

Nonstoichiometry in line compounds

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Received: 30 November 2005 / Accepted: 20 March 2006 / Published online: 9 January 2007
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Abstract Phases having compositional fields narrower than about 1 at.% and appearing as lines in binary phase diagrams often are assumed to have properties independent of composition. That such an assumption can be seriously in error is illustrated by recent measurements on pairs of samples prepared to have compositions at opposing phase boundaries. Two microscopic properties, lattice locations of highly dilute solutes and diffusional jump frequencies, were studied, respectively, through measurement of static and dynamic nuclear quadrupole interactions using the method of perturbed angular correlation of gamma rays (PAC). At opposing boundary compositions, PAC probe atoms have been observed to occupy different lattice sites or to have jump frequencies differing by a factor of 100. Such gross differences suggest measurements of other properties of line compounds should be made on pairs of samples having the opposing boundary compositions in order to avoid inconsistent or unreproducible results.

Introduction

Line compounds are intermediate phases that appear as vertical lines in binary phase diagrams [1]. Although the line suggests a definite composition at some stoichiometric ratio of mole fractions of elements,

intermediate phases must have fields of finite compositional extent at non-zero temperatures (excepting unique points such as peritectoids and eutectoids). Boundaries of a phase are determined by X-ray analysis as the compositions beyond which second phases begin to appear. The uncertainty in determinations of this type is typically 1 at.%, so that line compounds generally may be assumed to have phase fields of indeterminate width less than or about 1 at.%. Usually, the field spans a stoichiometric composition, with deviations in composition on either side accommodated by the presence of structural point defects such as antisite atoms or lattice vacancies.

Recently, we studied two microscopic properties in series of intermetallic line compounds [2–6]. Measurements were made using the nuclear quadrupole interaction of ^{111}In radioactive probe atoms, which decay with a mean-life of 4.0 days into ^{111}Cd . Samples were made by arc-melting constituent elements and carrier-free ^{111}In activity together under argon, followed by an annealing treatment to coarsen and order the crystal structure. Mole fractions of ^{111}In were typically $\sim 10^{-8}$, much lower than concentrations of constitutional or thermal defects, so that impurity probes did not disturb intrinsic defect concentrations. The experimental method used is perturbed angular correlation of gamma rays (PAC), for which a heuristic description is now given. The reader is referred to Ref. [3] or to the book by Schatz and Weidinger [7] for more comprehensive descriptions of the methodology of PAC. Radioactive decay of ^{111}In leaves the daughter ^{111}Cd nucleus in its second excited state, after which two gamma rays are emitted in succession. The intermediate, first excited level has a mean-life of 120 ns, long enough for its nuclear quadrupole moment Q to

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precess through a number of revolutions during the lifetime of the state. The precession frequency is proportional to the product of the quadrupole moment and electric field gradient (EFG) at the nucleus due to external charges. Such precessions are detected through angular correlations between directions of emissions of each of the two gamma rays and the spin orientation of the intermediate state nucleus. The angular correlation between the two gamma rays precesses with the nuclear spin, so that the probability for detecting coincidences of the two gamma rays at a delay time Δt after creation of the intermediate state with fixed detectors oscillates with the precession frequency. By histogramming delay times measured over the ensemble of probe nuclei, one obtains an exponential lifetime decay curve for the intermediate state that is modulated by the precessions. By combining coincidence spectra measured at relative detector angles of 90° and 180° , one can determine the perturbation function, a kind of spin-rotation pattern, or PAC spectrum, that contains all information about the solid-state environment(s) of the probes. The perturbation function for a unique static quadrupole interaction with an axially symmetric EFG (which occurs when the probe site has a three- or higher-fold axis of charge symmetry) is

$$G_2^{\text{static}}(t) = \frac{1}{5} + \frac{13}{35} \cos(\omega_1 t) + \frac{10}{35} \cos(2\omega_1 t) + \frac{5}{35} \cos(3\omega_1 t) \quad (1)$$

in which the fundamental frequency is $\omega_1 = \frac{3\pi}{10} eQV_{zz}/h$, with V_{zz} equal to the principal component of the EFG tensor. The above function applies for a sample having random polycrystalline texture and for the spin 5/2 intermediate state of ^{111}Cd , with the three frequency harmonics corresponding to hyperfine splittings of the intermediate state. The EFG is given by a sum over all extra-nuclear charges: $V_{zz} = \sum q_i (3 \cos^2 \theta_i - 1)/r_i^3$. In the special case of cubic point symmetry, $V_{zz} = 0$ and $\omega_1 = 0$. When solutes occupy more than one lattice location, the experimental perturbation function is a sum of functions such as in Eq. 1 multiplied by the fractions of solutes in each site.

Lattice location measurements

Lattice locations of probe atoms in compounds were determined through measurements of quadrupole interaction frequencies in two studies. The first study was carried out on GdAl_2 [2], a line compound [1] having the cubic Laves Cu_2Mg , or C15, structure, in

which the Gd-site is cubic and the Al-site is not. As a consequence, one can immediately identify the lattice location of a solute according to whether the observed nuclear quadrupole interaction frequency of the solute is or is not zero. Figure 1 shows experimental perturbation functions measured at 823 K for four samples [2]. The compositions are believed to span the phase field from the more Gd-rich phase boundary to the less Gd-rich boundary. As can be seen, the experimental spectra exhibit superpositions of two functions of the form of Eq. 1 that correspond to the non-cubic Al-site and cubic Gd-site, with frequencies $\omega_1 = 45$ and 0 Mrad/s. Amplitudes of the two functions equal the fractions of probes in the sites. As can be seen, indium solutes are predominantly located on Al-sites at the more Gd-rich boundary (Fig. 1a), and predominantly on Gd-sites at the less Gd-rich boundary (Fig. 1d). Unusually large mass changes observed during preparation of GdAl_2 samples left their compositions uncertain by several tenths of an atomic percent. However, semi-quantitative information about boundary compositions can be obtained from an examination of inhomogeneous broadening of the perturbation functions caused by structural point defects. Figure 1a exhibits very little inhomogeneity of the dominant, Al-site

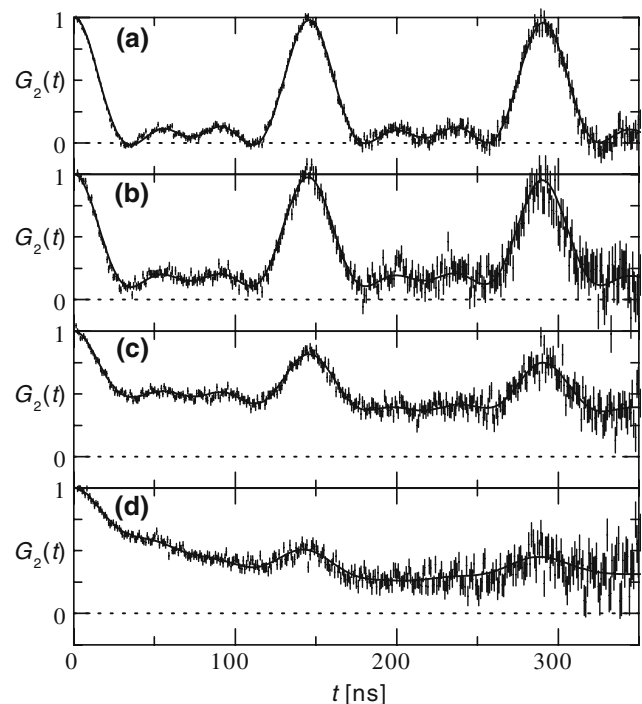


Fig. 1 PAC spectra of $^{111}\text{In}/\text{Cd}$ probes in four samples of GdAl_2 measured at 823 K (from Ref. [2], Fig. 1). From top to bottom, the samples are progressively more deficient in Gd. Lack of inhomogeneous broadening in (a) suggests that the Gd-rich phase boundary is very close to the 33.3% stoichiometric composition

signal. Based on extensive observations on many phases in this laboratory, the spectrum is consistent with a highly ordered compound having a very low concentration of intrinsic point defects, and is estimated to correspond to a composition within about 0.05 at.% of the stoichiometric composition. Figure 1d exhibits significant broadening of the zero-frequency, Gd-site signal, suggesting a greater concentration of intrinsic defects and consequently greater deviation from the stoichiometric composition. The damping reflects weak EFGs caused by “distant defects” located at random in the lattice. Such weak EFGs have a more pronounced effect on zero-frequency signals than when perturbing a strong EFG such as at the Al-site. Therefore, the Gd-poor boundary composition is estimated to be a few tenths of an atomic percent below the stoichiometric composition. In summary, observed inhomogeneous broadening suggests phase boundaries of the GdAl₂ phase at about 33.0 and 33.3 at.% Gd.

As a consequence, In solutes switch between Al- and Gd-sites over a composition range of only ~0.3 at.%. Clearly, the idea that a solute should have a unique preferred site in a compound is simplistic. Fractions of indium on Al- and Gd-sites additionally were measured as a function of temperature in Ref. [2]. It was observed that indium solutes prefer Gd-sites at low temperature and Al-sites at high temperature. For samples having five compositions that span the phase field, the ratio of site fractions was found to be thermally activated with an enthalpy of 0.343(7) eV, which represents the increase in enthalpy when an indium solute transfers from a Gd-site to an Al-site. This study of GdAl₂ study showed that site preferences can be strong functions of both composition and temperature. For further details, the reader should consult Ref. [2].

A second study was made of lattice locations of indium solutes in phases having the Ni₂Al₃ structure [3], including the aluminides Ni₂Al₃, Pd₂Al₃ and Pt₂Al₃ and gallides Ni₂Ga₃ and Pt₂Ga₃. The first two phases are reported to have field widths of about 4 at.% while the last three appear as line compounds in Ref. [1]. The crystal structure is complex, having two inequivalent Al-type sites, one Ni-type site, and a sublattice of empty sites. Observed site-preference behavior was found to be correspondingly rich. At the more transition-metal-rich phase boundaries of all five phases, indium solutes were found to exclusively occupy one of the two Al-type sites, with a large EFG and quadrupole frequency. At less transition-metal-rich boundaries, the behavior differed between gallides and aluminides. For gallides, indium solutes were observed to occupy Ni-type sites, with a low EFG, whereas for aluminides spectra exhibited strongly inhomogeneous

quadrupole interactions attributed to solutes in “lattice sink sites” such as grain boundaries. Finally, for Ni₂Ga₃ a second low frequency signal was observed for compositions close to stoichiometry that was attributed to solutes on empty lattice sites, which have interstitial character. Thus, as in the study of GdAl₂, solutes were observed to “switch” between different substitutional lattice sites in compounds. However, for Ni₂Al₃ phases one also observed occupation of sites having interstitial character and non-crystallographic sites such as in grain boundaries. Using a thermodynamic model and numerical simulations, a number of heuristic rules were formulated for use in predicting site preference behavior [3]. Perhaps the most important rule is that solutes tend to occupy substitutional sites of an element in which there is a deficiency. Following that rule, the overall defect count is one (the solute replaces a host atom) whereas the defect count is two if the solute displaces a host atom from its normal site (solute plus displaced host atom). This rule is consistent with the composition dependences observed in GdAl₂ and in gallides having the Ni₂Al₃ structure. The reader is referred to Ref. [3] for additional discussion and rules.

Jump frequency and diffusion measurements

Jump frequencies of probe atoms were determined through analysis of dynamically relaxed quadrupole perturbation functions for a series of RIn₃ phases (R = rare-earth) having the cubic Cu₃Au or L1₂ crystal structure [4–6]. All RIn₃ phases appear as line compounds in R-In binary phase diagrams [1] and no evidence of static inhomogeneous broadening was observed in room temperature spectra for any of the samples. Thus, it is estimated that widths of the L1₂ phase fields are less than or about 0.2 at.%. Sites on the indium sublattice have tetragonal symmetry and the interesting property that each jump of an atom leads to reorientation of the axis of the EFG by 90°. Such jumps lead to decoherence of the quadrupole precessions that appears as damping of the static quadrupole perturbation function, with the dynamical perturbation function given in good approximation by

$$G_2^{\text{dynamic}}(t) \cong \exp(-wt)G_2^{\text{static}}(t). \quad (2)$$

Here w is the mean jump frequency, or inverse of the mean residence time, of a Cd daughter-probe at a site, and Eq. 2 applies for low jump frequencies ($w < \omega_1/6$; slow fluctuation regime) [6, 8]. The diffusion mecha-

nism presumably involves vacancies that move very rapidly on the In-sublattice, thereby shuffling atoms from site to site, although the detailed mechanism is not yet known [4]. PAC spectra for a CeIn_3 sample having the In-rich phase boundary composition measured at four temperatures are shown in Fig. 2 (from Ref. [6]). Damping in the form of Eq. 2 is evident and the jump frequency w can be seen to increase with temperature up to 954 K. The spectrum at the highest temperature, 1112 K, is in a fast fluctuation regime ($w > \omega_1/6$) for which jump frequencies are so high that the perturbation function has a fundamentally different form than Fig. 2, as discussed in detail elsewhere [4, 6, 8]. Precise values of the jump frequency were obtained by fitting experimental perturbation functions with exact numerical results calculated using a detailed relaxation model [4]. Fitted jump frequencies in Fig. 2 are 128, 27, 7 and 1.2 MHz, respectively, from top to bottom.

Much different jump frequencies were observed for compositions at opposing phase boundaries. Temperature dependences of jump frequencies for samples of LaIn_3 and CeIn_3 having the more In-rich (A) and less In-rich (B) boundary compositions are shown in Fig. 3

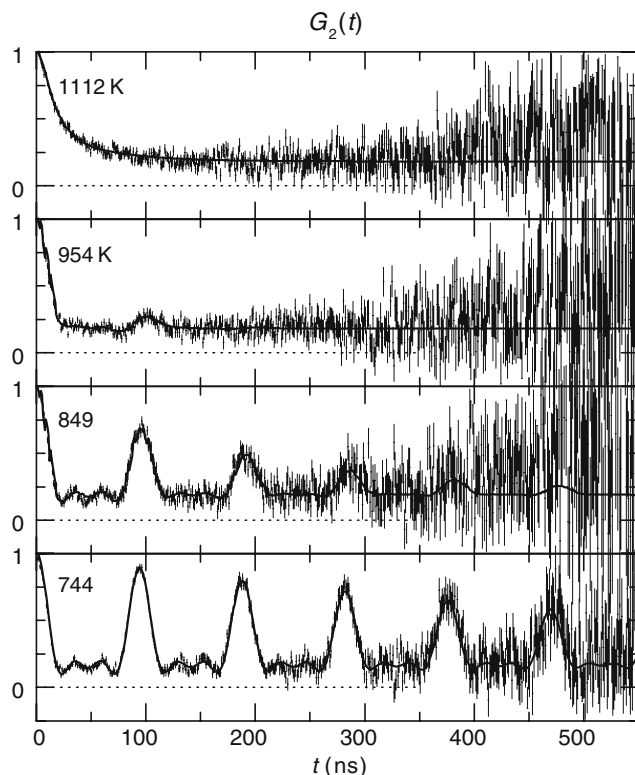


Fig. 2 PAC spectra of $^{111}\text{In}/\text{Cd}$ probes measured in CeIn_3 at the indicated temperatures (from Ref. [6], Fig. 2 right). The increase in damping at high temperature is attributed to nuclear relaxation caused by rapid jumping of ^{111}Cd probes on the indium sublattice

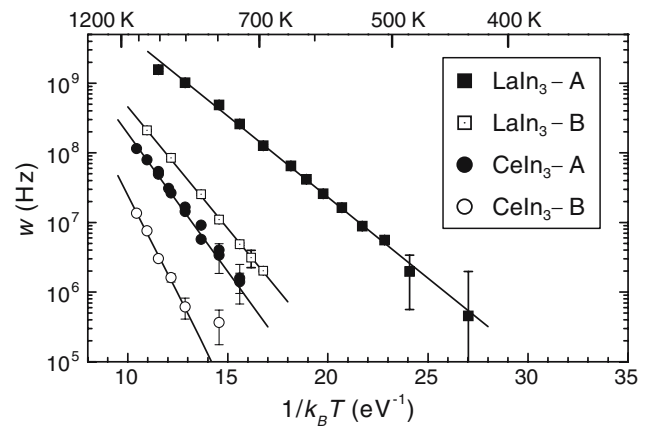


Fig. 3 Jump frequencies of ^{111}Cd tracer atoms on the In-sublattice in LaIn_3 and CeIn_3 (after Ref. [5], Fig. 3). A and B indicate compositions at opposing phase boundaries that are, respectively, more In-rich and less In-rich. As can be seen, jump frequencies are 10–100 times greater at the more In-rich phase boundaries

(from Ref. [5]). Fits of the data give activation enthalpies in the range 0.54–1.30 eV and prefactors in the range 1–10 THz [5]. For each phase, it can be seen that jump frequencies of Cd tracer atoms at the two boundaries differ by factors of 10–100. The diffusivity D of a tracer atom is related to the jump frequency w through $D = \frac{1}{6}fw\ell^2$ for jumps on a cubic sublattice, in which f is the correlation coefficient of diffusion and ℓ is the jump distance [5]. Taking the correlation coefficient to be a constant of order 1, and ignoring thermal expansion, the diffusivity is seen to be directly proportional to the jump frequency. Large jump-frequency ratios thereby imply large ratios of the diffusivity across the phase field of the compound. As a consequence, diffusivity measurements on line compounds would similarly lack reproducibility if one does not control for the composition. Diffusivity measurements on samples having a small amount of a second phase would be difficult to interpret since macroscopic measurements average over bulk diffusivities of the two phases and boundary diffusivities. Hyperfine measurements, on the other hand, provide a superposition of signals from the two phases and are unaffected by jumps in fast-diffusion paths such as grain boundaries since normally only a very small fraction of probe atoms are located there.

Discussion and conclusions

The above measurements demonstrate that some properties depend strongly on the exact composition within the phase field of a line compound. The

particular properties examined here may be especially sensitive to the composition. Atom movement in solids is commonly mediated by point defects such as lattice vacancies, so that the observed jump frequency is proportional to the mole fraction of available vacancies, $[V]$, the coordination number, z , and the exchange frequency of the tracer atom with a neighboring vacancy $\omega_2 : w \cong z\omega_2[V]$. At the stoichiometric composition there are only thermally activated elementary defects that occur in combinations that preserve the average composition of the compound (e.g., antisite atom pairs or mixed vacancy-antisite atom defects such as, possibly, a quintuple defect $\text{In}_{\text{La}} + 4V_{\text{In}}$ in LaIn_3 [9]). Deviations from the stoichiometric composition are normally accommodated by structural point defects that are one member or the other of the thermal defect combination (e.g., In_{La} in In-rich LaIn_3). Due to couplings among concentrations of intrinsic defects given by defect reactions, mole fractions of all elementary defects, including vacancies, depend sensitively on the deviation from stoichiometry. Thus, a strong dependence on composition is expected.

Lattice locations of solutes are similarly sensitive position at the very dilute mole fractions of solutes in this study, $\sim 10^{-8}$, much lower than mole fractions of elementary intrinsic defects. Thus, it is possible for all solute atoms to occupy sites of an element in which there is a deficiency even when deviations from stoichiometry are immeasurably small and to switch sites as the composition changes. This is a generic problem in hyperfine studies when using carrier-free radioactive hyperfine probes as solutes, such as in PAC or Mössbauer source experiments. Historically, it has been common to infer lattice locations of solutes using simplistic arguments based on comparison of atomic radii and valences of solute and host atoms, and some site attributions were undoubtedly mistaken. In studies of site preferences by other methods such as AL-CHEMI [10], much higher mole fractions of solutes

have to be used, ~ 1 at.%, that may be in excess of defect concentrations. Then, the site occupation of a solute may change much more gradually with composition and, for a line compound, may be essentially constant. Properties strongly dependent on the composition of a line compound are likely to involve low concentrations of intrinsic or extrinsic point defects such as vacancies and solutes; possible examples are color centers in insulators and channeling of electrons emitted by radioactive impurities in single crystals to determine their lattice locations [11]. In summary, the present findings suggest that it may be prudent to make pairs of measurements of other properties at compositions of the opposing phase boundaries.

Acknowledgments I thank Aurélie Favrot, Li Kang, Egbert Rein Nieuwenhuis, Denys Solodovnikov, Jipeng Wang and, especially, Matthew O. Zacate, who contributed significantly to the measurements and analysis. This work was supported in part by the National Science Foundation under Grants DMR 00-91681 and 05-04843 (Metals Program).

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