

A perturbed angular-correlation study of the electric-field gradient at the In site in compounds of the Hg-In alloy system

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 6711

(<http://iopscience.iop.org/0953-8984/6/33/018>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 20:20

Please note that [terms and conditions apply](#).

A perturbed angular-correlation study of the electric-field gradient at the In site in compounds of the Hg–In alloy system

P R J Silva†, H Saitovitch†, M Olzon-Dionysio‡ and M Forker†§

† Centro Brasileiro de Pesquisas Físicas, Rua Dr Xavier Sigaud 150, 22290 Rio de Janeiro, Brazil

‡ Departamento de Física da Universidade Federal de São Carlos, São Carlos, SP, Brazil

Received 30 March 1994, in final form 23 May 1994

Abstract. The electric-field gradient (EFG) of dilute ^{111}Cd nuclei in compounds of the Hg–In alloy system has been investigated by perturbed angular correlation (PAC) measurements of the electric quadrupole interaction (QI) of ^{111}Cd on In sites. It has been found that, as in the pure metals Hg and In, the quadrupole frequency decreases with increasing temperature according to the relation $\nu_q(T) = \nu_q(0)(1 - BT^{3/2})$. The strength constant B in the intermetallic phases, however, is up to 35% smaller than in the pure metals. The QI parameters are consistent with an orthorhombic γ -Pu-type lattice for β -Hg ($\text{Hg}_{30}\text{In}_{20}$), but are difficult to reconcile with the structures proposed for HgIn. An intermetallic compound HgIn₂ has not been observed.

1. Introduction

In this paper we report on an investigation of the electric-field gradient (EFG) of the nuclear probe ^{111}Cd at the In site in compounds of the Hg–In alloy system, which has been carried out by perturbed angular-correlation (PAC) measurements of the electric quadrupole interaction (QI) of ^{111}Cd .

A study of the EFG of Cd in Hg–In intermetallic compounds is of interest from two aspects. First, the EFG at nuclear probes in non-cubic sp metals has been found to decrease with increasing temperature according to a $BT^{3/2}$ relation (Christiansen *et al* 1976), a behaviour generally attributed to the lattice vibrations of the host atoms (Nishiyama *et al* 1976). This interpretation is supported e.g. by the observation of a correlation between the strength parameter B and the inverse spring constant $(M\theta_D^2)^{-1}$ of the lattice, where θ_D is its Debye temperature and M the atomic mass (Mahnke *et al* 1979).

While pure sp metals and dilute impurity systems have been extensively investigated, much less is known about the temperature behaviour of the EFG in sp intermetallic compounds (Radhakrishna and Mungurwadi 1969). It is for example an open question whether the $T^{3/2}$ relation is maintained and as universally followed in compounds as in the pure metals.

The Hg–In alloy system appears particularly interesting for a study of the EFG in sp compounds: both In and Hg are non-cubic metals, in both the EFG of dilute Cd probes follows the $T^{3/2}$ relation (Haas and Shirley 1973, Mahnke *et al* 1979, Christiansen *et al* 1976) and in spite of the large mass difference of these metals, for Cd probes they have practically the same strength parameter B , which in the lattice vibration concept is a

§ On leave of absence from Institut für Strahlen- und Kernphysik der Universität Bonn, Nussallee 14–16, D-53115 Bonn, Germany.

consequence of the smaller Debye temperature of the low-melting Hg. The Hg–In system contains several non-cubic intermetallic compounds and therefore offers the opportunity to study the temperature behaviour of the EFG as a function of the concentration of two constituents with the same relative temperature dependence of the pure metals.

The second aspect of interest concerns the crystal structure of some of the In–Hg intermetallic compounds. In is soluble in rhombohedral α -Hg up to about 15 at.%. For higher In concentrations the intermetallic compounds HgIn and HgIn₂ and single-phase fields around Hg₈₀In₂₀ (β -Hg) and Hg₁₀In₉₀ (β -In) have been reported to exist in the phase diagram (Gubbels 1990).

There are discrepancies in the crystal structures proposed by different authors for HgIn and Hg₈₀In₂₀. According to Mascarenhas (1970) HgIn is a disordered compound with a rhombohedral unit cell, while Segnini and Giessen (1972) deduce an ordered CuPt-L1₁-type rhombohedral structure from the x-ray diffraction pattern. For the single-phase field around Hg₈₀In₂₀ Mascarenhas (1970) proposes an FCT structure, while Mahy and Giessen (1979) find that the structure is orthorhombic, of γ -Pu type, with eight random Hg₈₀In₂₀ atoms in position (8a). The EFG is sensitive to the lattice symmetry and in the case of disordered compounds EFG distributions are expected. A study of the EFG in these compounds may therefore help to clarify their crystal structure.

Using the PAC nucleus ¹¹¹Cd as a probe, we have investigated the EFG in the In–Hg alloy system as a function of temperature at the compositions Hg₉₂In₈ (α -Hg), Hg₈₇In₁₃ (α -Hg), Hg₈₀In₂₀ (β -Hg), HgIn, HgIn₂, Hg₁₀In₉₀ (β -In) and Hg₆In₉₄ (α -In).

2. Experimental details

The PAC measurements were carried out with the 172–247 keV cascade of ¹¹¹Cd, which is populated in the EC decay of the 2.8 d isotope ¹¹¹In. The radioactivity was produced via the reaction ¹⁰⁹Ag(α , 2n)¹¹¹In by irradiating a natural Ag foil in a cyclotron with 28 MeV α -particles. The irradiated spot of the Ag foil was dissolved in concentrated HNO₃ and AgCl was precipitated by adding HCl. After separating the precipitate, the radioactive solution was dried and washed several times with distilled water and then dropped onto a thin In foil. The foil was melted in an H₂ flux and kept at 400 °C for about 1 h. After cooling, the sample was briefly washed in dilute HNO₃. The PAC spectrum measured after this procedure (the topmost spectrum in figure 1) corresponds to the well known PAC pattern of ¹¹¹Cd in metallic In, with the quadrupole frequency $\nu_q(302\text{ K})=17.6(2)$ MHz in agreement with the values given in the literature (Vianden 1987). At room temperature, metallic In was found to dissolve readily in liquid Hg up to concentrations of about 70 at.%. For the preparation of the compositions Hg₉₂In₈, Hg₈₇In₁₃, Hg₈₀In₂₀, HgIn and HgIn₂ the ¹¹¹In-doped In metal was brought into contact with a drop of liquid Hg at room temperature on a thin teflon foil and after at most a few minutes the In metal was completely dissolved. For the compositions Hg₁₀In₉₀ and Hg₆In₉₄ the constituents were heated in vacuum to about 200 °C.

The PAC measurements were carried out with a standard four-NaI(Tl)-detector set-up. A closed-cycle He refrigerator was used to vary the sample temperatures between 26 K and 300 K. Typical spectra for the different compositions are shown in figure 1.

3. Data analysis and results

The electric quadrupole interaction (QI) between the nuclear quadrupole moment Q and the EFG tensor can be expressed by two independent parameters, the quadrupole frequency

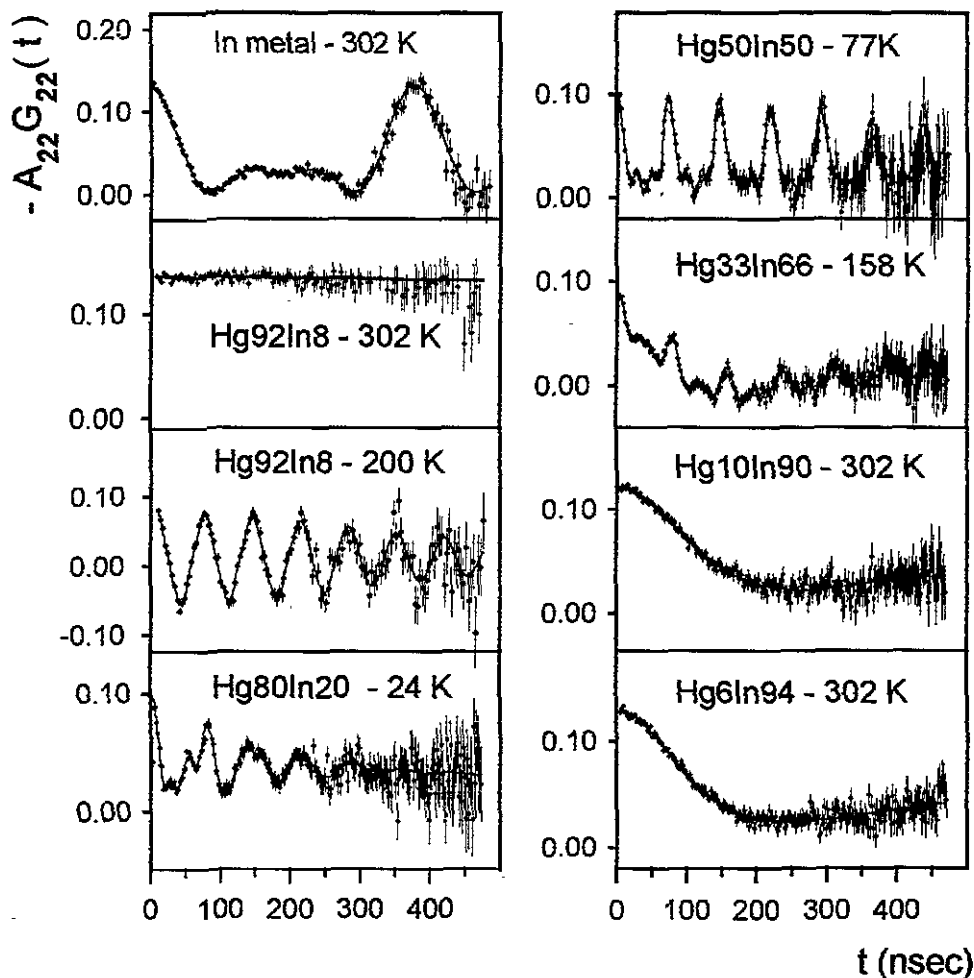


Figure 1. PAC spectra of ^{111}Cd in compounds of the Hg-In alloy system.

$v_q = eQV_{zz}/h$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, where V_{ii} ($i = x, y, z$) are the principal-axis components of the EFG with $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$.

The time modulation of the angular correlation caused by a hyperfine interaction can be described by the perturbation factor $G_{kk}(t)$ (see e.g. Frauenthal and Steffen 1965 for details). Here we are dealing with perturbations by dynamic and static QIs in the liquid and solid phases of the investigated compounds, respectively.

Rapidly fluctuating, isotropic interactions caused by the Brownian motion in a liquid lead to an exponential attenuation of the angular correlation: $G_{kk}(t) = \exp(-\lambda_k t)$, with the relaxation parameter $\lambda_k \propto \omega^2 \tau_c$, where ω is the average interaction frequency and τ_c the correlation time of the fluctuation (Abragam and Pound 1953). For all compositions $\text{Hg}_{100-x}\text{In}_x$ we observed practically unperturbed angular correlations in the liquid phase ($\lambda_2 \leq 3$ MHz), consistent with the fact that the correlation times in liquids are usually much shorter than the time window of the PAC probe ^{111}Cd ($\sim 10^{-6}$ s). As an example the spectrum of liquid $\text{Hg}_{92}\text{In}_8$ at 302 K is shown in figure 1.

For a static QI in a polycrystalline sample the perturbation factor $G_{kk}(t)$ has the general

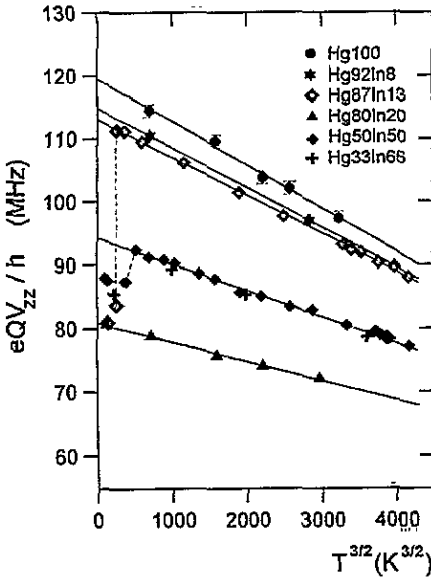


Figure 2. The temperature dependence of the quadrupole frequency ν_q of ^{111}Cd in compounds of the Hg-In alloy system. The solid lines are fits of the relation $\nu_q(T) = \nu_q(0)(1 - BT^{3/2})$ to the experimental data.

form

$$G_{kk}(t; \nu_q, \eta, \delta) = s_{k0} + \sum_n s_{kn} \cos \omega_n t \exp[-1/2(\delta\omega_n t)^2]. \quad (1)$$

The hyperfine frequencies ω_n are the transition frequencies between the hyperfine levels into which a nuclear state is split by the QI. These frequencies depend on the quadrupole frequency ν_q and the asymmetry parameter η . In polycrystalline samples the amplitudes s_{kn} are functions of η only. The number of terms in (1) depends on the nuclear spin of the nuclear state under consideration. The exponential factor accounts for possible distributions of the hyperfine frequencies caused by defects and other imperfections. The parameter δ is the relative width of a Gaussian distribution. Frequently, several fractions of nuclei with different QIs are found in the same sample. The effective perturbation factor is then given by

$$G_{kk}(t) = \sum_i f_i G_{kk}(t; \nu_{qi}, \eta_i, \delta_i) \quad (2)$$

where f_i (with $\sum_i f_i = 1$) is the relative intensity of the i th fraction with the QI parameters $[\nu_{qi}, \eta_i, \delta_i]$. These parameters were determined for the different compositions $\text{Hg}_{100-x}\text{In}_x$ and temperatures by a least-squares fit of (2) to the measured PAC spectra.

At practically all compositions the amplitudes s_{kn} of the various oscillatory terms of the perturbation factor (1) were found to differ more or less strongly from the theoretical values for polycrystalline samples, which occurs when the interaction has a preferred orientation relative to an external frame of reference. This effect was most pronounced in the case of $\text{Hg}_{92}\text{In}_8$, which—as shown by the PAC spectrum of this composition at 200 K in figure 1—solidified as an almost perfect single crystal with the symmetry axis perpendicular to the detector plane. To allow for these texture effects, the oscillation amplitudes s_{kn} of the perturbation factor were treated as free parameters in the least-squares-fit procedure. In the following we shall summarize the results of the fits concerning the number of sites and their relative intensities, the symmetry of the EFG and the relative width of the frequency distribution. The values of the quadrupole frequency obtained for different compositions are collected in figure 2, where ν_q is plotted versus a $T^{3/2}$ temperature scale.

$Hg_{92}In_8$. Single-site spectra with axial symmetry of the interaction ($\eta = 0$) are observed. The width of the Gaussian frequency distribution is $\delta \simeq 0.025(5)$ at all temperatures.

$Hg_{87}In_{13}$. For $T \leq 40$ K single-site spectra are observed with QI parameters identical to those of β -Hg ($Hg_{80}In_{20}$, see below): $\eta = 0.36$, $\delta \simeq 0.08(1)$, $\nu_q = 81.2(5)$ MHz at 26 K. Upon heating above 40 K, a second, axially symmetric site appears with a relative intensity of about 65% and the same frequency ν_q as in $Hg_{92}In_8$ (α -Hg). When temperatures $T > 40$ K are reached by cooling from higher temperatures, the axially asymmetric component does not appear in the spectra. These observations indicate that for $Hg_{87}In_{13}$ the β -Hg \rightarrow α -Hg transition occurs at about 40 K and that a considerable fraction of the sample is retained in the β -phase when the compound is heated across the transition temperature. The values of $\nu_q(Hg_{87}In_{13})$ shown in figure 2 for $T > 40$ K correspond to the quadrupole frequency of the majority fraction, i.e. α - $Hg_{87}In_{13}$.

$Hg_{80}In_{20}$. Single-site spectra are observed with $\eta = 0.36(1)$ and $\delta = 0.079(5)$ at 24 K. The asymmetry parameter decreases by less than 20% between 4 K and 240 K. The width of the frequency distribution is temperature independent.

$Hg_{50}In_{50}$. Single-site spectra are observed with $\eta = 0$ and $\delta = 0.015(5)$ at all temperatures.

$Hg_{33}In_{67}$. Two-site spectra, showing a rapid oscillation of small amplitude superimposed on a slow decay of the anisotropy, are observed. The QI parameters of the dominant site ($f_1 \simeq 0.65(5)$) correspond to those of β -In ($In_{90}Hg_{10}$, see below): a broad frequency distribution ($\delta \simeq 0.4$, $\eta \simeq 0.4$) with a centre frequency ν_q varying from 11(1) MHz to 8(1) MHz between 26 K and 235 K. The QI parameters of the minority site ($f_2 = 1 - f_1 = 0.35$, $\eta = 0$, $\delta = 0.030(5)$, ν_q given by the crosses in figure 2) are identical to those of the composition $In_{50}Hg_{50}$.

$Hg_{10}In_{90}$. A weakly perturbed, single-site spectrum, measured at 302 K only, is observed. The best fit is obtained for a broad frequency distribution ($\delta \simeq 0.3$, $\eta \simeq 0.4$) centred at $\nu_q \simeq 7(1)$ MHz, but as the perturbation is very weak, a description by a unique, axially symmetric interaction cannot be completely excluded.

Hg_6In_{94} . Weakly perturbed single-site spectra are observed, measured at 30 K and 302 K. As for $Hg_{10}In_{90}$, the best fits are obtained with a broad frequency distribution ($\delta \simeq 0.3-0.4$, $\eta \simeq 0.4$) with centre frequencies of $\nu_q \simeq 11.0(5)$ MHz and 8.0(5) MHz at 30 K and 302 K, respectively.

4. Discussion

The information obtained by this study on the temperature dependence of the EFG in compounds of the Hg-In alloy system is collected in figure 2, where we have plotted the quadrupole frequency ν_q of dilute ^{111}Cd in pure α -Hg, α - $Hg_{92}In_8$, α - $Hg_{87}In_{13}$, β - $Hg_{80}In_{20}$ and $HgIn$ versus a $T^{3/2}$ temperature scale. The values for pure Hg were taken from Mahnke *et al* (1979). The crosses in figure 2 indicate the frequency of the minority fraction of the composition $Hg_{33}In_{66}$ (see above). It is safe to assume that ^{111}Cd occupies the In site in these alloys. The possibility of a site change by the $^{111}In \rightarrow ^{111}Cd$ transmutation can be excluded because the threshold energies for atomic displacements are much larger than the recoil of ^{111}Cd caused by the neutrino emission in the EC of ^{111}In (3.2 eV), also for metals with low melting points (Landolt-Bornstein 1991).

The data in figure 2 have two interesting aspects: first, the quadrupole frequency follows a $T^{3/2}$ relation very accurately in all cases and second, the compounds differ in the relative

temperature dependence of the EFG: in the compounds β -Hg and HgIn the decrease of ν_q with temperature is considerably slower than in pure and In-doped α -Hg.

The values of the strength parameter B and the saturation frequency $\nu_q(0)$, obtained by fitting the expression $\nu_q(T) = \nu_q(0)(1 - BT^{3/2})$ to the experimental data, are listed in table 1, which also shows the $V_{zz}(0)$ component of the EFG calculated from $\nu_q(0)$ with the quadrupole moment $Q = 0.83(13)$ barns (Herzog *et al* 1980) of the 247 keV state of ^{111}Cd . The errors given for $V_{zz}(0)$ consider only the uncertainty of the time calibration and not the error of the quadrupole moment.

Table 1. The saturation value $\nu_q(0)$, the corresponding EFG component $V_{zz}(0)$ and the strength parameter B of ^{111}Cd in compounds of the Hg-In alloy system, obtained by fitting the expression $\nu_q(T) = \nu_q(0)(1 - BT^{3/2})$ to the experimental values of $\nu_q(T)$.

Compound	$\nu_q(0)$ (MHz)	$V_{zz}(0)$ (10^{17} V cm $^{-2}$)	B (10^{-5} K $^{-3/2}$)
Hg ₁₀₀	119.2(22)	5.9(1)	-5.74(30)
Hg ₉₂ In ₈	114.8(5)	5.7(1)	-5.48(30)
Hg ₈₇ In ₁₃	113.0(5)	5.6(1)	-5.31(15)
Hg ₈₀ In ₂₀	80.9(5)	4.0(1)	-3.79(15)
Hg ₅₀ In ₅₀	93.0(5)	4.6(1)	-4.27(15)

According to the data in table 1, the addition of In to Hg causes a decrease of the strength parameter B . In the α -phase of Hg the effect is small: within the errors the relative temperature dependence within the series Hg₁₀₀, Hg₉₂In₈, Hg₈₇In₁₃ may be constant or decrease at most by a few per cent. Compound formation, however, leads to a pronounced decrease of the strength parameter: in β -Hg (Hg₈₀In₂₀) the parameter B is 35% smaller than in the pure and the In-doped α -phase of Hg. If one accepts lattice vibrations as the main source for the temperature dependence of the EFG, the decrease of the parameter B implies smaller mean square displacements $\langle x^2 \rangle$ of the atoms. Since the addition of In reduces the average mass of the nearest neighbours of the probe, smaller values of $\langle x^2 \rangle$ correspond qualitatively to an increase of the Debye temperature relative to that of α -Hg. A quantitative analysis is difficult, as the relation of the strength parameter B and the mass in the case of two different atoms is not known. If one assumes that the relation between B and the spring constant ($M\theta_D^2$) for pure metals and dilute impurity systems (Mahnke *et al* 1979) also holds for binary sp compounds, with M the average mass of the constituents, one estimates from the measured B values Debye temperatures $\theta_D = 100$ K and 110 K for β -Hg and HgIn, respectively, which can be compared to $\theta_D = 90$ K and 110 K for pure Hg and In, respectively.

In both α -phases of the Hg-In system the quadrupole frequency ν_q at a given temperature decreases with increasing concentration of the other element. For α -Hg the effect is small: between Hg₁₀₀ and Hg₈₇In₁₃ $\nu_q(0)$ decreases at most by 5% (see table 1). The addition of Hg to α -In, however, has a strong influence on ν_q : at 300 K the quadrupole frequency in Hg₆In₉₄ ($\nu_q(302\text{ K}) = 8$ MHz) is about 50% smaller than in pure In ($\nu_q(302\text{ K}) = 17.6$ MHz). This is in agreement with previous NMR measurements of the ^{115}In QI in In-rich In-Hg alloys at 4.2 K by Thatcher and Hewitt (1970). Qualitatively, the different concentration dependence of the QI in α -In and α -Hg can be related to the lattice parameter variation in the two phases: the c/a -ratio of BCT α -In ($c/a > 1$) decreases considerably with increasing Hg concentration towards cubic symmetry (Thatcher and Hewitt 1970), whereas the parameters of the rhombohedral unit cell of α -Hg are practically unaffected by the addition of In (Mascarenhas 1970).

The QI parameters [ν_q, η, δ] also carry some information on the Hg-In phase diagram and the lattice structure of the different compounds.

(i) The observation of the β -Hg \rightarrow α -Hg transition in $\text{Hg}_{87}\text{In}_{13}$ at 40 K, clearly visible in figure 2, confirms (Gubbels 1990) that at low temperatures the α -phase of Hg extends up to an In concentration of about 12–13 at.%. The axial symmetry of the EFG in α -Hg is consistent with its rhombohedral crystal structure.

(ii) The QI parameters of HgIn are difficult to reconcile with either of the two structures proposed for this compound. In table 2 we compare the experimental EFG values to the ionic EFG contribution $(1 - \gamma_{\infty})V_{zz}^{\text{latt}}$ determined by a point-charge lattice-sum calculation for rhombohedral Hg, orthorhombic γ -Pu-type $\text{Hg}_{80}\text{In}_{20}$ and the two structures proposed in the literature for HgIn. In the following the HgIn structure proposed by Mascarenhas (1970) (disordered, with one atom in the rhombohedral unit cell) shall be denoted as HgIn-A, and the ordered PtCu-L1₁-type structure proposed by Segnini and Giessen (1972) as HgIn-B. For ordered structures charges 2+ and 3+ have been used for Hg and In, respectively. In the case of disordered structures the lattice-sum calculation has in principle to be carried out for a statistical distribution of atoms of different charges, which results in an EFG distribution. For the present discussion we mainly require the order of magnitude of the lattice EFG. For disordered $\text{Hg}_{80}\text{In}_{20}$ and HgIn we have therefore calculated only the average EFG by assuming the same charge 2.2+ and 2.5+, respectively, for all lattice sites. $(1 - \gamma_{\infty}) = 30.3$ is the Sternheimer correction for Cd^{2+} . As expected from the lattice symmetry, the calculated EFG of Hg and both structures proposed for HgIn is axially symmetric ($\eta = 0$) in agreement with the experimental observation. For Hg, $\text{Hg}_{80}\text{In}_{20}$ and the structure of HgIn proposed by Mascarenhas (1970) (HgIn-A) the enhancement of the ionic EFG by valence and conduction electrons, expressed in table 2 by the ratio $\alpha = V_{zz}/(1 - \gamma_{\infty})V_{zz}^{\text{latt}}$, is of the same order $\alpha \simeq 1$ –3 as generally found for the pure sp metals. For the ordered PtCu-L1₁-type structure proposed for HgIn by Segnini and Giessen (HgIn-B), however, the calculated ionic EFG is more than a factor of 10 smaller than the measured value. This small value results from the fact that for one Hg atom in (a):0, 0, 0 and one In atom in (b): $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ of the rhombohedral PtCu unit cell the contributions of the Hg^{2+} and In^{3+} sublattices to the ionic EFG at the In site have very similar magnitudes, but opposite sign, and therefore cancel to a large extent. So, for a PtCu L1₁ structure of HgIn the measured EFG is much larger than expected from the systematics of the enhancement factor α in sp systems and under this aspect one would favour the structure proposed by Mascarenhas (1970) for which α is of the correct order of magnitude.

Table 2. A comparison of the experimental value V_{zz} (sign undetermined) of the EFG of ^{111}Cd in Hg-In compounds and the result $(1 - \gamma_{\infty})V_{zz}^{\text{latt}}$ of a point-charge lattice-sum calculation. In the case of HgIn $(1 - \gamma_{\infty})V_{zz}^{\text{latt}}$ has been calculated for the disordered rhombohedral lattice proposed by Mascarenhas (1970) (denoted below HgIn-A) and the ordered CuPt L1₁ structure proposed by Segnini and Giessen (1972) (denoted as HgIn-B).

Compound	$V_{zz}(0)$ (10^{17} V cm $^{-2}$)	$(1 - \gamma_{\infty})V_{zz}^{\text{latt}}$ (10^{17} V cm $^{-2}$)	$\alpha = V_{zz}/(1 - \gamma_{\infty})V_{zz}^{\text{latt}} $
Hg ₁₀₀	5.9(1)	2.70	2.2
Hg ₈₀ In ₂₀	4.0(1)	2.05	1.9
HgIn-A	4.6(1)	3.48	1.3
HgIn-B	4.6(1)	-0.35	13.2

On the other hand, in an ordered lattice containing two different atoms A and B the EFG has the same value on all equivalent sites, whereas in the disordered case each probe will

see a different distribution of atoms A and B on the available lattice sites and if the EFG contributions of A and B differ, due e.g. to different charge states, an EFG distribution will result. We have found only a very small frequency distribution ($\delta = 0.015(5)$) for HgIn, which argues against the disordered lattice proposed by Mascarenhas (1970).

The temperature dependence of the quadrupole frequency in HgIn shows a discontinuity around 50 K (see the dotted line in figure 2), which possibly indicates a change in symmetry at low temperatures.

(iii) The finite asymmetry of the EFG ($\eta = 0.36$) and the rather large frequency distribution ($\delta = 0.08$) observed in the single-phase field around $\text{Hg}_{80}\text{In}_{20}$ are consistent with the orthorhombic, disordered structure of γ -Pu type proposed by Mahy and Giessen (1979) for β -Hg, but incompatible with the FCT structure suggested by Mascarenhas (1970). In a tetragonal lattice the EFG is axially symmetric. The lattice-sum calculation yields an asymmetry parameter of $\eta = 0.52$ in reasonable agreement with the experimental value of $\eta = 0.36$, considering that the same average charge has been used for Hg and In.

(iv) The phase diagram of the Hg-In system given by Gubbels (1990) shows an intermetallic compound HgIn_2 , which decomposes into HgIn and β -In at $T \geq 200$ K. We have not been able to find this intermetallic phase between 32 K and 230 K. At the composition $\text{Hg}_{33}\text{In}_{66}$ the PAC spectra show a mixture of two distinct compounds (see figure 1), which can be identified unambiguously from their QI parameters as HgIn and β -In. (See the perfect agreement of the quadrupole frequencies of HgIn (diamonds) and of the minority component of $\text{Hg}_{33}\text{In}_{66}$ (crosses) in figure 2).

(v) Although the single-phase field around $\text{Hg}_{10}\text{In}_{90}$ (β -In) is known to be FCC (Cu type, Coles *et al* 1963), we have observed a weak QI in this phase, which reflects the perturbation of the cubic symmetry by the disordered occupation of the lattice sites with two different types of atom. The same effect leads to an EFG distribution when a few Hg and In atoms are dissolved in α -In and α -Hg, respectively. At first sight the distribution in α -Hg ($\text{Hg}_{92}\text{In}_8$: $\delta = 0.025$) seems to be much smaller than in α -In ($\text{Hg}_6\text{In}_{94}$: $\delta = 0.3$ – 0.4), but actually both distributions have the same absolute width: $\delta\nu_q \simeq 3$ – 4 MHz.

In summary, we have investigated the EFG of dilute ^{111}Cd nuclei in compounds of the Hg-In alloy system and found that as in the pure metals Hg and In the quadrupole frequency decreases with increasing temperature according to the relation $\nu_q(T) = \nu_q(0)(1 - BT^{3/2})$. The strength constant B in the intermetallic phases, however, is up to 35% smaller than in the pure metals, suggesting that the compound formation is accompanied by an increase of the Debye temperature relative to α -Hg. The QI parameters are consistent with a disordered orthorhombic γ -Pu-type crystal structure for $\text{Hg}_{80}\text{In}_{20}$, but difficult to reconcile with either of the two structures proposed for HgIn (Segnini and Giessen 1972 (CuPt L1₁), Mascarenhas 1970 (disordered rhombohedral)). An intermetallic compound HgIn_2 has not been observed.

Acknowledgments

One of the authors (MF) would like to express his appreciation of the kind hospitality extended to him by the Centro Brasileiro de Pesquisas Fisicas. The cyclotron irradiations were carried out by the Instituto de Engenharia Nuclear, Rio de Janeiro. Dr Marta Marszalek, Cracow helped with the lattice-sum calculations. This work was supported by CNPq, Brazil.

References

Abragam A and Pound R V 1953 *Phys. Rev.* **92** 943

- Christiansen J, Heubes P, Keitel R, Loeffler W, Sandner W and Witthuhn W 1976 *Z. Phys.* B 24 177
- Coles B R, Merriam M F and Fisk Z 1963 *J. Less-Common Met.* 5 41
- Frauenfelder H and Steffen R M 1965 *Alpha, Beta, Gamma-ray Spectroscopy* ed K Siegbahn (Amsterdam: North-Holland)
- Gubbels G H M 1990 *Z. Metallk.* 81 203
- Haas H and Shirley D A 1973 *J. Chem. Phys.* 58 3339
- Herzog P, Freitag K, Reuschenbach M and Walitzki H 1980 *Z. Phys.* A 294 13
- Landolt-Börnstein New Series* 1991 Group III, vol 25, ed H Ullmaier (Berlin: Springer) p 1
- Mahnke H E, Dafni E, Rafailovich M H, Sprouse G D and Vapirev E 1979 *Phys. Lett.* 71A 112
- Mahy T X and Giessen B C 1979 *J. Less-Common Met.* 63 257
- Mascarenhas Y P 1970 *J. Appl. Crystallogr.* 3 294
- Nishiyama K, Dimmling F, Kornrumpf Th and Riegel D 1976 *Phys. Rev. Lett.* 37 357
- Radhakrishna Setty D L and Mungurwadi D B 1969 *Phys. Rev.* 183 387
- Segnini M and Giessen B C 1972 *Acta Crystallogr.* B 28 320
- Thatcher F C and Hewitt R R 1970 *Phys. Rev.* B 1 454
- Vianden R 1987 *Hyperfine Interact.* 35 1079