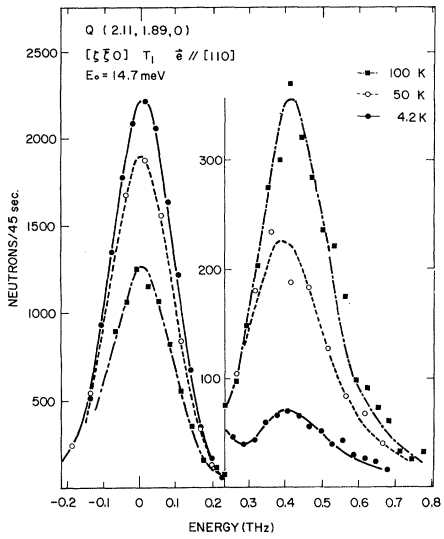

FIG. 3. Temperature dependence of the scattered neutron spectra observed at (2.11, 1.89, 0). $\vec{e}$ is the polarization vector of the phonons.

4 K, but no intrinsic energy width exceeding that of the instrumental resolution, 0.21 THz, was detected throughout the present experiment.

The three-peaked cross sections, accompanied by softening of the phonons, have been observed in many other systems such as Nb_3Sn [15] and $SrTiO_3$,[17] in the vicinity of the structural phase transition temperature. They have been interpreted in terms of the dynamical coupling between the soft mode phonons and other fluctuations. In the present case, however, the intensity of the central component tends to saturate towards 4 K and no phase transition was observed down to this temperature. Furthermore the intensity of phonon side peaks at any temperature was well explained by the one-phonon cross section formula. No notable temperature dependence could be observed in both phonon energy and their line shape at low temperatures. The phenomenological theory[18,19] tells us that a three-peaked frequency spectrum observed in the present experiment is only adapted to the slow relaxation case; the relaxation rate of the fluctuating motion is extremely slow compared with the bare phonon frequency. This assumption seriously conflicts with the fact that the sound velocities measured by neutron scattering and ultrasonic method agree. Obviously the fractional integrated intensity of the central component to the total intensity cannot be analyzed with the simple expression used by Axe and Shirane[18] for many coupled systems. Therefore we expect that the central peak is static in origin as would occur from a local crystal deformation. In this connection, we note that the ordered Fe_3Pt undergoes the reversible martensitic transformation at low temperatures.[20] The magnetic anisotropy measurements have also predicted[21] such reversible crystalline transformation by few percents in volume at about 60 K for stoichiometric, ordered Fe_3Pt. The central peak might be related to this reversible transformation. A detailed structural analysis is now in progress.

The softening of the acoustic shear modes was observed to extend over a wide wave vector range, and sound velocities determined by two methods show a similar anomaly below T_C. Therefore the fast relaxation mechanism is concluded to be responsible for this softening. The softening cannot be explained by the Bain's model[22] which has been successful to explain the martensitic transformation in Invar alloys and which does not predict an anomaly in the shear modes of $[100]TA$ and $[110]TA_1$. The origin could be the magnetoelastic coupling as suggested by Hausch, because the anomaly begins to occur around T_C, and is nearly proportional to the square of the relative magnetization, as mentioned above. Introducing both the spontaneous magnetization M and the volume strain ω, the free energy may be expressed as

$$F = \tfrac{1}{2}AM^2 + (2\kappa)^{-1}\omega^2, \tag{1}$$

where A and κ are the exchange stiffness constant and the compressibility, respectively. The volume magnetostriction ω_m is obtained by minimizing F;

$$\omega_m = -2\kappa \frac{\partial A}{\partial \omega} M^2 = -\frac{2}{B}\frac{\partial A}{\partial \omega} M^2, \tag{2}$$

where B is the bulk modulus. Since the bulk modulus, $B = \frac{1}{3}(C_{11} + 2C_{12})$, increases below T_C in the usual manner, the origin of the Invar effect does not lie in the anomaly of the mean lattice energy. In general the magnetostriction apparently modifies the elastic modulus. This effect is very small for this particular substance because the change of the bulk modulus expected by this effect is opposite to what is observed. The effect is much smaller for the shear modulus, because the shear magnetostriction is smaller than the volume magnetostriction.[23]

The elastic anomaly, therefore, couples with the second derivative of A, $\partial^2 A/\partial\epsilon_{ij}\partial\epsilon_{jk}$, via the magnetoelastic interaction. The softening of the shear modes is thus a direct consequence of the change of the magnetic energy by shear deforma-

tion, possibly through the deformation of the d electron energy band. The two conflicting results obtained on FeNi and Fe_3Pt Invar alloys by neutron scattering experiments could be caused by a difference in the relaxation mechanism for electron-phonon coupled systems. We hope that our results will encourage further theoretical studies on the magnetoelastic coupling in the Invar-type alloys.

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Tunneling as a Probe of Nonequilibrium Superconducting States*

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The $I(V)$ characteristic of a superconductor-insulator-superconductor tunneling junction in which both of the superconductors are driven out of equilibrium is investigated. We show that the steady-state quasiparticle distribution function is related to the $I(V)$ characteristic by a linear integral equation. Modifications of the $I(V)$ characteristic due to nonequilibrium distributions produced by phonon and microwave irradiations are discussed.

A thin superconducting film can be driven out of equilibrium by exposing it to light,[1,2] microwaves,[3] phonons,[4] or injected quasiparticles.[5] Present theoretical descriptions view the nonequilibrium state as characterized by the distribution of quasiparticles and phonons in a superconductor with a gap which is self-consistently calculated using the modified distributions.[6] Within this framework a variety of different theoretical models have been suggested: Eliashberg[7]