Anomalous Phase Fluctuations Accompanying
the Crystallographic Phase Transition in UNi$_2$Sn

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The phase transition in the Heusler compound UNi$_2$Sn has been investigated by means of neutron powder diffraction and ^{119}Sn Mössbauer spectroscopy. It is shown that the low-temperature orthorhombic structure is gradually transformed into the high-temperature cubic structure between 200 and 330 K. Although the Mössbauer spectra for these two phases are virtually identical, an extraordinary line broadening is observed in the transition region. The broadening is explained in terms of the thermal excitation of domain walls, moving on the Mössbauer time scale. The atoms must hop continuously between cubic and orthorhombic positions. [S0031-9007(96)01427-5]

Recently the low-temperature structure of UNi$_2$Sn has been determined [1]: at 80 K UNi$_2$Sn is orthorhombic, space group *Pnma*, while above room temperature it is cubic, space group *Fm$\bar{3}$m*. Here we describe an extraordinary behavior at the transition in this structurally well-defined compound, which was investigated by means of neutron diffraction and ^{119}Sn Mössbauer spectroscopy. In powder diffraction experiments with thermal neutrons the pair correlations within small ($\sim$100 nm) crystallites are observed with a typical interaction time $\sim$10^{-11} s. Mössbauer spectroscopy provides a valuable extension in determining structural order, because it gives a local probe and because the interaction time is several orders longer ($\sim$10^{-8} s). It will be shown that the combination of these two techniques allows for a clear—but surprising—"mesoscopic" description of the structural transition.

The neutron powder diffraction measurements have been carried out at the high flux reactor with a wavelength $\lambda = 2.5717$ Å. High-accuracy diffractograms of 45 h each were recorded between $2\vartheta = 5$ deg and 155 deg. The structure refinements were performed using a multiphase Rietveld program. The hysteretic transformation between cubic and orthorhombic structure was followed between 80 and 410 K with decreasing and increasing temperature. After the measurement cycle in the cryostat the hysteresis was not yet completed at room temperature, so we went up to 410 K in a furnace. The variation of the cubic weight fraction, resulting from the refinement, is displayed in Fig. 1(a) and shows that the hysteresis loop extends from about 200 to 330 K. The cell parameters a_{cub} and b_{ort} increase smoothly with increasing temperature, while a_{ort} and c_{ort} are almost temperature independent [1]. This gives a ratio of the unit cell volumes V_{ort}/V_{cub} between 1.01 and 1.02 at all temperatures. The free (x, z) parameters of the atomic positions in the orthorhombic structure are different from the cubic ones at every temperature [Figs. 1(b) and 1(c)],

i.e., the atoms do not move gradually but hop between their orthorhombic and cubic positions during the transition. No irregularity in the half-width parameters nor in the isotropic temperature factor was observed, so the structures remain well defined throughout the transition.

In the ^{119}Sn Mössbauer measurements we used 30 mg/cm^2 of the powder from the neutron experiments,
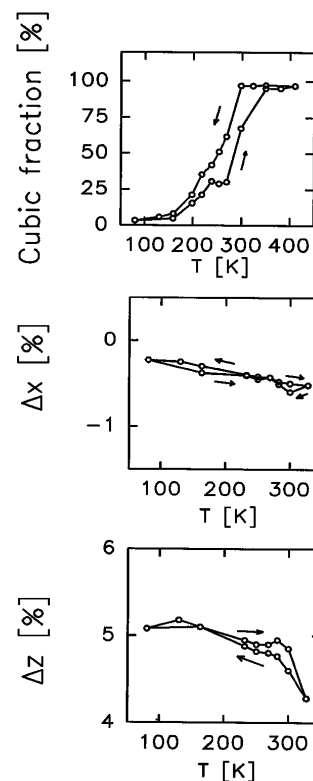

FIG. 1. (a) The cubic weight fraction as a function of temperature. (b),(c) Temperature dependence of the relative change of the x and z coordinates of the lattice positions of Sn in the cubic and orthorhombic structure [1]: $a_{ort} = 9.62$ Å, $c_{ort} = 6.59$ Å.

and a $BaSnO_3$ source at room temperature. The velocity calibration was done by Michelson interferometry, recording in all channels. In analyzing the spectra, the transmission integral method was used, with the source linewidth calibrated using a tin metal foil. Mössbauer spectra recorded at different temperatures are presented in Fig. 2. Except for a minor change in peak position there is no difference between the Mössbauer spectrum at room temperature and at 77 K (the larger absorption at 77 K reflects the larger Debye-Waller factor). This shows that in this compound the ^{119}Sn spectrum is not influenced by the change in symmetry of the surroundings; the spectra give no reason to assume a quadrupole splitting. It is surprising therefore to note that between 230 and 290 K the linewidth Γ *increases drastically* and also the recoilless fraction decreases slightly [Figs. 3(b) and 3(c)]. The isomer shift values vary only slightly with temperature [Fig. 3(a) and are all in a region expected for Sn^{2+}.

Combining our results, we find that during the first-order transition in UNi_2Si, the low-temperature orthorhombic and high-temperature cubic structure coexist. In general, the sample grains will consist of orthorhombic and cubic domains, which will be separated by domain walls. The number of atoms in the domain walls will mainly be determined by the large local stresses. The neutron diffractograms show at any temperature sharp Bragg peaks and a low background. This means that the pair-correlation functions probed by the neutrons take basically constant and well-defined values [2]. Also the minimum domain length has to be of order 0.1 μm. Therefore practically all atoms are in one of the two well-defined crystallographic phases. The number of atoms present in the domain walls has to be a small fraction of the total number of atoms. However, the Mössbauer measurements show a completely different picture: around $T = 260$ K all tin atoms participate in the phase transition, since the whole spectrum is broadened. In this Letter we show that this seeming contradiction is resolved when the different time scales of the two measurement techniques are taken into account. The Mössbauer time scale is determined by the average lifetime $\tau = 2.7 \times 10^{-8}$ s of the excited state of the ^{119}Sn nucleus, corresponding to an observed, natural Mössbauer linewidth of 0.62 mm/s. In the neutron diffraction experiment the average interaction time is at least of the order $\sim 10^{-11}$ s, depending on the
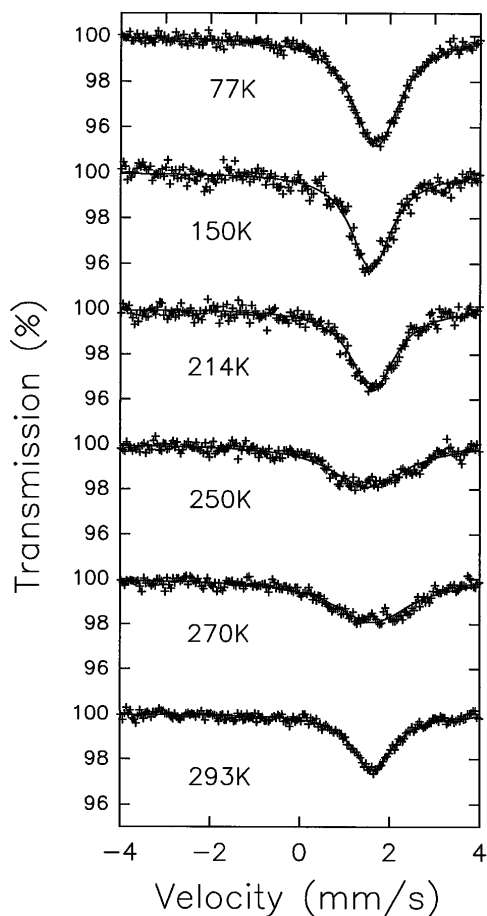
FIG. 2. Mössbauer spectra in chronological order from the top at the indicated temperatures. Before the series of measurements started, the sample was heated to 450 K. The fits are performed using Eq. (3) with ν as an adjustable parameter.
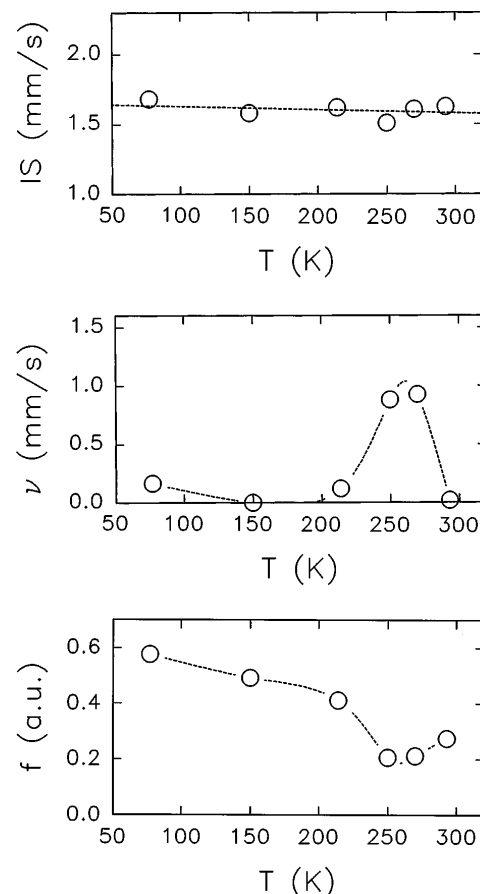
FIG. 3. Plotted as a function of temperature: (a) the isomer shift values, (b) ν, and (c) the Debye-Waller factor f.

domain size distribution. When the domain walls move through the sample, they sooner or later will pass all tin atoms, despite the fact that the number of atoms *in* a domain wall is negligibly small at any moment. If this movement takes place on the Mössbauer time scale, the Mössbauer line will be broadened, whereas well-defined structures within the domains are probed by neutrons. An exact description of the Mössbauer line broadening will be given below, but now we will first give a global outline.

An increase of the Mössbauer linewidth due to diffusive motion of atoms has been reported on many occasions in biological systems (see, e.g., [3]), and also in crystals (see, e.g., [4]). The phase fluctuations which result in the line broadening as described here have not been reported before, however, which gives an altogether new perspective for this type of transitions in well characterized bulk crystals.

The line shape and intensities in the Mössbauer spectrum basically follow from the Fourier transform of the autocorrelation function $G_s(\mathbf{r}, t)$ and from the evolution of the excited nuclear level (see, e.g., [5]). $G_s(\mathbf{r}, t)$ gives the chance to find the nucleus at time t at position $\mathbf{r}$ when it was at the origin at $t = 0$. Here we can consider three cases: the spatial position of the nucleus changes on time scales (a) much faster than $\hbar/\Gamma$, (b) comparable to $\hbar/\Gamma$, and (c) much slower than $\hbar/\Gamma$ (Γ is the natural line width in μeV). Case (a) can be found for the normal vibrational motions of atoms in a lattice under influence of high frequency phonons ($\omega_{\text{phonon}} \approx 10^{12}$ Hz). In the Fourier transform (the spectrum) this leads to additional phonon δ peaks (not observable since the splittings are $10^4 \times$ typical hyperfine splittings). The main result of this contribution is to decrease the total intensity of the observable line(s) down to the Debye-Waller factor (f). Case (b) is most interesting, since here the amplitude as well as the width of the spectrum is modulated, while the total cross section remains constant. Case (c) is the situation as applied in a standard Mössbauer setup: the source moves with low frequency and large amplitude relative to the absorber. This results in a line with natural linewidth, of intensity determined by f, and—when treated relativistically correct—a Doppler shifted position.

In UNi$_2$Sn, the line broadening is *not* caused by the fact that the Mössbauer spectra are different for the two crystallographic phases, which is the usual concept of a line broadening accompanying a phase transition. (For example, in low-dimensional magnetic systems soliton excitations have been reported, corresponding to magnetic domain walls moving on the Mössbauer time scale [6]). The broadening is caused by the sheer fact that the atoms move between different crystallographic positions at a rate which modulates the autocorrelation function G_s.

In order to describe the Mössbauer line shape $\sigma_a(E)$, we need to evaluate

$$\sigma_a(E) = \frac{\sigma_0 \Gamma}{4\hbar} \int \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)$$
$$- (\Gamma/2\hbar)|t|]G_s(\mathbf{r}, t) \, d\mathbf{r} \, dt$$
$$= \frac{\sigma_0 \Gamma}{4\hbar} \int \exp[-i\omega t$$
$$- (\Gamma/2\hbar)|t|]I(\mathbf{k}, t) \, dt, \qquad (1)$$

where σ_0 is the nuclear cross section, $\mathbf{k}$ the gamma ray wave vector, Γ the natural linewidth, and E the energy of the photon. The Fourier transform of $G_s(\mathbf{r}, t)$, $I_s(\mathbf{k}, t)$ is the so-called intermediate scattering function [7]. $I_s(\mathbf{k}, t)$ can be determined directly in the following way: $I_s(\mathbf{k}, t) = \mathbf{I}(\mathbf{k}, t) \cdot \mathbf{I}(\mathbf{k}, 0)$, where $\mathbf{I}(\mathbf{k}, t)$ follows from $\frac{\partial}{\partial t}\mathbf{I}(\mathbf{k}, t) = \mathbf{A} \cdot \mathbf{I}(\mathbf{k}, t)$. $\mathbf{A}$ is the jump matrix characteristic for the movement of the Sn atoms in the system. In our system the cubic symmetry can be transformed into the orthorhombic one in 12 different ways. In total there are 13 positions that a specific Sn atom can occupy, and the transition probability from one position to another is determined by the domain wall movements. Therefore $\mathbf{A}$ has the form

$$\mathbf{A}_{i,j=1,\ldots,13} = \frac{\nu}{12}\exp[i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)](1 - \delta_{i,j}) - \nu\delta_{i,j}.$$
$$(2)$$

The vectors $\mathbf{r}_i - \mathbf{r}_j$ give the jump of a Sn atom between positions $\mathbf{r}_i$ and $\mathbf{r}_j$; they follow from the differences given in Figs. 1(b) and 1(c). ν equals the frequency with which domain walls pass.

The solution for $\sigma_a(E)$ reads

$$\sigma_a(E) = \int \frac{d\hat{k}}{4\pi}\frac{1}{14\pi}\sum_{n=1}^{12}\frac{|v_n(\hat{k})|^2[\Gamma + \Gamma_n(\hat{k})]}{(E - E_0)^2 + \frac{1}{4}[\Gamma + \Gamma_n(\hat{k})]^2}.$$
$$(3)$$

The line shape is given by a sum of Lorentzians with total "effective linewidths" $\Gamma + \Gamma_n(\hat{k})$, where $\Gamma_n(\hat{k})$ are the eigenvalues of $\mathbf{A}(\hat{k})$, and $v_n(\hat{k})$ the eigenvectors. [Express $\Gamma_n(\hat{k})$ in mm/s by multiplication with $hc/2E_\gamma$. c is the velocity of light, and E_γ the Mössbauer gamma energy of 23.9 keV.] We have to integrate over the directions $\hat{k}$ of the gamma rays since we work with powdered samples.

The hopping frequency can be estimated from fitting with the line shape (3). In the middle of the transition, at $T = 260$ K, the fitted value of $\nu \times hc/2E_\gamma$ amounts to 0.9 mm/s, which makes the total apparent linewidth about $2\frac{1}{2}$ times the natural linewidth. At this temperature, the time between the passing of two domain walls clearly has become closest to the typical Mössbauer time τ. For other temperatures, one of the two phases prevails and the number of domain wall passages decreases. Thus the time between two passages becomes larger than the Mössbauer time scale and the line broadening disappears. The hop itself takes place in a very short time compared to the Mössbauer time scale. Otherwise the domain

walls would be so large that the incoherent scattering in the neutron experiment would visibly increase. We estimate a maximum fluctuation rate in the order of 10^9 Hz. This time lies indeed within the Mössbauer time window for ^{119}Sn.

The measurable decrease of the Mössbauer Debye-Waller factor near the transition temperature indicates a softening of the relevant phonon modes. A softening of phonon modes near a phase transition has been observed before (see, e.g., [8]), and may be explained by the notion that the microscopic domain structure may modulate the density of the (mainly long wavelength) phonons if they are incommensurate with the microscopic domains.

There is an apparent discrepancy between the neutron diffraction results presented here and earlier experiments. Endstra *et al.* [9] measured resistivity and magnetization on a different sample and observed a much smaller transition region, extending from 210 to 250 K. Therefore dc magnetic susceptibility measurements were performed on 100 mg of our powder and hysteresis was found between 220 and 300 K, in fair agreement with the diffraction data. This means that the disparities are stoichiometry dependent, and not due to the different measurement techniques. By electron-probe microanalysis the composition of our sample was determined as $U_{1.00}Ni_{1.93}Sn_{0.98}$, whereas the composition of the sample in Ref. [9] was $U_{1.00}Ni_{2.03}Sn_{1.01}$. A third sample, $U_{1.00}Ni_{1.89}Sn_{1.01}$, did not show a transition below room temperature and is cubic. Obviously the transition region strongly depends on stoichiometry and this might explain the absence of a transition in Takabatake's sample [10], which also remains cubic. In view of the proposed importance of moving domain walls in the compounds, it may be that these walls are easily pinned when the stoichiometry is slightly different. This apparently makes the structural transition impossible.

In conclusion, we have observed a phase transition in the Heusler compound UNi_2Sn with neutron diffraction and Mössbauer spectroscopy. The different time scales of these experiments make it possible to observe that during this transition thermally excited domain walls move through the sample. The structural transition can be visualized as a gradual change of the size and average lifetime of the domains as a function of temperature, which gives an altogether new perspective for this type of transition.

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