Study of an Order-Disorder Phase Transition on an Atomic Scale: The Example of Decagonal Al-Ni-Co Quasicrystals

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In the present paper we succeeded in studying structural phase transitions from an atomistic point of view by positron annihilation Doppler broadening. This differs and is complementary to conventionally used diffraction experiments with large coherence lengths. In the exemplary case of the 1140 K order-disorder transition in decagonal $Al_{71.5}Ni_{14}Co_{14.5}$ quasicrystals the importance of this atomistic approach and its wide scope of application is demonstrated.

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Structural phase transitions in condensed matter can be studied by scattering experiments or by macroscopic techniques such as dilatometry, electrical resistivity, magnetization, etc. The characterization of phase transitions becomes more challenging in structurally complex systems as, e.g., aperiodic quasicrystals. In this situation, local probes such as, e.g., positrons may yield specific information on an atomic scale by the characteristic radiation emitted when a positron is annihilated with the electrons of a condensed system. In the present study, positron annihilation spectroscopy is performed on decagonal Al-Ni-Co quasicrystals over a wide temperature range and directly correlated to structural order-disorder transitions detected by x-ray diffraction and neutron scattering [1–4].

Decagonal Al-Ni-Co quasicrystals exhibit a wealth of structural modifications in dependence of composition, temperature, and time-temperature history as compiled in the phase diagram of Ritsch *et al.* [5] and modeled by Hiraga *et al.* [6] in dependence of composition. Chemical ordering between Al and transition metal (TM) atoms, which is detected by electron microscopy [6,7] as well as x-ray diffraction [8,9] and which is favored theoretically [7,10], may play a pivotal role for understanding why quasicrystals with their aperiodic structure form. The ordered quasi-unit-cell decagons exhibit a central cluster rich in transition metals which eventually may give rise to a symmetry breaking of the decagon structure [7,10,11]. This may be a prerequisite for perfect quasiperiodic tiling [7,12] since it yields the same overlap rules as in the Gummelt coverage model [13]. In this sense specific investigation of chemical order-disorder processes in Al-Ni-Co quasicrystals, as reported earlier [1], is of particular interest. For a better understanding of this transformation, atomic-scale structural information is desirable.

Structural information on atomic processes as, e.g., formation and migration of thermal vacancies, on dislocations or on structural transformations may be obtained by positron lifetime measurements for probing the electron densities at the annihilation site. In the case of a multinary system, an even more powerful tool is available when positron lifetime spectroscopy is combined with a coincident Doppler broadening measurement of the electron-positron annihilation photons. The latter technique is sensitive to the chemical environment of the annihilation site by probing the core electron momentum densities [14]. In the present paper we focus on high-temperature studies of structural transformations in decagonal $Al_{71.5}Ni_{14}Co_{14.5}$ quasicrystals by means of positron lifetime and coincident Doppler broadening measurements.

A cylinder of the decagonal $Al_{71.5}Ni_{14}Co_{14.5}$ quasicrystal with a length of 7 mm, an outer diameter of 3.5 mm, and a 1.5 mm diameter axial borehole was prepared by ultrasonic techniques. A 3.7×10^5 Bq positron source of $^{44}TiSO_4$ was deposited in the borehole, oxidized, and covered by a Al-Ni-Co cap with subsequent evacuation and sealing in a quartz tube.

The positron annihilation lifetime spectra ($> 2 \times 10^6$ coincidence counts) with a time resolution of 280 ps full width at half maximum (FWHM) were analyzed numerically [15].

The coincident measurements of the Doppler broadening were performed by measuring the energies of the two annihilation quanta E_1 and E_2 with a collinear setup of two high-purity Ge detectors with 1.2 keV (FWHM) energy resolutions. The Doppler spectra (see Fig. 3, $>3 \times 10^7$ coincidence counts) were obtained by cutting the E_1, E_2 spectra along the energy conservation line $E_1 + E_2 = (1022 \pm 1)$ keV taking into account the annihilation events within a strip of ± 1 keV. For measuring the reference spectra of the pure components Al, Ni, and Co at ambient temperature, a $^{22}NaCl$ positron emitter was stacked between two disks of the specimen material. In order to examine the core electron contributions of the positron-electron annihilation radiation, the W parameter was defined by the ratio of the wing area $\pm(18–25) \times 10^{-3} m_0 c$ and the total area of the Doppler broadening spectrum (m_0 is the electron mass, c the velocity of light).

Positron lifetime spectroscopy yields one dominant component with the lifetime τ_1 which is characteristic for the $Al_{71.5}Ni_{14}Co_{14.5}$ quasicrystal as reported earlier [16] and an additional weak $\tau_2 \approx 600$ ps source component in the whole temperature range. The positron lifetime $\tau_1 = 198$ ps at ambient temperature, which is substantially higher than the positron lifetime in the defect-free case as expected from the mean valence electron density [17], demonstrates that structural vacancies with an atomic concentration $>10^{-4}$ are available.

The temperature variation of the positron lifetime τ_1 is shown in Fig. 1. Two narrow reversible changes in dependence of temperature are observed centered at 650 and 1140 K. The temperature dependence of the Doppler broadening W parameter is shown in Fig. 2.

We first consider the prominent change of the W parameters at 1140 K (see Fig. 2). In this temperature range structural changes were observed for d-AlNiCo quasicrystals with compositions similar to the present one by dilatometry [18], by x-ray diffraction [2], and by neutron scattering [3]. From the width FWHM of the diffuse neutron scattering peak in decagonal $Al_{72}Ni_{12}Co_{16}$ [3], ordered domains of the width $d = 2\pi/\mathrm{FWHM} = 3.7$ nm within the decagonal planes and a length exceeding 1 μm along the periodicity axis can be derived at ambient temperature [4,19]. In the 1140 K stage chemical disordering is observed by a shrinkage of the domains and the disappearance of scattering peaks. In the simple model comprising both the atomic-scale positron data as well as the temperature-dependent domain size from neutron scattering [3,4], we denote the Doppler broadening parameters characteristic for the vacancies in the ordered domain by W_0 and that for the vacancies in the disordered structure by W_d. The mean volume-averaged Doppler broadening parameter is then given by

$$W = f_0 W_0 + f_d W_d \tag{1}$$

taking into account the volume fractions

$$f_0 = \frac{d^2}{d_{\max}^2} \tag{2}$$

of the ordered domains and $f_d = 1 - f_0$ of the disordered structure. For the fully ordered state the relations $d = d_{\max}$ and $f_0 = 1$ hold.

A fit of this model [Eqs. (1) and (2)] to the 1140 K stage of the W parameter (Fig. 2) with the temperature-dependent domain size $d(T)$ from neutron scattering data [3,4] demonstrates that the 1140 K stage of W in Fig. 2 coincides with disordering. This fit yields $W_0 = 2.5 \times 10^{-3}$ below the 1140 K stage, which is intermediate between the values of pure Ni (4.9×10^{-3}) and of pure Co (1.7×10^{-3}). In the above comparison with pure metals we neglect that the W parameter in vacancies is by about 15% lower than in the defect-free pure metal [20], because this difference is much smaller than that of the W parameters between the transition metals and of Al taken from the data in Fig. 3.

Based on the present data novel specific information on phase transitions in complex systems can be deduced by a comparison to the structural information recently derived

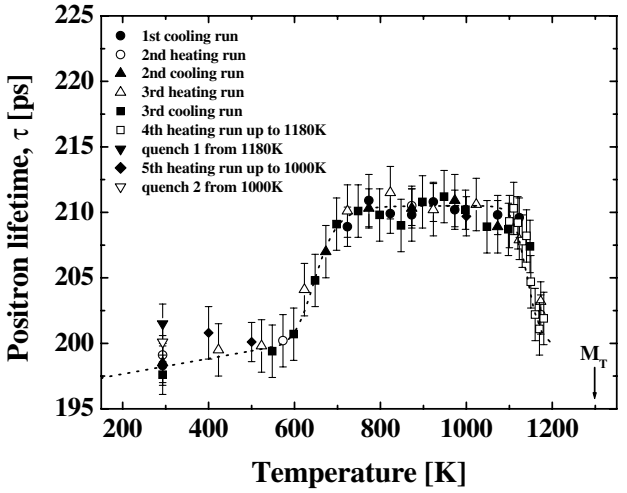

FIG. 1. Reversible temperature variation of the positron lifetime τ_1 in the decagonal $Al_{71.5}Ni_{14}Co_{14.5}$ quasicrystal with data from various measuring runs. Positron lifetimes measured at ambient temperature after quenching from 1180 or 1000 K are given additionally together with isochronal annealing data (full diamonds). The dotted line is drawn for guiding the eye.

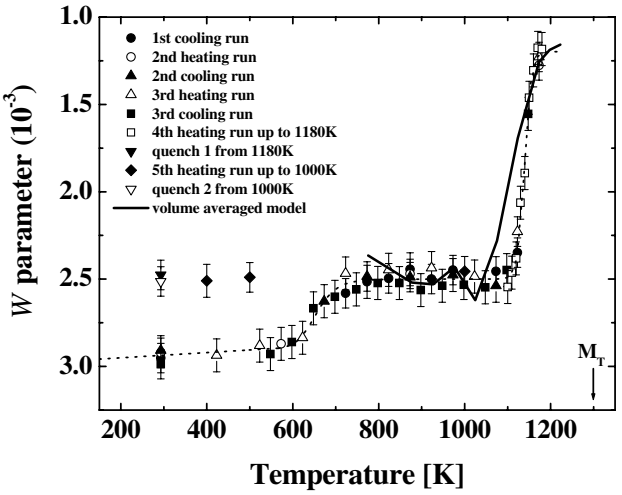

FIG. 2. Reversible temperature variation of the W parameter in the decagonal $Al_{71.5}Ni_{14}Co_{14.5}$ quasicrystal with data from various measuring runs. W parameters measured at ambient temperature after quenching from 1180 and 1000 K are given additionally together with isochronal annealing data (full diamonds). The bold line indicates a fit of the volume averaged positron annihilation in the ordered domains and in the disordered structure (see text) taking the temperature dependent domain size from neutron scattering [3] into account. The dotted line is drawn for guiding the eye.

for decagonal Al-Ni-Co quasicrystals from Z-contrast electron microscopy [6,7] and x-ray diffraction [9]. These studies yield in the 2.0 nm decagon a central cluster with a transition metal concentration exceeding that of the mean value of the quasicrystal. This may be the very environment selected by the present positron annihilation W parameter between the 650 K stage and the 1140 K stage. At high temperatures, upon disordering, the atomic composition of the central cluster appears to be enriched in Al [21] as expected according to the mean composition of the $Al_{71.5}Ni_{14}Co_{14.5}$ quasicrystal. This is specifically detected by the positron annihilation Doppler parameter W (Fig. 3) characteristic for pure Al.

We want to point out here that the change of the W parameter in the 1140 K stage due to chemical changes around the vacancies is accompanied by a decrease of the positron lifetime (Fig. 1). This may originate from the Al rich high-temperature vacancy environment contributing a high number of valence electrons, thus increasing the mean valence electron density.

At 650 K an additional reversible transition unknown from the literature is observed by the positron lifetime (Fig. 1) and the W parameter (see Fig. 2) signifying a change from a Ni rich vacancy surrounding (see Fig. 3) to more Co or some small addition of Al. Thermal vacancy formation can be excluded for an explanation of this stage or of the 1140 K stage as discussed briefly in the following.

For an interpretation by thermal vacancy formation the two stages are by far too narrow. This can be demonstrated by a model of positron trapping of thermal vacancies formed with the atomic concentration $C_2(T)$ at high temperatures in addition to structural vacancies with the constant concentration C_1. This model yields the temperature variation

$$W(T) = \frac{W_1 + \frac{\sigma_2}{\sigma_1 C_1} W_2 C_2}{1 + \frac{\sigma_2}{\sigma_1 C_1} C_2} \tag{3}$$

of the W parameter with

$$C_2 = \exp(S_V^F/k_B)\exp(-H_V^F/k_B T), \tag{4}$$

where W_1 is the specific parameter for structural vacancies, W_2 that of thermal vacancies, σ_1 and σ_2 the corresponding specific positron trapping rates, H_V^F the vacancy formation enthalpy, and S_V^F the vacancy formation entropy.

This model yields for the 650 K stage the apparent parameters $H_V^F = 1.56$ eV and $(\sigma_2/\sigma_1 C_1)\exp(S_V^F/k_B) = 10^{12}$. With the values $\sigma_2/\sigma_1 \approx 1$ and $C_1 \approx 10^{-3}$ as derived from positron diffusion experiments in quasicrystals [22] a value is obtained for $S_V^F/k_B = 21$ which is far beyond the values $S_V^F/k_B = 2$ to 5 usually obtained for intermetallic compounds [23] and therefore excludes this type of process for the 650 K stage. For interpreting the 1140 K stage thermal vacancy formation is even more inappropriate as evidenced by the apparent parameters $H_V^F = 11$–15 eV and $(\sigma_2/\sigma_1 C_1)\exp(S_V^F/k_B) = 10^{50}$–$10^{65}$ leading to a value $S_V^F/k_B = 110$–150 unreasonably high for this type of process.

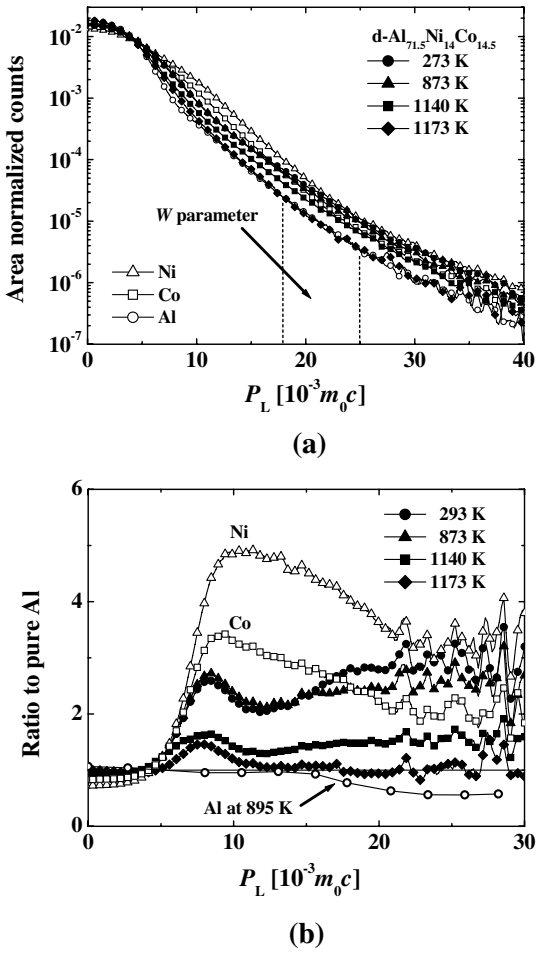

FIG. 3. (a) Coincident Doppler broadening spectra in the momentum range of 0–$40 \times 10^{-3} m_0 c$ of the decagonal $Al_{71.5}Ni_{14}Co_{14.5}$ quasicrystal measured at various temperatures, together with the spectra for pure Al, Ni, and Co. Each spectrum is normalized to the total number of counts. (b) Ratio curves of the coincident Doppler broadening spectra of the decagonal $Al_{71.5}Ni_{14}Co_{14.5}$ quasicrystal measured at various temperatures together with those for pure Al, pure Ni, and pure Co. All spectra are normalized to that of pure Al.

About the quenching behavior of the 650 and 1140 K effects only little information is available. After fast cooling ($\sim$1 K/s) from 1180 K a W parameter (see Fig. 2) similar to that above the 650 K stage is observed at 295 K. By this treatment obviously the 650 K effect but not the 1140 K effect can be quenched in. As demonstrated in Fig. 2 the quenching effect is still visible after heating to 500 K so that annealing is expected in the 650 K stage. In this stage disordering between Ni and Co atoms may occur since the Ni-Co ordering energy is predicted to be much smaller than the Al-TM ordering energy [7] involved in the 1140 K stage. Short-range

atomic transport for disordering is well available as concluded from the Co diffusivity D_{Co} [24,25] which yields within the present measuring time of $t = 10^5$ s a mean diffusion length $L = \sqrt{2D_{Co}t} = 1$–2 nm at 650 K. Atomic mobility in this stage is also evidenced by internal friction studies [26]. In addition, pairs of Al atoms in the Startile section of the basic decagons are predicted to rotate between five equivalent orientations [10,11].

In conclusion we point out that order-disorder phase transformations in complex multinary systems as exemplified in decagonal $Al_{71.5}Ni_{14}Co_{14.5}$ quasicrystals are studied for the first time by positron annihilation techniques yielding element-specific information on an atomic scale. This is of importance for the future studies of phase diagrams of complex systems and therefore of wide interest. The prominent stage of the W parameter in decagonal Al-Ni-Co quasicrystals at 1140 K can be quantitatively correlated to an order-disorder transition detected in neutron scattering experiments [3].

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