

Electric-field gradients used to measure atomic short range order: $U(\text{In}_{0.5}\text{Sn}_{0.5})_3$ as a case-study

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Abstract. A scheme is presented in order to obtain complete information on atomic short range order in crystalline materials based on measuring the electric-field gradient on a probe nucleus. Limitations and possible improvements of the method are discussed. When applied to $U(\text{In}_{0.5}\text{Sn}_{0.5})_3$, short range order with In–Sn attraction is found.

PACS. 75.40.-s Critical-point effects, specific heats, short-range order – 76.80.+y Mössbauer effect; other γ -ray spectroscopy – 71.27.+a Strongly correlated electron systems; heavy fermions

1 Introduction

Extended X-ray Absorption Spectroscopy (EXAFS) and diffuse scattering of X-rays on single crystals [1, 2] are the techniques most often used to study atomic Short Range Order (SRO). However, they are not always applicable. Less standard methods are to be used when either no – or only small – single crystals can be grown or when the disordered atoms have comparable atomic numbers. The use of synchrotron radiation can circumvent the limitation due to small single crystals. The limitation due to constituents of similar Z can be encompassed by preparing samples with mono-isotopic atoms and investigating them by diffuse scattering of neutrons. Recently also the possibility to measure SRO by the production of γ -ray holograms has been proposed [3, 4]. All these methods however are in one way or another difficult to apply. Hyperfine interaction techniques may offer an alternative approach at least in some particular cases. Hyperfine interaction quantities, especially the electric-field gradient (efg), are extremely sensitive to the local electronic environment, and hence to the nature of the nearest neighbours. In this paper we describe a scheme to derive from the measured efg the SRO-parameters and discuss possible improvements to overcome the (still severe) limitations in the present approach. By applying this scheme to $U(\text{In}_{0.5}\text{Sn}_{0.5})_3$ we collect evidence for the existence of SRO in this material.

As a function of Sn-concentration, the pseudo-binary system $U(\text{In}_{1-x}\text{Sn}_x)_3$ shows an evolution from a mainly

localized magnetic material ($U\text{In}_3$) to delocalised band-like behaviour ($U\text{Sn}_3$) [5]. In the region near $x = 0.6$ it is not yet clear whether the system behaves as a heavy-fermion or rather as a spinfluctuating system. U sits at the Au-position in this AuCu_3 -structure, In and Sn are distributed over the Cu-sublattice. In the discussion on the electronic behaviour in material, the possible influence of atomic SRO is as yet ignored. However one cannot *a priori* exclude that a *non-random* (In, Sn)-distribution leads to a different ground state as compared with a random distribution. This system is also a typical example where diffuse X-ray scattering cannot be used to study SRO because only small single crystals can be produced, and In ($Z = 49$) and Sn ($Z = 50$) are next to each other in the periodic table. Furthermore, ^{111}In is not only the favorite perturbed angular correlation (PAC) probe and as such not an impurity in the compound, it also makes the PAC technique ideally suited for SRO studies in this particular system.

2 SRO and electric-field gradients

It lies in the nature of the problem that SRO-information is contained in diffuse, broad features. In a hyperfine interaction experiment, the presence of SRO is seen as a distribution in the measured quantities. As far as the electric-field gradient (efg) is concerned, the reason for this distribution is that each particular environment around the probe nucleus yields its own efg (characterized by its strength V_{zz} , asymmetry parameter η and possibly its absolute orientation). A Mössbauer, Perturbed Angular Correlation (PAC) or NMR-spectrum will hence contain

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many sub-spectra, each of them corresponding to slightly different types of environments. The classical way of analysis is unraveling such a complex spectrum in its components. This method may be applicable within the dilute impurity concentration range, but fails for a non-dilute mixture of two elements on the same sub-lattice. Such an impossible classical fit can be avoided by taking into account the distribution function $P(V_{zz}, \eta)$ rather than each particular environment. If both the relationships between $P(V_{zz}, \eta)$ and the experimental spectrum as well as between $P(V_{zz}, \eta)$ and the SRO are known, then SRO-information can be extracted from the experiment. The former relation is straightforward to obtain for each experimental technique. On the connection between $P(V_{zz}, \eta)$ and SRO, a quite general formulation has been given by Czjzek *et al.* [6, 7], where the point charge model was used to describe the charge distribution. In the present work, we follow a more brute-force oriented approach: many different SRO-situations are generated by computer. For each one, $P(V_{zz}, \eta)$ is obtained in a numerical/statistical way. The corresponding PAC-spectrum can then be compared with experiment.

The first step is to give a quantitative description of SRO. This can be done by the well-known Warren-Cowley parameters [1, 8, 9], which describe the probability to find a B-type atom at a certain neighbour position around an A-atom. In principle an infinite number of Warren-Cowley parameters is needed to describe the SRO completely, but in practice a set describing the probabilities for the first few neighbour shells is sufficient. Given such a set, a computer simulation can yield a piece of crystal with a type of SRO obeying these Warren-Cowley parameters. We wrote a program according to an algorithm given by Gehlen *et al.* [10] to obtain a piece of crystal with 60 000 atoms and periodic boundary conditions. The last step – determining which experimental Mössbauer, PAC or NMR spectrum will result from the simulated type of SRO – is the most difficult one. It is very feasible nowadays to calculate the efg at any position in a periodic structure by *ab initio* methods [11, 12]. The time needed to perform such a calculation highly depends on the number of atoms in the unit cell, and something like 100 atoms takes already weeks of CPU-time on a midrange server. Unfortunately, in our SRO-case there is no periodicity, hence the complete simulated crystal with its 60 000 atoms would have to be taken as the unit. Smaller cells are hardly possible: the smaller the simulated crystal the more (unphysical) constraints are put on the allowed types of SRO. Therefore we can exclude at the moment the efg-calculation by reliable *ab initio* methods. Instead we are forced to use the older and much less reliable, but computationally much faster, point charge model: the efg is thought as to arise from the lattice of ions in the neighborhood of a given position in the crystal [13]. We note that a point charge model largely fails in predicting the magnitude V_{zz} of an efg, but is most often correct as far as the symmetry is concerned (asymmetry parameter η and orientation). Hence we can to some degree justify the use of a point charge model

if our analysis is built on symmetry arguments only. The following procedure is practical:

- (1) measure the efg on some (impurity) probe nucleus;
- (2) simulate a crystal according to a set of Warren-Cowley parameters;
- (3) calculate by the point charge model (or by any method allowed within the computing facility at hand) the efg on any position available to the probe nucleus;
- (4) for any of the efg's found under (3) and properly weighted: calculate the experimental spectrum and add it to the sum of the already obtained spectra;
- (5) repeat (2) to (4) until the average spectrum obtained under (4) stabilizes;
- (6) compare the calculated spectrum from (5) with the measured spectrum from (1);
- (7) repeat from (2) on, until a suitable set of Warren-Cowley parameters is found.

For this scheme, it is required that the parent of the probe atom is a constituting element of the studied material. If not the probe atoms may not be equally distributed over all environments but preferentially attracted by some specific ones. In the latter case an erroneous conclusion about the SRO would be made. For a PAC- measurement on ^{111}Cd (parent ^{111}In) or a Mössbauer experiment on $^{119\text{m}}\text{Sn}$ in $\text{U}(\text{In}_{1-x}\text{Sn}_x)_3$, this condition is fulfilled. Note also that the weighting as indicated under (3) poses no problem: in the simulated crystal *e.g.* each In-position can be thought as to decay to a ^{111}Cd probe. Hence, if the efg is calculated on a ^{111}Cd -nucleus subsequently sitting at every In-position, then the most likely environments are automatically encountered most often.

All essential approximations are made in the point charge model under (3) and in no other part of the scheme. Within the point charge model, (possibly non-integer) ionic charges have to be attributed to the different atoms. These values have no clear physical meaning in a metallic compound like $\text{U}(\text{In}_{1-x}\text{Sn}_x)_3$. Also other doubtful parameters as the electronic enhancement factor k and the Sternheimer antishielding factor γ_∞ enter the point charge model. In order to render the use of this model nevertheless as justified as possible in our case, we need to distinguish between parameters which affect either the *magnitude* V_{zz} of the efg or its *asymmetry*. In an experiment, the latter category determines the shape of the experimental spectrum and the former its absolute “strength” (amount of splitting for Mössbauer, main frequency for PAC and position on the frequency axis for NMR). The symmetry of the efg is fully determined by the ionic charge distribution (it is not very likely in the case of a ^{111}Cd probe that local contributions to the efg have another symmetry than the ionic lattice) and not at all influenced [13] by the extra parameters k and γ_∞ . The role of the ionic charges is however more complicated. It can be proven that for a AuCu_3 structure the shape of the spectrum is determined by a shape parameter α :

$$\alpha = \frac{Z_{\text{U}} - [(1-x)Z_{\text{In}} + xZ_{\text{Sn}}]}{Z_{\text{Sn}} - Z_{\text{In}}}. \quad (1)$$

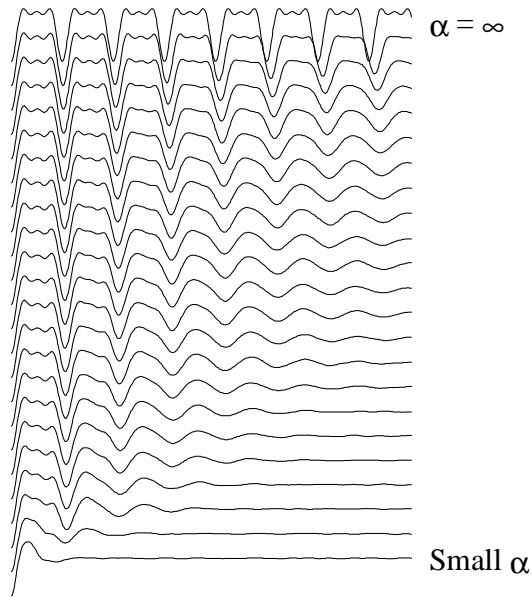


Fig. 1. PAC-spectra from a probe at the In-position, obtained by the point charge model from a simulated $\text{U}(\text{In}_{0.5}\text{Sn}_{0.5})_3$ -crystal with 60 000 atoms and without short range order. The shape parameter α is varied from a low value (below, large charge difference between In and Sn) to infinity (above, In and Sn have same charge).

Z_i is the ionic charge (valence) of the atom of type i . This can be understood from the fact that in a AuCu_3 -structure the strength of the efg is proportional to $Z_{\text{Au}} - Z_{\text{Cu}}$ [14]. Hence, the numerator of α gives the valence difference between U and an average (In, Sn)-atom, and thus measures the strength of an average efg. If the valence difference between In and Sn (the denominator) is very small with respect to the average efg (the numerator), then α is large and the spectrum will look almost like the one for pure UIn_3 or USn_3 . For large α (In and Sn very different) the spectrum is heavily damped. Note that α itself contains no strength-information, as both numerator and denominator are proportional to the strength. A different triplet of charges (Z_{U} , Z_{Sn} , Z_{In}) which gives the same α (obtained *e.g.* by doubling all Z_i) will yield a spectrum with the same shape but with a different strength. As the point charge model is unreliable as far as the magnitude (strength) of the efg is concerned but gives good results for the symmetry (shape), we completely neglect the strength-related parameters. In practice this means we fix all but one of the parameters k , γ_∞ , Z_{In} , Z_{Sn} and Z_{U} to an arbitrary value. By varying the remaining one, α is controlled, and hence the shape of the spectrum. Then the spectrum is compared with the measurement by simply rescaling it by an amount needed to give a best fit. Actually, this is nothing else than supposing that the magnitude of the efg as calculated by the point charge model is off by the same factor for all possible environments. As the environments are similar to a large degree (due to the similarity of In and Sn), this is not too bad an assumption.

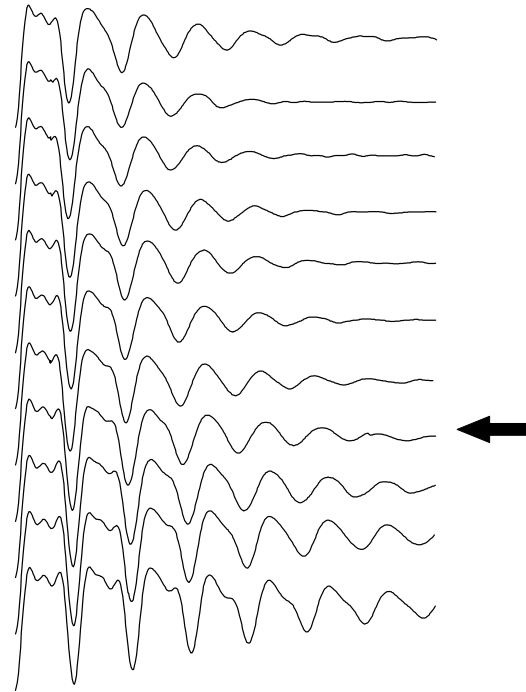


Fig. 2. Same conditions as in Figure 1. Now the shape parameter α is kept fixed at 6.0, while the In–Sn interaction for the first neighbour shell is varied from maximal In–Sn attraction (below) over no-interaction (arrow) to maximal In–Sn repulsion (above).

Before tackling a real experiment, we demonstrate the influence of some parameters on a PAC-spectrum for polycrystalline $\text{U}(\text{In}_{0.5}\text{Sn}_{0.5})_3$. In Figure 1, for a situation without SRO the shape-parameter α is varied from $\alpha \approx 0$ (below, the charge difference between In and Sn relative to the charge difference between U and an average (In, Sn)-atom is large) up to $\alpha \approx \infty$ (above, In and Sn have identical charges). The larger the difference between the ionic charges on In and Sn, the faster the PAC-spectrum is wiped out. In Figure 2, α is kept fixed at 6.0, and the first Warren-Cowley parameter describing the interaction of the parent In-atom with the first nearest neighbour shell is varied from In–Sn attraction (below) over no interaction (arrow) to In–Sn repulsion (above). In Figure 2 no Warren-Cowley parameters for higher shells are specified, which leaves a lot of freedom. In an actual calculation, the values of non-specified order parameters are implicitly determined by the algorithm used to produce the crystal. We checked that specifying the values for the first 4 nearest neighbour shells was sufficient in order to reproduce a calculated spectrum within experimental error. Note that when comparing Figure 2 with Figure 1, no obvious feature immediately signals the presence of SRO. The SRO manifests itself rather as small changes distributed over the PAC-spectrum as a whole.

Table 1. For the first 8 types of (In, Sn)-neighbours around an In-atom the following information is listed: number of atoms of that type, distance to the central In-atom, direction of the neighbour as seen from the central atom and Sn-concentration for neighbours of that type (in brackets: deviation of this local concentration from the bulk concentration 0.5). The interaction for the first 4 types was imposed to the simulation program. For all other neighbours further away no freedom appeared to be left.

(In, Sn) neighbour type	Number of (In, Sn)- neighbours	Distance from central In-atom	Direction	Sn-fraction and (difference from $x_{bulk} = 0.5$)
1	8	0.70711	(1 0 1)	0.65 (+0.15)
2	2	1.00000	(0 0 1)	0.15 (−0.35)
3	4	1.00000	(1 0 0)	0.25 (−0.25)
4	16	1.22474	(1 2 1)	0.58 (+0.08)
5	4	1.41421	(1 1 0)	0.34 (−0.16)
6	8	1.41421	(1 0 1)	0.30 (−0.20)
7	8	1.58114	(3 0 1)	0.60 (+0.10)
8	8	1.58114	(1 0 3)	0.60 (+0.10)

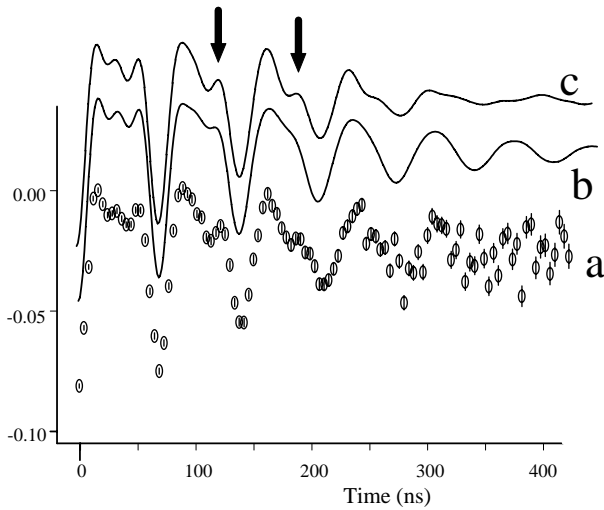


Fig. 3. (a) Room temperature ^{111}Cd PAC measurement on $\text{U}(\text{In}_{0.5}\text{Sn}_{0.5})_3$ (axes valid for this measurement). (b) Best fitting simulation with $\alpha = 6.0$ and no SRO. (c) Best fitting simulation with $\alpha = 6.0$ and SRO imposed for the 4 nearest types of neighbours. Arrows indicate the significant improvements of (c) over (b). Both simulations are shifted for clarity.

3 SRO in $\text{U}(\text{In}_{0.5}\text{Sn}_{0.5})_3$

Figure 3 shows a room temperature PAC-measurement on polycrystalline $\text{U}(\text{In}_{0.5}\text{Sn}_{0.5})_3$. When compared with a similar measurement for USn_3 (Fig. 4), it is clear that the disorder on the (In, Sn)-sublattice indeed causes a damping of the spectrum, as expected from Figure 1. The damping is not particularly strong however, indicating that there is not so much difference between In and Sn. In principle one should now, in the parameter space spanned by $(\alpha, WC_1, WC_2, WC_3, WC_4) - WC_i$ are Warren-Cowley parameters for the 4 nearest types of neighbour positions – find the quintet which yields a spectrum with the same shape as the measured one. Even with the point charge

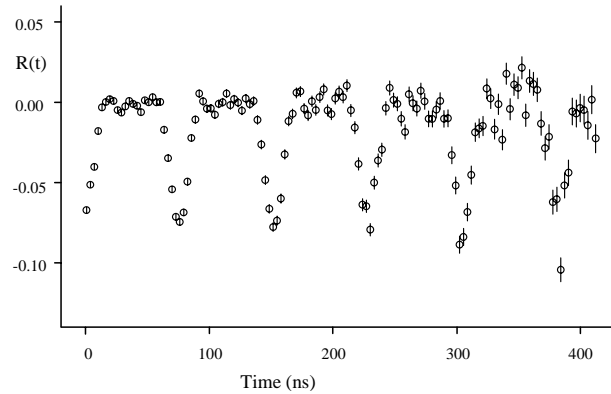


Fig. 4. ^{111}Cd PAC spectrum of USn_3 ($x = 1$) at 40 K.

model, this is extremely demanding with respect to CPU-time. Therefore we determined first the best α when a random (In, Sn)-distribution was assumed (*i.e.* the best fitting function from Fig. 1). This value turned out to be about 6. As the influence of α on the shape is much larger than the effect of WC_1 (Figs. 1, 2), which is again much larger than the influence of WC_2 , this approach is justified. It may be seen from Figures 1 and 3 that no zero-interaction spectrum has really the same shape as the measurement (follow the structure of the simulated spectra at the positions of the two arrows in Fig. 3). This implies that SRO must be present. After varying the first 4 Warren-Cowley parameters, the best shape was found to be the one labeled as (c) in Figure 3, which fits the data rather well. Translated into the Sn-fraction present in the n th neighbour shell around an In-atom (Cd-probe) this yields Table 1. There appears to be more Sn than average in the first shell (In–Sn attraction), less in the second, and so on with an oscillating behaviour.

A direct consequence of the existence of SRO in $\text{U}(\text{In}_{1-x}\text{Sn}_x)_3$ is the position where the magnetic/non-magnetic boundary lies. From previous PAC-measurements on this system with $x = 0.3$ [15], we know

a minimal *local* In-concentration should be reached in order to observe a stable local magnetic field. When In–In attraction is present, a macroscopically detectable long range magnetic order will occur at lower x than if In–Sn attraction happens. It can not be excluded that different sample growing techniques induce different types of SRO, which could help explain the variety of boundary-values found in $\text{U}(\text{In}_{1-x}\text{Sn}_x)_3$. To examine this, we annealed two samples with $x = 0.5$ for 24 h at 500 °C. One was cooled quickly by dropping in liquid nitrogen, while the other sample steadily cooled during a week. The resulting PAC-spectra were however the same, indicating that the type of SRO is rather independent of sample treatment.

4 Discussion

We do *not* claim that the SRO in $\text{U}(\text{In}_{1-x}\text{Sn}_x)_3$ really is of the type as given in Table 1, because the uncertainties contained in the point charge model are too crude. But we might at least conclude that there is a strong indication for a non-random (In, Sn)-distribution with possibly In–Sn attraction. The main conclusion from this paper – which we estimate far more important than the particular case of $\text{U}(\text{In}_{1-x}\text{Sn}_x)_3$ – is that by measuring the efg it is possible to characterize the SRO in a situation where conventional X-ray techniques would certainly fail due to the similarity of the disordered elements, provided an accurate and fast method to calculate the efg in a non-periodic structure is available. Further advantages of the efg-approach are that it can be used for both poly- and single crystals, while X-rays are limited to single crystals. It is also straightforward to incorporate higher order correlations in the analysis (X-rays are inherently sensitive only to pair correlations between atoms). This can reduce the remaining ambiguity when only a few neighbours can be detected [1]. Disadvantages are the fact that (the parent of) the nuclear probe should not be an impurity in the material. Also the disordered elements may not be too far apart in the periodic table, otherwise there will be not much detail in the experimental spectrum (but in such a case it is usually no problem to use X-rays). The main disadvantage is the heavy computational load, and related therewith the need to use

the inaccurate point charge model. Much improvement could be achieved by a substitution of the point charge model by an *ab initio* method capable of treating non-periodic materials. Such methods exist – *e.g.* the Coherent Potential Approximation [16] – but they should be extended first in order to be able to calculate hyperfine interaction quantities. A further refinement of the scheme can be made by allowing atomic displacements (see *e.g.* [17]), although this would again drastically increase the amount of freedom and hence the calculation time.

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