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Electric Quadrupole Interaction of ^{192}Tl(8$^-$) Nuclei in Hexagonal Tl and in Tetragonal In Metals

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ABSTRACT

The TDPAD technique has been used to measure the electric quadrupole coupling constants for the ^{192}Tl(8$^-$) isomer in hexagonal Tl at different temperatures and in tetragonal In at room temperature. The values measured were e^2qQ/h=24.0(15) MHz extrapolated to T=0 K, and 33.1(16) MHz at 293 K for the Tl and In hosts, respectively. The electric field gradient for Tl impurities in In was determined from systematics of isoelectric systems, yielding $|Q[^{192}Tl(8^-)]|$=0.44(7)b.

The almost perfect symmetry of the Tl crystalline structure makes this metal a sensitive probe to current models for electric field gradients in metals. The magnitude and temperature dependence of the field gradient in thallium metal are discussed within the framework of such models.

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1. Introduction

The electric field gradient (EFG) tensor in non-cubic metals has been extensively studied in recent years, both experimentally and theoretically[1]. Such studies are motivated by the sensitivity of that quantity to the exact charge distribution in the metal. Traditionally, an approximate expression

$$eq = eq_{latt}^{Coul}(1-\gamma_\infty) + eq_{el}(1-R) \qquad (1)$$

was used to describe the EFG. One contribution, eq_{latt}^{Coul}, originates from the Coulomb potential of the point charge ions in the lattice while $(1-\gamma_\infty)$ is the antishielding due to quadrupole polarization of the probe core electrons by charges which are further away. eq_{el} is the contribution to the EFG from the conduction electrons, having a non-uniform distribution reflecting the non-cubic crystal structure and (1-R) is a shielding factor for charges which are within the Wigner-Seitz cell, having a value closed to 1 for sp metals.

A different view of the EFG arose with discovery of the "Universal Correlation", relating the contribution from conduction electrons to that from the ions in the lattice[2]. According to that phenomenological correlation

$$eq_{el} \approx -K\, eq_{latt}^{Coul}(1-\gamma_\infty) \qquad (2)$$

K being a constant whose value is around 3. Another stimulating observation was that the temperature dependence of the EFG in many metals follows the rule[3]

$$eq(T) = eq(T=0)(1-BT^{3/2}) \qquad (3)$$

referred to as the $T^{3/2}$ law. Various theoretical approaches have been able to reproduce the temperature dependence in some cases[4-6], but none of them has

predicted an exact $T^{3/2}$ temperature dependence, as is observed for all sp metals in the intermediate temperature range, from first principles. The B coefficient in eq. (3) can be predicted from systematics for pure systems but as yet is not well understood, in particular for impurity systems.

The present work includes measurements of the electric quadrupole interaction for the ^{192}Tl(8^-) isomer, implanted into Tl at different temperatures and into In at room temperature. No previous experiments on quadrupole interaction of Tl isotopes were carried out since the ground states of the stable Tl isotopes have spin 1/2, and no suitable isomers for Mössbauer effect or perturbed angular correlation experiments were known until recently. The recent discovery of the 8^- ($T_{1/2}$=296(5)ns) isomer in ^{192}Tl [7] enabled the present work. Another Tl isomer reported recently[8] is not as suitable technically for quadrupole interaction studies.

The temperature dependence of the EFG for the pure system, Tl in Tl is of particular interest. In the framework of lattice vibration models this dependence is expected to be strong due to the low Debye temperature of Tl(θ_D=89K) [9]. The temperature dependence of the EFG for ^{111}Cd [10] and ^{69}Ge [11] impurities in Tl was indeed found to be strong.

The lattice parameters ratio, c/a, for the Tl hcp crystal (c/a=1.599 at room temperature[12]) is close to the value $\sqrt{8/3}$=1.633 at which the lattice symmetry results in a vanishing EFG. The EFG is expected then to be very sensitive to variations in the lattice constants. Indeed, at a pressure of 35 kbar, the EFG for ^{111}Cd in Tl is reduced by about 24% as compared to its value at zero pressure.[13] This result is reproduced fairly well by a simple lattice sum over the Coulomb point charges, assuming the screening electrons

to be in a uniform compensating background. A more sophisticated pseudo-potential approach of the type suggested by ref. 5 predicts , according to the authors of ref. 13, by far a stronger pressure dependence, in complete disagreement with the experimental results.

The nuclear quadrupole moment of the ^{192}Tl(8$^-$) isomer was determined from a measurement in the In host. Usually, the EFG for a given probe-host system is determined from a measurement of the quadrupole coupling constant, e^2qQ/h, of a reference level whose quadrupole moment, Q, was determined for instance from atomic beam hyperfine interaction, quadrupole interaction studies in ionic crystals or from reliable nuclear structure arguments. Once the EFG for the probe-host system is determined using a reference quadrupole moment, it can serve to measure other nuclear quadrupole moments of levels in isotopes of the same element as the probe since the EFG is believed to be isotopic mass independent. Strictly, the EFG for Tl in In is not known. It is shown below, however, that under favourable conditions, such as in the present case, the requirement of a known reference quadrupole moment in an isotopic probe can be relaxed and the EFG for a host-probe combination can be estimated from a reference level in an isoelectric element.

2. Experimental Procedure and Results

The experiments were carried out using the time differential perturbed angular distribution (TDPAD) technique in the presence of an EFG in non-cubic hosts. A pulsed ^{16}O beam from the 14UD Koffler accelerator in Rehovot was used to populate, align and recoil implant the ^{192}Tl(8$^-$) isomers via the ^{181}Ta(^{16}O,5n)

reaction at a beam energy of 100 MeV. The beam pulse width was around 1 ns fwhm and the pulse repetition time was 1.2 μs, exceeding the isomeric lifetime by a factor of three. For the ^{192}Tl$\underline{\text{Tl}}$ measurements the target consisted of a 850 μg/cm^2 natural Ta foil pressed against a ∿0,5 mm thick Tl disk which was cut from a 99.9% pure Tl rod and flattened by a slight pressure. Appropriate target handling procedure was used to avoid oxidation. Upon inspection with a microscope, the Tl disks appeared to consist of microcrystals approximately 0,5 mm in diameter. Since the beam spot diameter was about 3 mm, it is assumed that the Tl was effectively a polycrystal host. Care was taken not to overheat the Tl target in order to avoid recrystallization with unknown orientation.[11] The measurements were repeated with a different Tl disk, to ensure the validity of the results. For measurements with In host, it was desirable to improve the ratio between Ta and In in order to reduce γ-radiation from nuclear reactions in the In. Four layers, each consisting of 1.2 mg/cm^2 In evaporated onto 1 mg/cm^2 Ta were pressed against a thick ^{208}Pb backing and installed with the Ta sides towards the beam. An average beam energy of 100 MeV at the Ta layers was obtained by increasing the bombardment energy to 106 MeV. In either case, the target was mounted on a copper block that could be cooled by liquid nitrogen and/or heated by a resistance heater.

Gamma-rays from the isomeric decay were detected by two Ge(Li) spectrometers, placed at 0° and 90° relative to the beam direction. Energy and time of the radiation were detected with the usual fast-slow technique and time spectra for energy windows of interest were accumulated in an online computer. Windows were set on the 251 keV photopeak from the $8^- \rightarrow 7^+$ transition in ^{192}Tl,

and on the background above and below the photopeak. The two spectrometers were physically interchanged in the middle of each run to eliminate the dependence on the specific time response function of the individual spectrometers. For each measurement, a ratio function was derived, where:

$$R(t) = \frac{Y_1(0^o)+Y_2(0^o)-Y_1(90^o)-Y_2(90^o)}{Y_1(0^o)+Y_2(0^o)+Y_1(90^o)+Y_2(90^o)} \tag{4}$$

$Y_i(\theta)$ being the time spectrum of the detector i at angle θ, after background subtraction and normalization. Ratio functions for T1Tl and T1In are shown in Fig. 1 and Fig. 2 respectively.

The experimental ratio functions were least squares fitted to the expression

$$R(t) \approx \frac{3a_2G_{22}(t)}{4+a_2G_{22}(t)} \tag{5}$$

with

$$G_{22}(t) = \sum_{n=o}^{n_{max}} s_{2n} \cos(n\omega_o t) \tag{6}$$

where, a_2 is an angular distribution coefficient,[14] the s_{2n} coefficients are given in ref. 15 and $\omega_o=(\pi/80)e^2qQ/h$ for I=8. The fitting results are summarized in Table 1. Repeated results for the ^{192}T1Tl case were consistent with one another and the average value has been adopted.

Underlying the analysis procedure is the assumption that the Tl isomers were subject to a unique axial symmetric electric field gradient in the non-cubic polycrystalline hosts. Because of the low frequencies involved only a fraction of the period, $T_o=2\pi/\omega_o$, could be observed within few lifetimes.

Therefore, the measurements are rather insensitive to a possible distribution in the interaction strength and to the host being a single or polycrystal. In the Tl host, the initial alignment was somewhat reduced as compared to the In host, in particular at low temperatures. Similar loss of anisotropy is found for ^{69}GeTl at low temperature,[11] the measured frequency still being in agreement with the expected value. It is therefore believed that also the results for TlTl were not strongly affected by radiation damage.

3. EFG Calibration in Isoelectric Systems

Traditionally, in order to determine the absolute magnitude of the EFG for a probe nucleus in a given host, a reference nuclear quadrupole moment of a level in an isotope of the probe element must be known as only the product $|q.Q|$ is measured (the sign of the EFG or of Q cannot be determined with the present experimental technique). In the present case the quadrupole coupling constants have been determined for the ^{192}Tl(8^-) state in Tl and in In but the nuclear quadrupole moment was not known and could not be computed from nuclear structure considerations since the isomer has a rather complex configuration[16]. We have determined the EFG for Tl in Tl from the known EFG for In in In [17] using a calibration procedure which is described below.

We consider systems with impurity and host belonging to the same column of the periodic table. Presumably, the introduction of the isoelectric ion does not change the local electronic structure of the host metal. If so, then the EFG induced at the probe's site by the non cubic host does not depend on the specific impurity. Since the effective EFG at the nuclear site

is the external contribution times an ionic antishielding factor, the relative EFG for different isoelectric impurities should depend only on the probes' antishielding factors. This situation has been noticed before for group IIB elements[18]. It is not expected that the suggested systematics will hold for ions with EFG from localized d or f electrons. We have checked all other cases in the literature, where the EFG is known for at least one probe in a host which is in the same column of the periodic table in addition to the pure system. The data are listed in Table 2, where the parameter:

$$R = [|eq|/(1-\gamma_\infty)]_{\text{impur. sys.}}/[|eq|/(1-\gamma_\infty)]_{\text{pure sys.}} \qquad (7)$$

is calculated for each case. To avoid the effect of different temperature dependence of the EFG in a given host for different impurities we have extrapolated the eq data to T=0K, using the known or an estimated temperature dependence of each system.

Our hypothesis predicts values of R close to unity for each one of the impurity-host systems in Table 2. With the exception of the group VA data, all the R values are in striking agreement with the predicted value, i.e. 1, suggesting that the assumptions behind the derivation are correct. The prediction is not borne out for the Bi host, probably due to the limited metallic nature of group VA elements. The EFG for PbBi is much reduced as compared with the BiBi EFG, while for PoBi the EFG is increased drastically[27], suggesting that in bismuth the outer p electrons have a sizeable effect on the EFG. Further, the very weak EFG's found for In in As and in Sb are explained well in a model assuming a covalent bonding picture via the valence p electron in group VA[28].

A similar analysis of isovalent, but not isoelectric, impurity-host systems (e.g. CdBe and WTe) yield R values distant from 1.

Following the above hypothesis which is strongly borne out for group IIIA elements, we derive the EFG for Tl<u>In</u> at T=0K as

$$|eq|(Tl\underline{In}) = |eq|(In\underline{In})(1-\gamma_\infty)_{Tl}/(1-\gamma_\infty)_{In} = 4.6(6)\times10^{17}V/cm^2 \quad (8)$$

A value of $|eq|(In\underline{In})=2.2(1)\times10^{17}V/cm^2$ at T=0K[17] and $(1-\gamma_\infty)$ values from ref. 19 were used. The error due to our calibration procedure is estimated to be 10%. We have measured $|e^2qQ/h|$ for $^{192}Tl(8^-)\underline{In}$ to be 33.1(16) MHz at 293 K. The B coefficient for In<u>In</u> is $6.5\times10^{-5}K^{-3/2}$, very close to our value Tl<u>Tl</u>, $B=7.0(11)\times10^{-5}K^{-3/2}$ (see below). Assuming the temperature dependence of Tl<u>In</u> to be the same as for In<u>In</u>[3], we derive $|e^2qQ/h|=49(4)$ MHz at T=0K. From these results we determine

$$|Q[^{192}Tl(8^-)]| = 0.44(7)\ b \quad (9)$$

From the ratio between the measured frequencies for Tl in Tl and in In, extrapolated to T=0K(see below), we arrive at the value

$$|eq|(Tl\underline{Tl}) = 2.3(4)\times10^{17}V/cm^2 \quad (10)$$

EFG's calibration via data on isoelectric systems may be useful in other cases as well. In particular, much experimental effort was dedicated to Ge isomers but the nuclear quadrupole moments are unknown. The EFG for Ge in Sn is determined as $|eq|=1.74(33)\times10^{17}V/cm^2$ from the data of Sn and Pb probes in Sn host (Table 2). A 10% error due to uncertainty in the calibration procedure is included. Using the qudrupole coupling constant of $^{69}Ge\underline{Sn}$ extrapolated to T=0K[29] and data from ref. 17 we arrive at

$|Q|$=1.3(3), 1.0(2), and 0.23(5)b for the ^{67}(Ge(9/2$^-$), ^{69}Ge(9/2$^+$), and the ^{71}Ge(5/2$^+$) states respectively.

4. The EFG in the Metal Thallium

The lattice contribution to the EFG of T1T1 is calculated using the lattice parameters of ref. 12., extrapolated to T=0K, and the formula of Das and Pomerantz for hcp metals (z is the ionic valeace).

$$eq_{latt}^{Coul} = \frac{z}{a^3}[0.0065-4.3584(c/a-1.633)] \qquad (11)$$

and a value of $(1-\gamma_\infty)eq_{latt}^{Coul}$=0.52x10^{17} V/cm^2 was found. Within the framework of the universal correlation (eq. 2), we calculate the conduction electron contribution to the EFG (assuming a negative sign for the measured EFG) to be eq_{el}=-2.8(4)x10^{17} V/cm^2, Our data are then consistent with a value of K=5.4, almost twice as large as suggested by ref. 2. A refined universal correlation is proposed in ref. 31, where the empirical formula

$$eq_{el} = -K_z\, eq_{latt}^{Coul}(1-\gamma_\infty) + eq_z^{min} \qquad (12)$$

is sugested. For z=3, K_3=3.4 and eq_3^{min}=2.2x10^{17} V/cm^2, resulting in a predicted total EFG of 0.95x10^{17} V/cm^2 for T1T1, also in disagreement with our experimental results. A similar computation for room temperature yields $(1-\gamma_\infty)eq_{latt}^{Coul}$=0.9x10^{17} V/cm^2 and eq_{el}=-0.89x10^{17} V/cm^2, the sum of which is a vanishing total EFG.

A new approach for calculation of electric field gradients in metals was suggested by Bodenstedt and Perscheid.[6] They approximated the conduction

electrons charge distribution by a static point charge sublattice, superimposed on the ionic lattice so that there is a negative charge center between every two neighbouring ions. The positive ion in the hcp lattice is surrounded by 12 electronic charge centers, 6 in the hexagonal plane, each having a charge Q_{hp}, and 6 above and below the plane, having a charge Q_{el}. The deviation of the c/a ratio from the ideal value, $\sqrt{8/3}$ is associated with an imbalance of the in vs. out to plane electronic charges, e.g.

$$Q_{hp} = -\frac{1}{6} Z_{eff}\, e(1+\delta) \qquad (13a)$$

$$Q_{el} = -\frac{1}{6} Z_{eff}\, e(1-\delta) \qquad (13b)$$

In the model, the δ parameter is expected to have the same sign as $(c/a - \sqrt{8/3})$. The magnitude of δ is estimated in ref. 6 for Zn from data on elastic coefficients but in general it is a rather non trivial quantity. Z_{eff} is the part of ionic charge which is not screened by conduction electrons overlapping with the core. In the case of Zn, Z_{eff}=1.5 gave agreement with EFG data.[6] The introduction of Z_{eff} seems to be justified since only the contribution to the EFG from electrons outside the ionic sphere is enhanced by the large $(1-\gamma_\infty)$ factor. The total EFG at the nuclear site is obtained by a lattice sum over the Coulomb point charges of the ionic and electronic lattices, and is enhanced by $(1-\gamma_\infty)$. The results of lattice sums for different c/a ratios are tabulated in ref. 6, enabling a calculation of the total EFG for any hcp metal, for given values of Z_{eff} and δ . In the case of Tl, the experimentally observed EFG at T=0K is reproduced with Z_{eff}

values ranging from 1.5 to 3 for δ parameters varying from -0.053 to -0.025 respectively. A negative value of the total EFG is adopted to be consistent with a negative sign of δ . The values of δ which are consistent with the measured EFG in Tl are very reasonable for a metal whose structure only slightly deviates from the ideal one. We are encouraged to believe that the basic picture is a good approximation.

5. Temperature Dependence of the EFG of Tl in Tl

The weak electric field gradient for Tl in Tl and the moderate quadruple moment of the ^{192}Tl(8^-) isomer and the high spin, result in a small quadrupole frequency, thereby limiting the experimental accuracy. An additional difficulty arose from the limited statistics which could be obtained within a reasonable counting time. Nevertheless, since the variation of the observed quadrupole coupling constants with temperature (Table I) is large, a meaningful discussion is possible in spite of the limited accuracy of each measurement by itself. Assuming a $T^{3/2}$ temperature dependence according to eq. (3) the values e^2qQ/h=24.0(15) MHz at T=0Kand B=7.0(11)x10^{-5} $K^{-3/2}$ were found by a least squares fit. The data and the fitted curve (solid line) are shown in fig. 3. A $T^{3/2}$ temperature dependence was found for the EFG for ^{111}Cd [10] and ^{69}Ge [11] impurities in Tl with the B coefficient having the values 5.9(2)x10^{-5} and 4.85(5)x10^{-5} $K^{-3/2}$ respectively, close to the TlTl value. Tl is a good sp metal as indicated by a band structure calculation of Holtham et al.[32] and it is expected that the $T^{3/2}$ law will be valid also for TlTl.

As pointed out, first by Quitmann et al.[33] and later by numerous other authors, the strength of the temperature dependence, i.e.the coefficient B, is approximately proportianal to $1/M\theta_D^2$ (M is the atomic mass and θ_D is the Debye temperature). This dependence is due to the fact that in the Debye approximation the high temperature mean square displacement, $\langle u^2 \rangle$, is proportional to that quantity. The experimental verification of the proportionality between B and $1/M\theta_D^2$ for pure systems supports those theoretical models in which the dominant contribution to the temperature dependence in due to lattice vibrations. It is not, however, a proof for any specific phonon model. The strong temperature dependence found for ^{192}TlTl is related to the small value θ_D=89 K [9] of this metal. A plot of log(M·B) vs. log(θ_D) for pure systems including Tl (fig. 4) demonstrates that Tl fits well into this systematic.

Before discussing our data in detail within the framework of specific models which include lattice vibrations, it is interesting to consider the temperature effect on the lattice sum over contributions from point Coulomb charges. Using the lattice parameters at different temperatures[12] and the approximate formula for hcp metals (eq. 11) we have calculated $eq_{latt}^{Coul}(T)/eq_{latt}^{Coul}(0)$, which is displayed as a dashed line in fig. 3. The relevant parameter is [c/a(T)-1.633] since at c/a=$\sqrt{8/3}$=1.633 the lattice symmetry results in a vanishing EFG. For Tl, c/a is very close to 1.633 (c/a=1.615 at T=0K) and a modest reduction of c/a at higher temperatures is related to a very significant change in lattice symmetry.

Jena[4] has argued that the conduction electrons contribution to the EFG, when calculated in a pseudopotential due to the vibrating ions, contains a

term which is proportional to the Debye integral, which in turn is approximately proportional to $T^{3/2}$ at intermediate temperatures. In that model, the $T^{3/2}$ temperature depe ..e is due only to conduction electrons while the contribution from the lattice ions, calculated as above, is assumed to be temperature independent. This approach seems rather inappropriate for Tl, where the lattice contribution increases drastically with temperature, yet an overall very strong reduction of the total EFG is found.

Nishiyama and Riegel[5] have described the EFG as a lattice sum over screened ions, the screening electrons density being calculated in the pseudopotential approach and having an oscillatory nature. In their model an approximate expression is:

$$eq = (1-\gamma_{eff}) eq_{ion}^{sc} \, e^{-4k_F^2 \langle u^2 \rangle / 3} \qquad (14)$$

$(1-\gamma_{eff})$ is an effective antishielding factor. eq_{ion}^{sc}, the lattice sum, is temperature dependent due to the variation in the lattice parameters. Most of the temperature dependence is due to isotropic lattice vibrations and is described by the Debye-Waller factor, k_F being the free electron Fermi momentum and $\langle u^2 \rangle$ is the mean square displacement.

It was pointed out recently that at high temperatures $\langle u^2 \rangle$ behaves as[5,39]

$$\langle u^2 \rangle (T) = \langle u^2 \rangle (0) + \beta T^{3/2} \qquad (15)$$

High temperature resistivity being proportional to $\langle u^2 \rangle$, behaves in the same manner[40]. For Tl, the resistivity was measured in the temperature range 298 to 423 K[41], and found to be in agreement with eq(15). Phonon frequency

distributions for Tl have been measured at 77 and 296 K by neutron inelastic scattering[42]. We have calculated $\langle u^2 \rangle$ from these data as $\langle u^2 \rangle = 0.020$ and $0.113\ \text{Å}^2$ at T=77 and 296 K, respectively. Assuming eq. (15) to be valid for Tl, these values are found to have the same temperature dependence as the high temperature resistivities. For Tl, we extrapolate

$$\langle u^2 \rangle(T) = (5.87 \times 10^{-3} + 2.11 \times 10^{-5} T^{3/2}) \text{Å}^2 \qquad (16)$$

The Fermi momenta, calculated in the free electron gas model, depend only slightly on the temperature due to volume variation. The Debye-Waller factor contribution to the temperature dependence of the EFG (eq. 14) is plotted as a dotted-dashed line in fig. 3. The lattice sums for eq^{sc}_{ion} were done by P. Heubes[43] using the asymptotic form[1]

$$eq(r) \simeq A(2k_F^2) \frac{-\cos(2k_F r)}{(2k_F r)^3} \qquad (17)$$

The sums converged when approximately 3×10^4 neighbouring ions were included and the final results for 8×10^4 ions, normalized to the sum at T=0K, are shown as a dotted-dotted-dashed line in fig. 3. The dependence of this term on the temperature through the variation in the c/a ratio is regular. This is in disagreement with a similar calculation of ref. 13 which predicted a zero crossing of eq^{sc}_{ion} at a pressure of about 7 kbar . At this pressure the lattice dimensions are similar to those at zero pressure below room temperature[12,44]. The overall prediction of thl (eq. 14) is plotted as a dotted line in fig. 3. This result, which is in fair agreement with the data, will be disussed further in the Conclusions section.

A different approach for the calculation of EFG's was through the static charge distribution picture of ref. 6, discussed before. According to this work, the EFG is temperature dependent since the vibrating probe ion is sampling the gradient from the static electric field at different locations. For a static potential isotropic variations in the nuclear site do not change the average EFG and therefore the temperature dependence is due only to the non-isotropic part of the vibrations. The following formula is derived:

$$eq(T) = eq + \frac{1}{2}\frac{\partial^2 eq}{\partial z^2}\langle z^2\rangle\ (1-\varepsilon) \qquad (18)$$

Where eq is the lattice sum over ionic and electronic contributions for a static probe ion, $\langle z^2\rangle$ is the mean square displacement in the C axis direction and

$$\varepsilon = \langle x^2\rangle/\langle z^2\rangle \qquad (19)$$

is a measure of the vibration anisotropy ($\langle x^2\rangle = \langle y^2\rangle$ is assumed). The second derivative of the EFG is also obtained by lattice sum and is tabulated for different values of c/a[6]. Unlike eq itself, this quantity is not strongly dependent on δ and c/a.

The temperature dependence for TlTl, calculated for Z_{eff}=2.0, δ=-0.04 and ε=2 is plotted as a dashed-dashed-dotted line in fig. 3 and marked as th2. Values of $\langle z^2\rangle$ where found from the temperature dependent $\langle u^2\rangle$values, assuming

$$\langle u^2\rangle = \langle x^2\rangle + \langle y^2\rangle + \langle z^2\rangle \qquad (20)$$

and therefore

$$\langle z^2 \rangle = \frac{\langle u^2 \rangle}{1+2\varepsilon} \qquad (21)$$

Possible temperature dependence of δ and ε were neglected. It is obvious that even for the large assumed value of ε , the correct result cannot be reproduced. To get agreement with the experiment, within the formalism of ref. 6, one has to use a value of ε=9, corresponding to vibration amplitudes in the hexagonal plane 3 times larger than the vibration amplitudes out of plane, which is unrealistic.

6. Conclusions

The electric coupling constants for the ^{192}Tl(8$^-$) isomer have been measured in Tl host at four different temperatures and in In host at room temperature (Table 1). An EFG calibration procedure for isoelectric probe impurities was developed and used to determine the magnitude of the EFG for Tl in Tl at T=0K as $2.3(4)\times10^{17}$ V/cm^2. This value is small in magnitude because of the closeness of the c/a ratio of Tl to the value for ideal hcp metals, $\sqrt{8/3}$. The EFG value is not in agreement with the prediction of the universal correlation[2] or the refined correlation[30]. The disagreement is more pronounced at higher temperatures. We conclude that the universal correlation, usually being confirmed for metals with a stronger EFG, is not quite applicable for the Tl lattice with almost perfect symmetry and a weak EFG.

The magnitude of the EFG was discussed also within the framework of the static charge distribution model of Bodenstedt and Perscheid.[6] We have

treated the parameters of this model , Z_{eff} and δ , as free parameters and found that the experimental EFG is reproduced with reasonable values of those parameters. For Z_{eff}=2, corresponding to 1/3 of the electronic charge overlapping with ionic cores, we get δ=-0.04, that is a 4% electronic charge shift from the hexagonal planes into the space between planes.

The temperature dependence of the EFG of Tl was analyzed within the framework of the $T^{3/2}$ law (eq. 3), resulting in a B coefficient value, $7.0(11)\times10^{-5}$ $K^{-3/2}$, larger than measured for any other pure system. This value fits into the systematic relating M·B to θ_D (fig. 4). The temperature dependence was computed in the framework of two specific models. Nishiyama and Riegel's model [5] of screened ions lattice sum along with vibrations (th1) predicts a temperature dependence which is slightly stronger than our obseved one. An interesting result is that this model predicts for Tl nonlinear dependence on $T^{3/2}$. While this could be a result of the c/a ratio being close to $\sqrt{8/3}$ it could also be caused by the approximations made in the calculations (eq. 14 and 17). In fact, the data seem to favour the curve of th1 over the linear $T^{3/2}$ dependence. However, the $T^{3/2}$ law found for ^{111}CdTl [10] and most convincingly for ^{69}GeTl [11] does not support such an interpretation.

In the framework of the static charge distribution model of Bodenstedt and Perscheid [6] (th2) it is impossible to reproduce the temperature dependence in Tl. We judge their approximation, in which the potential is static while the probe ion vibrates, to be non-realistic. Their assumption results in temperature dependence due only to the vibrations anisotropy which is not large enough in Tl. A more realistic model allowing for a potential change as the probe ion moves from its central position would probably produce

better results. Such potential change is expected from the interaction with the nearest neighbouring electronic clouds. As the ion vibrates, currents of electronic charges follow its motion adiabatically.

The availability of a better probe isomer in Tl in the future may enable an improved measurement of the EFG in Tl. This, in turn, will allow better testing of current theories at the limit of c/a close to $\sqrt{8/3}$. In particular, a prediction of a temperature dependence of the EFG in Tl nonlinear in $T^{3/2}$ (e.g. thl in fig. 3) is interesting. On the theoretical side, an improved treatment of the temperature dependence in the otherwise attractive model of ref. 6 is called for.

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Table 1

Results from Quadrupole Interaction Measurements of $^{192}Tl(8^-)$

Host	T[K]	a_2	$\frac{e^2qQ}{h}$[MHz]
Tl	81	-0.09(2)	25.7(18)
	200	-0.10(2)	19.0(17)
	293	-0.13(2)	14.3(8)
	410	-0.14(2)	12.0(13)
In	293	-0.17(3)	33.1(16)

Quadrupole coupling constants of isoelectric systems

Group	Host	Impurity	I^{π}	$\lvert Q \rvert$ [b][a]	$\lvert \frac{e^2qQ}{h} \rvert$ [MHz][b]	$\lvert eq \rvert$ [10^{17} V/cm^2]	R[c]
IVB	Ti	^{17,49}Ti	$5/2^+, 7/2^+$	0.27(1)[d]	7.7(-)	1.18(4)	1
		^{178}Hf	2^+	1.9(2)	390(9)	8.5(9)	1.04(12)
	α-Zr	^{91}Zr	$5/2^+$	0.21(2)	18.7(3)	3.7(4)	1
		^{178}Hf	2^+	1.9(2)	403(14)	9(1)	1.02(15)
IIB	Zn	^{67}Zn	$9/2^+$	0.61(6)[e]	48.7(2)[f]	3.3(3)	1
		^{111}Cd	$11/2^-$	0.85(9)	139(15)	6.8(10)	0.91(16)
		^{197}Hg	$5/2^-$	0.081(6)	36.0(4)[g]	18.4(15)	1.21(16)
	Cd	^{67}Zn	$9/2^+$	0.61(6)[e]	44.5(5)[h]	3.0(3)	1.00(19)
		^{111}Cd	$5/2^+$	0.83(13)	136.2(8)[f]	6.8(11)	1
		^{197}Hg	$5/2^-$	0.081(6)	26.0(5)[g]	13.3(11)	0.97(17)
	Hg	^{107}Cd	$11/2^-$	1.06(17)[i]	151.6(10)	5.9(9)	1.24(22)
		^{199}Hg	$5/2^-$	0.95(7)	220(20)[j]	9.6(11)	1
IIIA	α-Ga	^{69}Ga	$3/2^-$	0.168(17)[e]	22.505(1)[k]	5.5(6)	1
		^{119}In	$3/2^+$	0.65(4)	173(3)[l]	11.0(7)	0.81(9)
IVA	Sn	^{113}Sn	$11/2^-$	0.46(10)	50.8(4)	4.6(10)	1
		^{204}Pb	4^+	0.44(2)[m]	96(20)[n]	9(2)	0.88(18)
VA	Bi	^{112}Sb	8^-	0.70(8)[k]	107(2)[o]	6.3(7)	2.8(4)
		^{209}Bi	$9/2^-$	0.42(4)[p]	54(1)[q]	5.3(5)	1

Comments to Table 2

a) Unless otherwise noticed, quadrupole moment values are from ref. 17.

b) Unless otherwise noticed, data from ref. 17. Whenever values are reported only for T>4.2K we have extrapolated them assuming $eq(o)=eq(T)/(1-BT^{3/2})$. B values are from quoted references. In some cases we have fitted published data to obtain a value for B.

c) $R=[|eq|/(1-\gamma_\infty)]_{impur.\ syst.}/[|eq|/(1-\gamma_\infty)]_{pure\ syst.}$, $(1-\gamma_\infty)$ values are from ref. 19.

d) Average Q moment.

e) 10% error assumed.

f) B value from ref. 3.

g) B value from ref. 20.

h) B value from ref. 21.

i) The value of ref. 17 was revised according to the adopted value of $Q[^{111}Cd(5/2^+)]$[22] and the quadrupole moment ratio from ref. 23.

j) $B(\underline{Hg}Hg)=7\times10^{-5}\ K^{-3/2}$ assumed. See ref. 10.

k) Corrected for $\eta=0.179$.

l) $B(\underline{Ga}Ga)=0.80(1)\times10^{-5}\ K^{-3/2}$ from data of ref. 24 was used for $In\underline{Ga}$.

m) Ref. 25.

n) $B(\underline{Sn}Sn)$ from ref. 11 was used for $Pb\underline{Sn}$.

o) B value from ref. 18.

p) Ref. 18.

q) $B[\underline{Bi}Bi]=2.0(1)\times10^{-5}\ K^{-3/2}$ from data of ref. 26.

Figure Captions

Fig. 1: Ratio functions (eq. 4) for the ^{192}Tl isomer in Tl host at different temperatures. The solid lines are from a fit to eqs. 5 and 6.

Fig. 2: Ratio function (eq. 4) for the ^{192}Tl(8^-) isomer in In host. The solid line is from a fit to eqs. 5 and 6.

Fig. 3: Normalized quadrupole coupling constants for TlTl at different temperatures. The circles are the measured points while the solid line is from a fit to eq. 3. Also shown are the results from a Coulomb point lattice sum according to eq. 11 (eq_{latt}^{Coul}), the Debye-Waller factor (DWF) and lattice sum (eq_{ion}^{sc}) contributions for the temperature dependence in eq. 4 along with their product (th1), and the prediction of eq. 18 (th2).

Fig. 4: The empirical correlation between the Debye temperature and M·B where M is the atomic mass and B is the strength of the EFG temperature dependence (eq. 3) for pure systems. (Mg: ref. 17; Zn, Cd, In, Sb: ref. 3 and references therein; α-Ga: ref. 24; As: ref. 34; Sn: ref. 11; Re: ref. 35; Gd: ref. 36; Ta: ref. 37; Bi: ref. 26). For Be the datum is not shown (θ_D=1160K, M·B=0.0(40)x10^{-5} K$^{-3/2}$ a.m.u.[38]), but it is in agreement with the correlation.

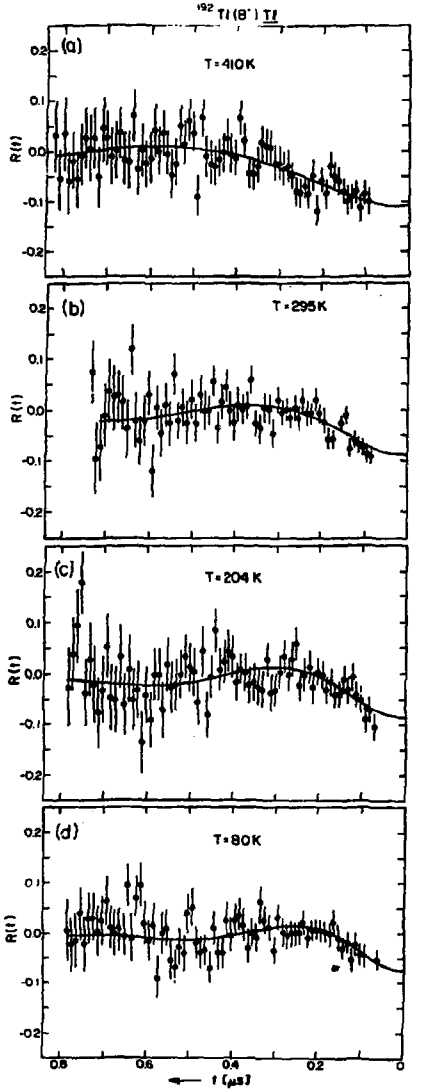

^{192}Tl(8^{-}) Tl
(a)
T=410K
(b)
T=295K
(c)
T=204K
(d)
T=80K
R(t)
0.2
0.1
0.0
-0.1
-0.2
0.8
0.6
0.4
0.2
0
t (μs)

Fig 1

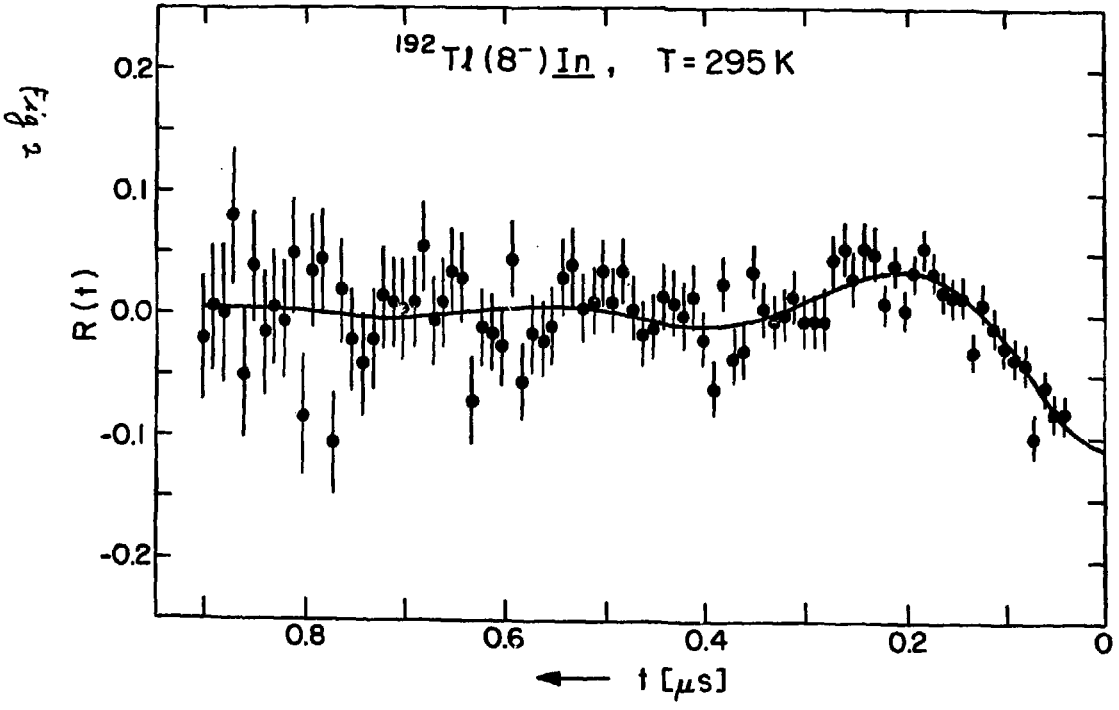
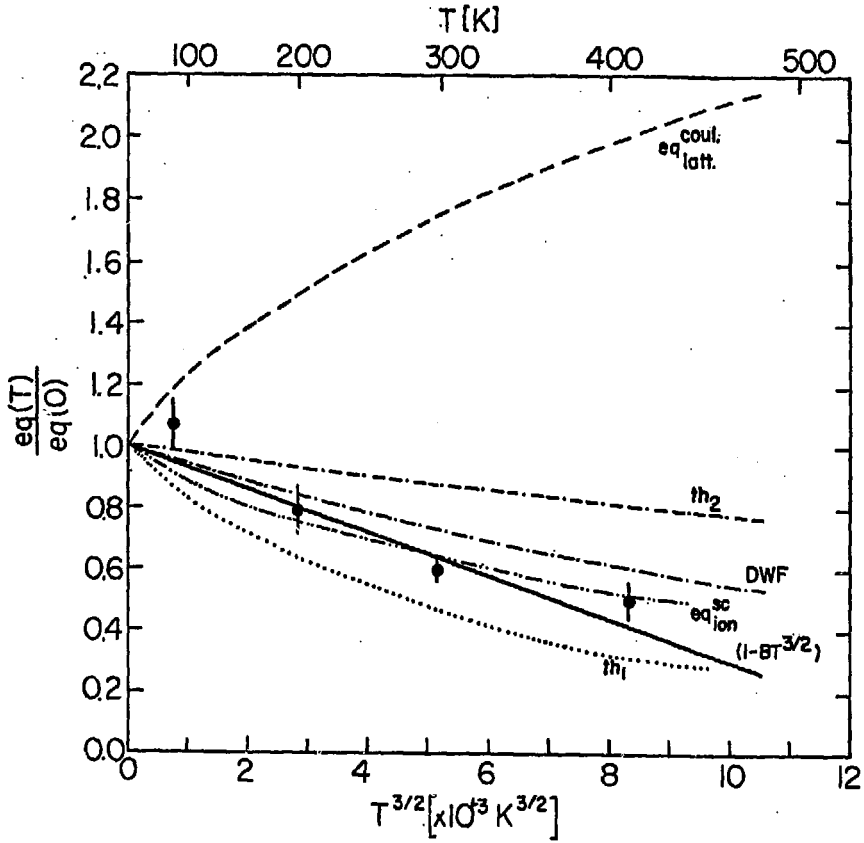


Fig 2

Fig 3


T [K]
100
200
300
400
500
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
eq(T) / eq(0)
eq coul. latt.
th2
DWF
eq sc ion
(1-BT^3/2)
th1
0
2
4
6
8
10
12
T^3/2 [x10^3 K^3/2]

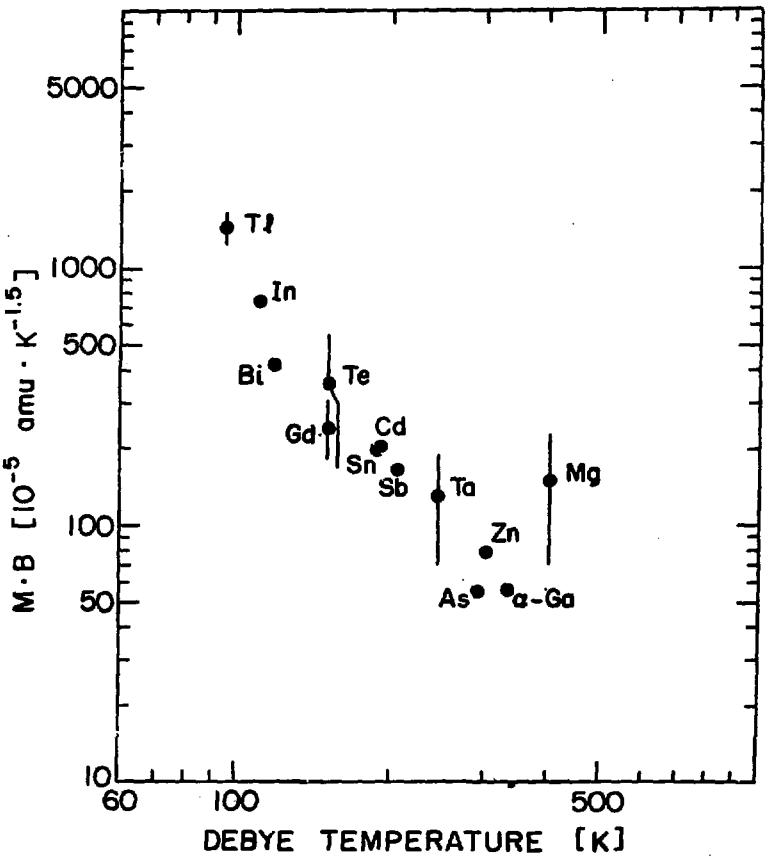

5000
1000
500
100
50
10
60
100
500
M·B [10⁻⁵ amu · K⁻¹·⁵]
DEBYE TEMPERATURE [K]
Tl
In
Bi
Te
Gd
Cd
Sn
Sb
Ta
Mg
Zn
As
α-Ga

Fig 4