Atomic Order Along the Half- to Full-Heusler Transition in Ni$_{1+x}$MnSb

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1. Introduction

Ever since Friedrich Heusler’s discovery that a compound of nonferromagnetic metals can itself display ferromagnetism more than a century ago,[1] the Heusler structure has become known as amenable for enabling a variety of functional properties attractive for application.[2,3] While the emergent ferromagnetism of the prototypical Cu$_2$MnAl system is nowadays understood to result from the increased distance between the local-moment Mn atoms compared to their antiferromagnetic coupling in elemental Mn, also from the band-structural point of view it is the hybridization of chemically distinct elements brought about by the ordered structure that gives rise to magneto-optical phenomena,[4] thermoelectric effects,[5] half-metallic[6] or topologically insulating behavior.[7] Indeed, as Heusler materials are susceptible to various kinds of site disorder, there is a growing awareness that for a material to be able to live up to its predicted properties, the realization of the theoretically assumed state of order in experiment is critical.[8,9]

The full-Heusler L$_2^1$ structure of general composition X$_2$YZ, with X typically a late transition metal, Y an early transition metal, and Z a main group element, results by assuming space group Fm$\overline{3}$m and occupying sites (4a) at (0,0,0), (4b) at ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$), and (8c) at ($\frac{1}{4}$,$\frac{1}{4}$,$\frac{1}{4}$) and ($\frac{3}{4}$,$\frac{3}{4}$,$\frac{3}{4}$) by distinct elements, here by Mn, Sb, and Ni (Figure 1). Reducing the symmetry to space group F$\overline{4}$3m breaks the former (8c) sites into the inequivalent sites (4c) at ($\frac{1}{4}$,$\frac{1}{4}$,$\frac{1}{4}$) and (4d) at ($\frac{3}{4}$,$\frac{3}{4}$,$\frac{3}{4}$). Leaving the latter empty corresponds to the so-called half-Heusler C$_{1b}$ structure of composition XYZ. NiMnSb is now the prototypical example for this structure,[10] but in addition, it is also the prototypical ferromagnetic half-metal:[11] while the Fermi level falls into a gap in the minority spin channel, it has a finite density of states in the majority channel, leading to theoretically perfect spin polarization of currents and thus to its potential for spintronics devices.[12] Meanwhile it has become accepted that such a behavior is not uncommon in theoretical investigations of hypothetical half-Heusler compounds.[13]

The idealized structures described above can be seen as end points of a potential continuum of states: the most intuitive way of accommodating an increasing Ni content in the composition series Ni$_{1+x}$MnSb is at the initially empty (4d) site in the C$_{1b}$ NiMnSb structure, leading to L$_2^1$ Ni$_2$MnSb as $x \to 1$. In contrast,
increasing temperature at a given composition will likely disorder the vacancies between (4c) and (4d), again leading to L2₁ symmetry at high temperatures. Indeed, low-temperature neutron diffraction data of the full composition series quenched from 973 K indicate a continuous transition,¹⁴ which is corroborated by the absence of indications for phase separation at this temperature in a recent determination of the ternary phase diagram,¹⁵ and ordering transition temperatures determined by differential scanning calorimetry (DSC) are available for the Ni-lean side.¹⁶ However, despite the relevance of these systems for application, the fundamental question of the relation between half- and full-Heusler states with respect to site disorder, in particular with respect to the ideally vacant sublattice in C₁₅, is still not settled. Due to the stability of full-Heusler NiₓMnSb, it does not seem natural to consider a small Ni excess over the half-Heusler composition accommodated at the ideally vacant sublattice as interstitial atoms, but rather to see the C₁₅ structure as the result of an ordering of constitutional vacancies in case of a Ni deficiency with respect to the full-Heusler composition. As off-stoichiometry, both in general and also in related Heusler systems, is much more frequently accommodated via constitutional antisite defects rather than vacancies, it is a priori quite plausible that these vacancies become unstable in the high-temperature L₂₁ phase, and that the transition thus goes along with a reduction of the number of unit cells via vacancy annihilation and antisite creation. Put in a broader context, the very large number of vacancies becoming redistributed at the C₁₅-L₂₁ transition is an unusual situation in alloy physics, and it is our intention here to shed light on this question.

Specifically, in this article we will present an investigation of the structural and magnetic states of order in the pseudobinary Niₓ₋₀.₅MnSb phase diagram. In terms of macroscopic characterization, we will report DSC measurements to complement existing phase transition temperatures, and we will give low-temperature SQUID magnetization measurements in different annealing states. Our main point will be room-temperature X-ray and high-resolution neutron diffraction data as well as in situ temperature-dependent neutron diffraction measurements, allowing us to determine temperature- and composition-dependent structure factors, ordered moments, lattice parameters, and atomic displacements, thus allowing us to arrive at a reliable and complete picture of the C₁₅-L₂₁ transition in this system, in particular of the dominant role of vacancies in this regard.

### 2. Experimental Section

#### 2.1. Sample Preparation

For these investigations, samples of the nominal compositions Niₓ₋₀.₅MnSb with x ∈ {0.05, 0.25, 0.50, 0.60, 0.75} have been prepared by induction melting of high-purity elements under argon atmosphere. According to the protocol set out by Nagasako et al.,¹⁶ the resulting bulk ingots were then encapsulated in quartz glass tubes, again under a rarefied argon atmosphere, and solution annealed at 1173 K for 3 days to eliminate potential concentration inhomogeneities due to liquid-solid phase separation during solidification. Subsequently, they were quenched in water by breaking the quartz tubes, leading to estimated cooling rates on the order of a few seconds to reach temperatures where structural kinetics are practically frozen. We confirmed the homogeneous nature of the resulting specimens by scanning electron microscopy.

The actual composition of our samples in this state was checked by wavelength-dispersive X-ray spectroscopy (WDS). Values averaged over eight distinct measurement points on a polished sample surface, together with their standard deviation, are given in Table 1. According to these results, we always have a slight excess of Mn compared with Sb. In a previous investigation of the related NiₓMnₓ₋₀.₅Gaₓ system,¹⁷ we found analogous deviations from the nominal compositions which were reproduced by inductively coupled plasma atomic emission spectroscopy, thus we believe the Mn excess to be real. This fact is actually desirable, as according to the ternary phase diagram,¹⁵ it shifts our samples toward the center of the L₂₁/C₁₅ region and thus

**Table 1.** Macroscopic properties of the samples: actual sample compositions according to WDS, transition temperatures, and spontaneous magnetization measured at 6 K. The magnetization of annealed Niₓ₋₀.₅MnSb denoted by an asterisk is affected by a larger uncertainty, as discussed in the text. Missing values have not been measured or, specifically for the calorimetric signal of the C₁₅-L₂₁ transition in Niₓ₋₀.₅MnSb and Niₓ₋₀.₇₅MnSb, were too weak to be determined.

| Nominal comp. | Analyzed comp. [atomic frac.] | Transition temperatures [K] | Magnetic | C₁₅-L₂₁ | Melting | Mₛ [μₜ / f. u.] at 6 K |
|---------------|--------------------------------|-----------------------------|----------|---------|---------|---------------------|
| Niₓ₋₀.₅MnSb   |                                 |                             |          |         |         |                     |
| Niₓ₋₀.₅MnSb   | 1.051(12)                       |                             | 719      | 1130    | 1333    | 4.14               |
| Niₓ₋₀.₅MnSb   | 1.025(14)                       |                             | 582      | 1096    | 1361    | 4.11               |
| Niₓ₋₀.₅MnSb   | 1.053(13)                       |                             | 468      | 940     | 1330    | 4.04               |
| Niₓ₋₀.₅MnSb   | 1.582(11)                       |                             | –        | –       | 1318    | –                   |
| Niₓ₋₀.₅MnSb   | 1.755(26)                       |                             | 436      | –       | 1297    | 3.88               |
| Niₓ₋₀.₅MnSb   |                                 |                             |          |         |         | 4.00               |
suppressed the parasitic formation of B8, NiSb that often appears as secondary phase in this system.\[^{18,19}\] As we will discuss in Section 4.3, theoretical point defect formation energies both for half- and full-Heusler systems\[^{20,21}\] imply that for all our compositions, the energetically most favored configuration should always be given by accommodating all Sb atoms and only then on their sublattice and having the excess Mn spill over onto the Ni sites. We have thus normalized the compositions in this way, and we use this convention for computing, e.g., magnetic moments per formula unit, but for simplicity will always quote only the nominal compositions.

After annealing and quenching, the ingots were portioned by a low speed diamond saw into pieces to be used for the respective measurements: for each composition, one sample for DSC characterization in the as-prepared state, two for magnetization measurements, of which one was subjected to additional low-temperature annealing at 573 K for 48 h, and the remaining sample material of a few grams for each composition was crushed and ground to a particle size below 0.1 mm. The X-ray diffraction measurements on the resulting powders, as discussed in more detail in Section 4.2, showed already ideally sharp peaks, so no additional strain recovery heat treatments were necessary, which can be understood by the materials’ very brittle nature. The same powder samples were then used for the temperature-dependent neutron diffraction measurements, and in the resulting state for the room-temperature high-resolution neutron diffraction measurements.

2.2. Experimental Methods

Differential scanning calorimetry measurements up to 850 K have been carried out in a Perkin Elmer DSC 8500 using Cu sample pans to probe the magnetic transition, whereas for the high-temperature measurements of the C1\textsubscript{1}–L\textsubscript{2}\textsubscript{1} transition and melting up to 1500 K a Netzsch DSC 404 C Pegasus was used. Both instruments have been calibrated via the known melting points of various elements. Field-dependent sample magnetizations up to 70 kOe at 6 K were determined by SQUID magnetometry in a Magnetic Property Measurement System by Quantum Design, Inc. Spontaneous magnetizations were measured by Arrott plot extrapolation.

X-ray powder diffraction was done on a laboratory Rigaku SmartLab diffractometer operating in \(\theta-\theta\) symmetric Bragg–Brentano geometry using Cu K\(x\) radiation, that is, a doublet of about 1.542 Å wavelength.

High-resolution neutron diffraction measurements were carried out at the SPODI diffractometer at the MLZ Garching\[^{22}\] at room temperature, using a wavelength of 1.5482 Å. SPODI uses a multidetector of 80 vertical position-sensitive \(^3\)He tubes that span 160° in 2\(\theta\), which permits the collection of data over a broad angular range. The recorded 2D diffraction patterns were radially integrated over the detector height using the standard variable-height approach.\[^{23}\]

The temperature-dependent neutron diffraction experiment was conducted at diffractometer 3T2 at the LLB, Saclay, at a wavelength of 1.23 Å. This instrument is equipped by a multidetector of 48 position-insensitive tubes, covering a \(2\theta\) range of 118° with reduced instrument resolution compared with SPODI. To correct for misalignments of detector collimator and sample, we calibrated the detector efficiencies so that the incoherent background was consistent with the SPODI measurements.

We modeled all diffraction data by Rietveld refinement\[^{24}\] using structure factors, lattice constants, and a single atomic displacement parameter (i.e., the displacements are assumed to be isotropic and the same for all elements) to describe all peaks up to (622), (640), and (644) for the XRD, SPODI, and 3T2 data sets, respectively. Angular corrections were considered by a constant shift, and for X-ray diffraction in addition by a term proportional to \(\cos(2\theta)/2\) due to vertical sample displacement in Bragg–Brentano geometry. For the neutron diffraction experiments, the instrumental resolutions were modeled via pseudo-Voigt peak shapes, with the angular dependence of the Gaussian component described by the classical \(U, V, \text{and} W\) parameters\[^{25}\] whereas the width of the Lorentzian component varied proportional to \(1/\cos(2\theta)/2\), corresponding to a constant width when seen as a function of Q. All these parameters were allowed to vary when fitting the high-resolution SPODI data, whereas the reduced resolution at 3T2 allowed us to keep them fixed over the whole experiment. For the X-ray diffraction measurements, the instrumental resolution shape was modeled solely in terms of the Lorentzian component, and the wavelengths used for the Cu K\(\alpha\) doublet were 1.5406449 and 1.5444834 Å for K\(\alpha_1\) and K\(\alpha_2\) (as the weighted averages of K\(\alpha_1\) and K\(\alpha_2\))\[^{26}\] with relative proportions of 1:0.52. In all cases, no asymmetry corrections were necessary to obtain satisfactory fits. For neutron scattering, the magnetic contribution was described via the Mn\(^{2+}\) form factor as fitted by Brown\[^{27}\] to Hartree-Fock wavefunctions\[^{28}\] while for X-ray diffraction the relativistic Hartree-Fock form factors given by Ref.\[^{29}\] were used. Quoted uncertainties always pertain to the statistical uncertainty due to Poissonian counting statistics.

3. Macroscopic Characterization

3.1. Calorimetry

We used differential scanning calorimetry to complement the pseudobinary Ni\(_{1+x}\)MnSb section of the ternary phase diagram, as given by Nagasako et al.\[^{16}\] Specifically, we investigated the magnetic transition, the C1\textsubscript{1}–L\textsubscript{2}\textsubscript{1} transition, and the melting transition. Plots of the calorimetric signal measured under heating with 10 K min\(^{-1}\) are given in Figure 2, with the scale in the distinct panels adapted to the magnitude of the respective signals. The determined transition temperatures are given in Table 1, and the corresponding phase diagram, along with earlier values from literature, is shown in Figure 3. We will now discuss the three transitions in turn.

At least for the samples with Ni excess \(x \leq 0.5\), the magnetic transition leads to textbook examples of \(\lambda\)-shaped peaks, as expected for a second-order transition. We thus identify the location of the endothermic signal’s maximum as the phase transition temperature. The steady decrease in the transition temperature with increasing \(x\) reproduces earlier reports (see Figure 3), and it would be tempting to relate it to the increase in lattice constant and thus separation between the Mn spins, the primary carriers of magnetism in these systems, with growing \(x\). Indeed, such a correlation between lattice constant and Curie temperature exists, but it is much weaker than the
The melting transition is now clearly of first order as an abrupt increase in endothermic heat flow. Note that the melting point defined in this way will fall between the solidus and liquidus points, between which the solid–liquid coexistence region in the equilibrium phase diagram is situated, as the limited diffusion rates in the solid together with the finite heating rate enforce a quite homogeneous melting transition.

Finally, we did find a further calorimetric signal at around 1225 K in the initial heating of Ni$_{1.05}$MnSb as already reported by Nagasako and co-workers, which however vanished during cycling through this feature. Thus, we do not think that it corresponds to an equilibrium transition, in particular, we have no indication to assume a transition to B2 before melting sets in.

3.2. Magnetization

Low-temperature field-dependent magnetization curves are given in Figure 4 for four compositions in two different states, namely first in the quenched state after solution annealing, and second after a subsequent low-temperature annealing at 573 K for 48 h. We see that in general, the magnetization reaches a true, constant saturation value quite quickly, with the sole exception of annealed Ni$_{1.25}$MnSb, where even at fields of 70 kOe no true saturation is reached. Also, the very small hysteretic effects of about 1 Oe indicate an ideal ferromagnetic state for these systems, again with the exception of annealed Ni$_{1.25}$MnSb with a comparatively larger hysteresis of 60 Oe. As all systems should be stable at low temperatures due to their small Mn excess as discussed previously, we can only conjecture that our sample of the nominal composition Ni$_{1.25}$MnSb, for which Table 1 suggests the largest Mn excess, perhaps shows incipient segregation of Mn to, e.g., the grain boundaries, increasing the material’s magnetic hardness.

The corresponding values for the spontaneous magnetization are reported in Table 1. We see that as $x$ increases from the half-Heusler to the full-Heusler structure, $M_s$ decreases steadily. At first view, this seems to be at odds with the intermediate maximum of magnetization at about $x = 0.5$ reported by Webster and Mankikar. Note, however, that the thermal histories of the samples are different: while our samples have been quenched from 1173 K, where the L2$_1$ phase is stable for all $x$, their samples have been quenched from 1173 K, where the L2$_1$ phase is stable for all $x$, their samples have been quenched.
were quenched from 973 K, which passes through the \( L_2_1 \rightarrow C_{1b} \) transition just at \( x = 0.5 \). Our low-temperature annealing increased the structural order, likely both with respect to the vacancies on the Ni sublattices and as well with respect to the Mn atoms with their large localized moments, thus increasing the spontaneous magnetization. However, our value of \( 4.46 \mu_B / \text{f.u.} \) for annealed \( \text{Ni}_{1.05} \text{MnSb} \) is clearly significantly larger than the typically reported \( 4.0 \mu_B / \text{f.u.} \) for \( \text{NiMnSb} \), which is also required by a half-metallic band structure\(^{[31]} \) with quenched orbital moments.\(^{[32]} \) We suspect that this is due to a vacancy supersaturation retained from the high-temperature quench that could also not relax for kinetic reasons during the 48 h of low-temperature annealing as we will discuss below.

4. Crystal Structure and Order

4.1. Peak Intensities for \( L_2_1 \) and \( C_{1b} \) Structures

Different from more simple superstructures like the textbook cases of \( B_2 \) or \( L_1_0 \) order, the \( L_2_1 \) structure can be seen as a superstructure of second order: first, there is the inequivalence between the \( 8c \) sites on the one hand and the \( 4a \) and \( 4b \) sites on the other hand—this doubling of the primitive unit cell compared with the body-centered cubic case corresponds to \( B_2 \) order. On top of that, in the inequivalence between \( 4a \) and \( 4b \) leads to another doubling of the unit cell. The resulting structure has face-centered cubic symmetry, whose reciprocal lattice consists of points \( hkl \) where \( h, k, \) and \( l \) are either all even or all odd integers. Due to the double superstructure, the diffraction peaks at the corresponding positions in reciprocal space can be grouped in three families: if all three indices are even and sum to a multiple of 4, all atoms scatter with the same phase, so that the intensities of the corresponding peaks are independent of order. They will be called fundamental or primitive (P) peaks. We call the other family of all-even indices \( S_0 \) superstructure peaks—in this case, the \( 4a \) and \( 4b \) sites have an opposite phase compared with the \( 8c \) sites, so the corresponding peak intensities are proportional to the degree of \( B_2 \)-type order. Finally, at the all-odd \( S_0 \) peaks, the \( 4a \) sites have phase 1 and the \( 4b \) sites have phase \( -1 \) (while one half of the \( 8c \) sites have phase \( i \) and the other half phase \( -i \), interfering destructively among themselves), indicating the degree of \( L_2_1 \)-type order.

\( C_{1b} \) can now be seen as yet an additional superstructure on \( L_2_1 \). However, the splitting of \( 8c \) into \( 4c \) and \( 4d \) does not lead to a further enlargement of the unit cell, and thus no additional peaks appear. The only indication of \( C_{1b} \) order lies in additional intensity in the \( S_0 \) peaks, as the perfect destructive interference among the \( 8c \) sites is lifted.

Due to the different variation of the scattering lengths over the elements, X-ray and neutron diffraction are sensitive to different aspects of the ordered structures: for X-rays, the scattering length is proportional to the atomic number \( Z \), so Ni and Mn are practically indistinguishable, whereas Sb and vacancies (with \( Z = 0 \)) deviate from this average Ni/Mn scattering length by the same absolute value but with opposite sign. Thus, in the idealized case of Ni progressively filling the \( 4d \) sites with increasing \( x \) in \( \text{Ni}_{1+x} \text{MnSb} \), \( S_0 \) and \( S_0 \) peaks have always about the same intensity. For neutrons, the strongest contrast is between Ni and Mn, with the latter having a negative scattering length. Due to partial cancellation between Ni and vacancies and between Mn and Sb, in particular for small \( x \), the \( S_0 \) peaks are expected to have clearly less intensity than the \( S_0 \) peaks. In contrast to X-ray diffraction, already a slight mixing between Ni and Mn would noticeably decrease both \( S_0 \) and \( S_0 \) peaks.

Finally, the magnetic dipole moment of neutrons is sensitive to unpaired electron spins. For unpolarized neutron diffraction as relevant here, conceptually the magnetic intensity is computed independently of the nuclear signal and added afterward to give the total diffraction intensity, where the magnetic scattering length is proportional in sign and magnitude to the magnetic moments per crystalline site. Thus, the same argumentation as given earlier shows that an enlargement of the primitive cell due to antiferromagnetic ordering would give additional magnetic superstructure peaks. In contrast, the spin structure under ferromagnetic order leads to magnetic peaks coinciding with the nuclear peaks. In the special case of the unpaired electrons being confined to a single site in the unit cell (the \( 4a \) Mn site in the present case), at any peak there is only constructive interference, so the magnetic contributions to the \( P \), \( S_0 \), and \( S_0 \) peaks are all equal.

4.2. Room-Temperature Diffraction

To ascertain the state of the powders after preparation, we conducted room-temperature X-ray diffraction experiments. The resulting data are illustrated in Figure 5. No indications of an
impurity phase are discernible, and the fact that the Kα1/Kα2 splitting is observable implies a very low level of internal strain. Both S₁ and S₂ superstructure peaks are visible and of comparable intensity, which means that a significant degree of C1₁ order exists in the quenched and crushed samples, even though they were quenched from the L2₁ regime. Any vacancy ordering can have happened only during the quenching on a time scale of seconds. It is thus remarkable that the S₂ superstructure peaks are as sharp as the primitive peaks, which implies a low density of antiphase domain boundaries also for the C1₁ order.

With the samples in their states after the temperature-dependent neutron diffraction experiments discussed in Section 5, we carried out high-resolution neutron diffraction. The data together with Rietveld fits are displayed in Figure 6. Even though these measurements were done at room temperature in the magnetically ordered phase, no additional peaks are visible, which confirms the expected ferromagnetic ordering.

The refined lattice constants a and isotropic atomic displacements uₘ₀ as obtained from the Debye–Waller factor \( \exp \left(-uₘ₀^2 q^2\right) \) are given in Table 2. We see that in general, the lattice constant increases with increasing Ni excess x and thus less vacancy content, which is in agreement with the results of Webster and Mankikar. We cannot expect a perfect quantitative coincidence of our lattice constants with published values, as the thermal history of the sample will have an effect on the states of order, which is also evident in the differences between the X-ray (measured before the temperature-dependent neutron diffraction experiments) and neutron values (measured afterward). We have to note here that no temperature-dependent experiments were carried out on Ni₁.₇₅MnSb, thus the slight disagreements of the X-ray and neutron values in this case give an indication of the systematic errors. Still, the information quality is quite high, as for instance the lattice contraction after temperature-dependent neutron diffraction of Ni₁.₂₅MnSb, which contrasts with the behavior of the other systems, is reproduced qualitatively and quantitatively in the consistent values obtained during the temperature-dependent diffraction that are presented in Figure 7.

Also, the atomic displacements uₘ₀ increase practically monotonically with Ni excess x. As the lattice constants vary comparatively insignificantly, the force constants and thus the phonon frequencies will do likewise, so we interpret this behavior of the room-temperature displacements to predominantly result from static displacements due to disorder. The observed increase is consequently less expected, as at least the end member Ni₂MnSb, assuming ideal site occupations, should show no disorder and therefore small displacements. The increased vacancy concentration compared with the idealized picture of a successively filled (4d) sublattice as discussed in the following sections will explain this observation.

### 4.3. Structure Solution

The diffraction data encompass two degrees of freedom with respect to the site occupations, namely the ratio of the two families of superstructure peaks’ intensities to the fundamental peaks. In contrast, with four chemical elements including the

![Figure 6. High-resolution room-temperature neutron diffraction—experimental data, Rietveld model, and residuals on linear scale.](image)

![Figure 7. Lattice constants as function of temperature. For being able to discern nonequilibrium behavior, here and in the following figures the temporal sequence of data points is indicated by the dash pattern of the connecting line that evolves continuously from closely spaced dots to large dashes.](image)

| Compound   | X-ray diffraction | Neutron diffraction |
|------------|-------------------|---------------------|
|            | a [Å]             | uₘ₀ [Å]             | a [Å] | uₘ₀ [Å] |
| Ni₁.₀₅MnSb | 5.930453(22)      | 0.0991(11)          | 5.94327(13) | 0.07963(27) |
| Ni₁.₂₅MnSb | 5.973103(27)      | 0.1346(10)          | 5.967625(15) | 0.08646(29) |
| Ni₁.₅₀MnSb | 5.992622(32)      | 0.1239(12)          | 5.998551(14) | 0.09984(24) |
| Ni₁.₆₀MnSb | –                 | –                   | 6.004738(12) | 0.10589(18) |
| Ni₁.₇₅MnSb | 5.999586(31)      | 0.1613(10)          | 6.002708(16) | 0.11201(21) |
vacancy to be distributed over three (for L21) or four (for C1b) inequivalent sites there are seven or ten free parameters in the model. Thus, we have used physical plausibility as a criterion to restrict the site occupancies.

According to density-functional theory (DFT) calculations of the defect formation energies both for the NiMnSb$^{20}$ and Ni$_2$MnSb$^{21}$ terminal compositions, for all our compositions the ground-state configuration would be to have the (4a) sublattice fully occupied by Mn, (4b) fully occupied by Sb, (4c) fully occupied by Ni and potentially excess Mn, and finally (4d) with Ni and vacancies so as to give the correct Ni content (see the Supporting Information for the detailed argumentation). In addition to these a priori constraints, our model has to be able to explain the remarkably high value of the S$_c$ intensities, in particular for X-ray diffraction, and also high S$_0$ intensities. The only consistent two-parameter model with these features we have found is to describe an increase in the number of unit cells by one parameter, putting all Mn onto (4a) and any excess Mn onto (4b) and filling up (4a) and (4b) by Ni, and using the other parameter to describe the asymmetry between the remaining Ni and the vacancies on (4c) and (4d).

Table 3 lists the corresponding site occupations. With one exception, all data sets can be described by this model. In all cases, C1$_b$ order is realized, with the asymmetry between (4c) and (4d) decreasing with increasing x as expected. What is remarkable is the high content of Ni on (4b) of a few percent, corresponding to an increase in vacancy content over the ground state as proposed earlier in a corresponding amount. The single exception pertains to Ni$_{1.05}$MnSb in X-ray diffraction, where it is logically impossible to reproduce the high S$_c$ and S$_0$ intensities simultaneously without introducing vacancies also on the Mn sublattice, which would be highly implausible. Thus, the corresponding values we report in Table 3 reproduce the S$_c$ intensity and fall short of the observed S$_0$ intensity by about 8%.

As usual, we use the Hartree–Fock atomic form factors computed for isolated atoms to model the X-ray diffraction intensities. One can now ask for the systematic errors due to aspects of charge transfer in an actual compound. For NiMnSb, a Wigner–Seitz cell analysis of DFT electronic densities shows that Ni gains one electron relatively to Sb.$^{[31]}$ Taking this effect into account by using the form factors for Cu instead of Ni and for Sn instead of Sb leads to differences in the occupations on inequivalent sites there are seven or ten free parameters in the model. Thus, we have used physical plausibility as a criterion to restrict the site occupancies.

Finally, Table 3 reports the refined ferromagnetically ordered moments in neutron diffraction. For stability of the fit, they have been calculated assuming all moments to reside on the Mn sublattice. As with the low-temperature macroscopic magnetizations in Table 1, they decrease with increasing x. Their lower value compared with the magnetizations, in particular for larger x, can be explained by a thermal reduction of magnetic order due to the decreasing Curie temperature, consistent with the temperature-dependent magnetizations measured by Webster and Mankikar.$^{[14]}$

### 5. Temperature-Dependent Neutron Diffraction

To follow the C1$_b$–L2$_1$ transition directly, we carried out temperature-dependent neutron diffraction measurements. Specifically, we did isothermal measurements of about 70 min each (accumulating until a set number of monitor counts), separated by heating or cooling ramps of typically about 10 min duration. In total, the measurements spanned 38, 41, 37, and 24 h for Ni$_{1.05}$MnSb, Ni$_{1.25}$MnSb, Ni$_{1.50}$MnSb, and Ni$_{1.60}$MnSb, respectively.

Figure 7 presents the increase in the lattice constant with temperature. In Ni$_{1.05}$MnSb, it is most evident that these measurements do not correspond to equilibrium situations—on cooling, the lattice constant is much larger than on heating from the quenched state—but also with the other samples measurements on heating and cooling do not coincide. We are certain that this effect is real, as it is mirrored by the independent room-temperature measurements by X-ray diffraction (corresponding to the initial state) and high-resolution neutron diffraction (final state) given in Table 2. To investigate this effect more closely, for Ni$_{1.25}$MnSb and Ni$_{1.50}$MnSb we covered the high-temperature range nonmonotonically and measured specific temperatures repeatedly (see the Supporting Information). This demonstrated that the observed lattice constant depends not only on the temperature of measurement, but also on the thermal history, with the strongest effect being a reduced lattice constant on first heating up to temperatures of about 900 K.

The temperature-dependent mean-squared displacements are given in Figure 8. With harmonic interactions and in the classical limit, which should be approximately fulfilled in the probed temperature range, a linear behavior would be expected for the

| Compound      | Ni on (4a) | Ni on (4b) | Ni on (4c) | Ni on (4d) | Ni on (4a) | Ni on (4b) | Mn on (4b) | Ni on (4c) | Ni on (4d) | moment ($\mu_0$) |
|---------------|-----------|-----------|-----------|-----------|-----------|-----------|------------|-----------|-----------|-----------------|
| Ni$_{1.05}$MnSb | 0.0224(15) | 0.0591(14) | 0.9075$^a$ | 0$^a$ | 0 | 0.0253(5) | 0.0062(3) | 0.8978(12) | 0.0948(12) | 3.968(15) |
| Ni$_{1.15}$MnSb | 0.0175(15) | 0.0652(15) | 0.9605(15) | 0.1393(35) | 0 | 0.0260(6) | 0.0116(3) | 0.9365(15) | 0.2530(15) | 4.005(19) |
| Ni$_{1.25}$MnSb | 0.0635(16) | 0.0926(16) | 0.9687(41) | 0.2391(41) | 0.0051(3) | 0.0359(3) | 0 | 0.9415(12) | 0.4665(12) | 3.305(22) |
| Ni$_{1.40}$MnSb | – | – | – | – | 0.0258(3) | 0.0268(3) | 0.9651(10) | 0.5219(10) | 2.890(20) | – |
| Ni$_{1.50}$MnSb | 0.0913(16) | 0.1082(16) | 0.9451(48) | 0.4204(48) | 0.0333(3) | 0.0513(3) | 0 | 0.8801(24) | 0.7003(24) | 2.585(25) |

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thermal displacements. Thus, the features above 1000 K in Ni$_{1.05}$MnSb and to a lesser degree in Ni$_{1.25}$MnSb clearly result from static displacements due to Ni/vacancy disordering at the C1b–L2$_1$ transition, which are largest for Ni$_{1.05}$MnSb and decrease with increasing $x$ as the number of disordering vacancies decreases.

Naturally, the most direct way to probe order–disorder transitions is via the intensity of the corresponding superstructure peaks. Specifically, after correcting for multiplicities, Lorentz factors and Debye–Waller factors, all peaks for a given family (here P, S$_0$, and S$_2$) should have the same intensity. Normalizing by the $P$ values cancels effects of the incident flux or sample volume, and these are the quantities we plot in Figure 9. In this way, we directly see the loss of intensity in the S$_0$ peaks toward the phase transition. The transition is evidently of second order, as already implied by the continuous concentration variation in diffusion couples.$^{[15]}$ Again, the signal of the phase transition diminishes with increasing $x$, being essentially invisible for $x > 0.5$. Note that in all our probed temperatures and by extrapolation likely also up to the melting point, the S$_0$ peaks stay clearly visible, as was already found for Mn-rich Ni$_2$MnSb.$^{[13]}$ Thus we cannot corroborate the previously conjectured transition to B2 at high temperatures.$^{[16]}$ For Ni$_{1.05}$MnSb and Ni$_{1.25}$MnSb, we fitted the behavior of the peak intensities by a phenomenological model, which gives phase transition temperatures of $T_c = 1063$ K and $T_c = 1034$ K, respectively. Counterintuitively, the S$_0$ peak intensities for Ni$_{1.05}$MnSb are larger on heating from the quenched state than on comparatively slow cooling, where one would rather expect more disorder and thus lower superstructure intensities. In contrast, the S$_2$ intensities show only a steady decrease with temperature, and are not noticeably affected by the C1b–L2$_1$ transition.

6. Discussion

According to the investigations we reported here, the system Ni$_{1+x}$MnSb shows a number of peculiar features, which are a consequence of the comparatively low energy cost for introducing a vacancy on sites (4c) or (4d).

First, our results indicate that at least in Ni$_{1.05}$MnSb a comparatively large amount of excess vacancies can be retained after quenching. They would congregate at low temperatures on the (4d) sublattice, increasing the (4c)–(4d) contrast and thus the S$_0$ intensity as observed, while during the temperature-dependent neutron diffraction with slow cooling they would partially annihilate. This explains the decreased S$_0$ intensity, and the resulting increase in lattice constant corresponds via the composition-dependent lattice constants as discussed in Section 4.2 to a reduced vacancy concentration consistent with the site occupation differences in Table 3.

The existence of excess vacancy concentrations after quenching in Mn-based full-Heusler systems per se is not unusual.$^{[34]}$ What is surprising is however that even with this very high concentration of constitutional vacancies, which will lead to an approximately half-occupied (8c) sublattice above the C1b–L2$_1$ transition, thermal excitations would lead to a further increase—one could equally have expected that with the loss of C1b order the system would move towards a more conventional full-Heusler configuration by annihilating vacancies and shifting...
Sb onto (4a) and Mn onto (8c). The reason for the observed behaviour clearly lies in the very small formation energy of vacancies on the Ni sublattice also in the L2₁ case compared to other systems according to DFT,[23] or put another way, a remarkable stability of the MnSb framework like in an interstitial compound, which is also reflected in the apparent stability of L2₁ order up to the melting point.

The large concentration of mobile vacancies at high temperatures leading to rapid atomic diffusive dynamics also makes it hard to conserve disordered states by quenching: in agreement with Ref. [16] we find our samples to display C₁b order even though they were quenched from the L₂₁ region, with no discernible broadening of the superstructure peaks that would point to the presence of antiphase domains.

The relevant time scales are a point worth noting: with these large vacancy concentrations, each given vacancy will have to perform only a few jumps until the site occupations have reached equilibrium with respect to order. However, for the vacancy concentration itself to reach thermal equilibrium, they need to reach crystalline defects or grain boundaries that act as vacancy sources or sinks. In these brittle materials, this can easily take on the order of 10⁸ vacancy jumps—note that, the lattice constant relaxation at high temperatures as probed by temperature-dependent neutron diffraction proceeds on the scale of a few hours, whereas ordering transitions in the same temperature region happen within some 20 K at heating rates of 10 K min⁻¹ in DSC, likely limited by heat flow rather than kinetics. Thus, we have here potentially the issue of ordering transitions that look conventional in all accessible respects (such as being reversible), but that indeed depend on the instantaneous nonequilibrium vacancy concentration. We think that it is quite possible that the discrepancy between DSC- and diffraction-derived C₁b–L₂₁ transition temperatures (1130 K compared with 1063 K for Ni₁.0₅MnSb, and a comparable difference for Ni₁.2₅MnSb) is due to such issues, whereas such a large discrepancy due to a temperature miscalibration or sample composition changes appears unrealistic.

Finally, we have noted that for small Ni excess x, we reach magnetizations of about 4.5 μᵣ / f.u. after annealing the quenched samples at low temperature, which is clearly larger than the 4.0 μᵣ / f.u. theoretically expected for a half-metallic band structure[31] and also found experimentally.[14] Our explanation is that this is again due to a vacancy supersaturation, which during low-temperature annealing will drive Ni atoms onto (4a) and (4b), where they will likely develop a significant magnetic moment. If these moments should align ferromagnetically, it would reproduce the observed increase of about 10% in macroscopic magnetization.

7. Conclusion

There are two main insights that result from the investigations we presented here: First, while physics as a whole has abandoned the concept of horror vacui, in metals physics it is still a commonly accepted rule that systems will tend to avoid empty space, and that vacancies are typically only present as thermal defects in concentrations below 10⁻³ at high temperatures. The ternary system Ni–Mn–Sb is now a contrary example, not only in the well-established fact that at low temperatures it forms the C₁b half-Heusler structure with voids of a size that an atom would fit comfortably, but that these vacancies are stable also in the high-temperature L₂₁ phase, and even increase further as thermal excitations. We see no reason why this should not apply also to other systems that host half-Heusler structures.

The other main consequence concerns the very different relaxation rates of atomic order and vacancies: in systems with low vacancy concentrations, the atomic structural arrangement is usually the most fundamental degree of freedom, dominating other aspects such as magnetic, martensitic or electronic transitions. With typical activation energies of diffusion of about 17kₐTₘ and attempt frequencies of a few THz,[15] already at 60% of the melting temperature Tₘ, atoms jump about once per second, so that order-disorder transitions at such temperatures measured with temperature ramps accessible in a DSC will happen practically in equilibrium, and any nonequilibrium vacancy concentrations can affect most the relaxation rates, but not the transition temperatures. In contrast, the large vacancy supersaturation of up to 10% additional vacant sites per formula unit in the present case will likely affect the thermodynamics of the system, and has to be considered in any quantitative interpretation of the properties of the materials.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
Financial support by the Deutsche Forschungsgemeinschaft (project no. 107745057, TRR 80) is gratefully acknowledged. P.N. acknowledges additional support from the Japan Society for the Promotion of Science (JSPS) via a short-term doctoral scholarship for research in Japan.

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
constitutional vacancies, half-Heusler, neutron diffraction, NiMnSb

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