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Quadrupole interaction of tantalum impurities in bismuth metal

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Abstract. The time differential perturbed angular correlation technique has been used in the measurement of the electric quadrupole interaction of Ta impuritiy in bismuth metal. The interaction frequencies at 293, 400 and 500 K have been observed to be 288 ± 1·5, 266·9 ± 3 and 244·5 ± 4·3 MHz respectively. The electric field gradient at 293 K is 4·75 ± 0·3 × 10^{17} V/cm² with the temperature coefficient $B = 2{\cdot}2 \pm 0{\cdot}2 \times 10^{-5}$ $(K)^{-3/2}$.

Keywords. Quadrupole interaction; electric field gradient; temperature coefficient; tantalum; bismuth.

1. Introduction

Specific heat (Phillips 1960; Collan *et al* 1970), nuclear quadrupole resonance (Bastow and Whitfield 1976; Williams and Hewitt 1966) and time-differential perturbed angular correlation (TDPAC) (Hass and Shirley 1973; Heubes *et al* 1977; Raghavan and Raghavan 1977; Keppner *et al* 1980), have been studied in rhombohedral bismuth metal. The values of electric field gradient (EFG) at the impurity nucleus in ^{69}GeBi (Raghavan and Raghavan 1977), ^{111}CdBi (Heubes *et al* 1977) ^{112}SbBi (Mahnke *et al* 1980) and ^{209}BiBi (Bastow and Whitfield 1976) have been reported to be $2{\cdot}51(12) \times 10^{17}$ V/cm², $4{\cdot}3(3) \times 10^{17}$ V/cm², $6{\cdot}3(7) \times 10^{17}$ V/cm² and $5{\cdot}32(19) \times 10^{17}$ V/cm² respectively. The temperature dependence of the EFG in the four cases is found to follow the $T^{3/2}$ power-law with the temperature coefficients $3{\cdot}35(4) \times 10^{-5}$ $K^{-3/2}$, $7{\cdot}65(5) \times 10^{-5}$ $K^{-3/2}$ $2{\cdot}3(2) \times 10^{-5}$ $K^{-3/2}$ and $2{\cdot}04 \times 10^{-5}$ $K^{-3/2}$ respectively.

The tantalum impurity is isovalent with bismuth. The size of the tantalum ion (0·73) Å is very close to that of bismuth (0·74) Å. It would be of interest to measure the EFG at the Ta nucleus in Bi and its temperature variation. This has been done by studying the TDPAC of the 133–482 keV gamma-ray cascade in ^{181}Ta. The quadrupole moment of the 482 keV ($5/2^+$) intermediate state of ^{181}Ta is reported to be 2·51(15)b (Netz and Bodenstedt 1973). The Sternheimer antishielding factor γ_∞ for the Ta^{5+} ion has been calculated to be −61 (Feiock and Johnson 1969).

2. Experimental

The ^{181}Hf activity was obtained by irradiating pure hafnium metal in the CIRUS Reactor, Trombay. Approximately 1 mg piece of the active hafnium metal was

heated with 168 mg of 99·999% pure bismuth in argon atmosphere at a temperature of 973K for 12 hr. On gradual cooling a globule was obtained, which was broken into small pieces for testing the activity. The activity was uniformly distributed. The pieces were used for the study without further treatment. The solubility of hafnium in bismuth at 973K is about twice (Weeks 1965) the amount of hafnium dissolved in bismuth in the present case.

The TDPAC set-up consists of three 1·75 inch diameter×2 inch long NaI (Tl) scintillation detectors in standard slow-fast coincidence set-up in which the fast coincidence circuit is replaced by a time-to-pulse-height-converter. In the fast channels, the fast pulses from 90° and 180° counters were added using proper lengths of cables. In the slow channels, the photo-peaks due to the 133–482 keV gamma-rays of ^{181}Ta were selected using single channel analysers with the window-width of 10% of the gamma-energies. The prompt resolution of the system FWHM was 2·3 nsec. The coincidences corresponding to 90° and 180° as a function of delay time t between the two gamma-ray photons of the cascade were recorded simultaneously in the two halves of the memory of ND 1100 multi-channel analyser. After subtraction of chance coincidences, the value of $R(t)$ defined as

$$R(t) = \frac{2\,[W(180°, t) - W(90°, t)]}{[W(180°, t) + 2\,W(90°, t)]}, \tag{1}$$

was calculated. In this expression $W(180°, t)$ and $W(90°, t)$ are true coincidence counting rates with 180° and 90° counters respectively. The angular correlation function for 133–482 keV cascade of ^{181}Ta as measured by Steffen (1955) is given by

$$W(\theta) = 1 + A_2 P_2(\cos\theta) + A_4 P_4(\cos\theta) + \ldots$$

$$= 1 - 0{\cdot}29\, P_2(\cos\theta) - 0{\cdot}07\, P_4(\cos\theta). \tag{2}$$

With the perturbation of the angular correlation, the correlation function becomes

$$W(\theta, t) = 1 + A_2 P_2(\cos\theta)\, G_2(t) + A_4 P_4(\cos\theta)\, G_4(t). \tag{3}$$

In view of the small value of A_4 the last term in the above equation is generally neglected and one has

$$R(t) \approx A_2 G_2(t) \tag{4}$$

If some of the atoms do not experience a hyperfine field, they show an unperturbed angular correlation with $G_2(t) = 1$. Equation (4) in such cases can be written as

$$R(t) = A_2^{\text{const}} + A_2^{\text{eff}} G_2(t) \tag{5}$$

At time $t = 0$, $G_2(t) = 1$ and hence

$$A_2^{\text{const}} + A_2^{\text{eff}} = A_2 \tag{6}$$

For an axial symmetric EFG and a polycrystalline sample (Frauenfelder *et al* 1965; Bodenstedt *et al* 1972)

$$A_2^{\text{eff}} G_2(t) = A_2^{\text{eff}} (a_0 + a_1 \cos \omega t + a_2 \cos 2\omega t + a_3 \cos 3\omega t)$$

$$= A_2^{\text{eff}} \left(\frac{7}{35} + \frac{13}{35} \cos \omega t + \frac{10}{35} \cos 2\omega t + \frac{5}{35} \cos 3\omega t \right). \quad (7)$$

If there are lattice defects in the vicinity of the probe nuclei or if the probe nuclei are shifted from the lattice positions due to the recoil, subsequent to the emission of β-particles, different probe nuclei may experience different EFG's. One may assume that under such circumstances the variation of the EFG has a Gaussian shape around a mean value. The width of this Gaussian distribution in EFG is represented by $\delta \omega$— the width in the interaction frequency. The expression for $R(t)$ in such a case is given by

$$R(t) = A_2^{\text{const}} + A_2^{\text{eff}} \left(a_0 + \sum_{n=1}^{3} a_n [\exp - \tfrac{1}{2} (n \delta \omega t)^2] \cos (n \omega t) \right). \quad (8)$$

Assuming that our sample of bismuth was polycrystalline, the experimental value of $R(t)$ was fitted with the above expression at computer DEC 10system at TIFR, Bombay. From the fitted values, the quadrupole frequency defined as $\nu_Q = e^2 q\, Q/h = 10\omega/3\pi$ was obtained. The experiment was performed at room-temperature 293, 400 and 500 K and the variation in ν_Q with temperature was obtained.

3. Results and discussion

Figure 1 shows the variation of $R(t)$ as a function of time, at different temperatures of the ^{181}TaBi source. The solid curves represent the computer fit of the data for which the values of the different parameters are shown in table 1. The base line in figure 1 seems to increase with time and this can be explained by a slight difference in the number of chance coincidences subtracted. It is seen that the value of A_2 ($= A_2^{\text{const}} + A_2^{\text{eff}}$) is less than the expected value (equation (2)). This can partly be attributed to the finite solid angle subtended by the detectors at the source and the finite time-resolution of the set-up for which no corrections were applied in the data. The finite resolution correction does not affect the value of the interaction frequency. The observed spread $\delta\omega/\omega$ is found to be 13%. The smaller value of $\delta\omega/\omega$ at 400 K is perhaps statistical in nature.

The sizes of both the Ta^{5+} (0·73 Å) and Bi^{5+} (0·74 Å) ions are very nearly the same and it is therefore, expected that the Ta would occupy the lattice site. The same valency and ion size for the probe and the host eliminate the possibility of distortion of the lattice or the electron distribution (valency effect) about the Ta atom. The quadrupole interaction frequency of 288 (1·5) MHz coupled with the quadrupole moment of the Ta state yields the EFG acting at the Ta nucleus to be 4·75 (3) $\times 10^{17}$ V/cm^2. The extrapolated value obtained from figure 2 at 4·2 K is 5·3(1) $\times 10^{17}$ V/cm^2

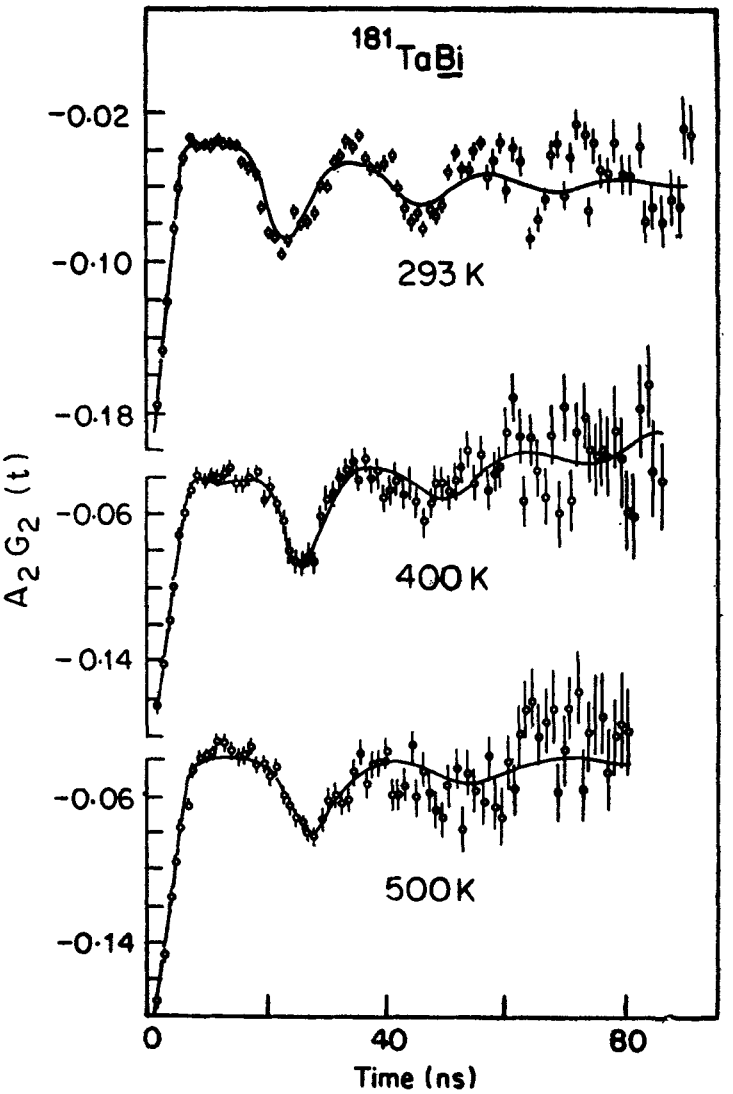

Figure 1. TDPAC spectrum of ^{181}TaBi at different temperatures.

which is to be compared with the EFG of $5{\cdot}32(19)\times 10^{17}$ V/cm^2 acting at the bismuth nucleus (Williams and Hewitt 1966). The EFG at the probe nucleus can be written as

$$eq_{exp} = (1-\gamma_\infty)\, eq_{latt} + (1-R)\, eq_{cond.\ el.} \tag{9}$$

Empirically Raghavan *et al* (1976) have suggested that $eq_{cond.\ el.}$ can be assumed to be proportional to eq_{latt} and with this the EFG at the probe nucleus becomes

$$eq_{exp} = (1-K)\,(1-\gamma_\infty)\, eq_{latt}. \tag{10}$$

Table 1. Computer fitted parameters for the TDPAC study of ^{181}TaBi at different temperatures.

Temp. (K)	$A_2(t=0)$ (without angular resolution correction)	A_2^{eff}	ν_Q (MHz)	$\delta\omega/\omega$
293	$-0{\cdot}188 \pm 0{\cdot}002$	$-0{\cdot}149 \pm 0{\cdot}002$	$288{\cdot}0 \pm 1{\cdot}5$	$0{\cdot}13 \pm 0{\cdot}006$
400	$-0{\cdot}172 \pm 0{\cdot}004$	$-0{\cdot}133 \pm 0{\cdot}004$	$266{\cdot}9 \pm 3$	$0{\cdot}10 \pm 0{\cdot}01$
500	$-0{\cdot}183 \pm 0{\cdot}005$	$-0{\cdot}135 \pm 0{\cdot}005$	$244{\cdot}5 \pm 4{\cdot}3$	$0{\cdot}16 \pm 0{\cdot}01$

On the basis of the experimental data, Raghavan *et al* (1976) have proposed a value of 3 for the universal correlation constant K. Taking the value of eq_{latt} for bismuth metal as calculated by Taylor and Hygh (1963), the value of $(1-\gamma_\infty)\, eq_{latt}$ is obtained as $-2{\cdot}44\times 10^{17}$ V/cm^2 which when compared with the experimental value eq_{exp} gives a value of $K=2{\cdot}95$, which is in good agreement with the proposed value of 3. Recently however, Raghavan and Raghavan (1981) have suggested that the electronic contribution to the EFG depends upon the valency of the probe atom. They give an empirical relation for eq_{el} as

$$eq_{el} = -K_Z\, eq_{latt}\,(1-\gamma_\infty) + eq_Z^{\min}, \tag{11}$$

where $eq_Z^{\min}$ is the minimum observable EFG even for vanishingly small ionic gradients and can be called the hard core electronic gradient and K_Z is the correlation constant for impurity of valency Z. Raghavan and Raghavan (1981) have suggested $K_2=2{\cdot}6$, $K_3=3{\cdot}4$ and $K_4 \approx 5$. For a pentavalent ion of Ta the value of K_5 could be greater than 6. The value of K_5 for ^{181}TaSb system is reported as 3·05 (Jaaffrey *et al* 1982) and for ^{181}TaZn system 2·3 (Bedi *et al* 1978). For ^{112}SbBi system K_5 is estimated to be 11. It is thus seen that the values of the correlation constant K_z-neglecting the hard core electronic gradient $eq_z^{\min}$ for different systems do not show any consistent trend. If one takes some value for $eq_z^{\min}$ the values of K_5 would reduce even further.

The temperature dependence of the quadrupole interaction (Heubes *et al* 1974) in ^{181}TaBi system has been examined by fitting the data as shown in figure 2 to the equation

$$\nu_Q(T) = \nu_Q(0)\,(1 - BT^{3/2}), \tag{12}$$

and is found to give the value of temperature coefficient $B=2{\cdot}2\ (2)\times 10^{-5}\ K^{-3/2}$. This is to be compared with the values of $B = 2{\cdot}04 \times 10^{-5}\ K^{-3/2}$ for ^{209}BiBi and $2{\cdot}3\ (2)\times 10^{-5}\ K^{-3/2}$ for ^{112}SbBi. It is a general observation that the temperature coefficient B of the EFG at the nucleus of an isoelectric impurity is nearly the same as at the host nucleus. A marked difference has however been observed in the value of B for the isoelectric system ^{111}CdCd ($B = 1{\cdot}81(8) \times 10^{-5}\ K^{-3/2}$, Christiansen *et al* 1976) and ^{197}HgCd ($B = 2{\cdot}90(6) \times 10^{-5}\ K^{-3/2}$, Krien *et al* 1975) as also ^{121}SbSb ($B = 1{\cdot}34\ (1) \times 10^{-5}\ K^{-3/2}$, Hewitt and Williams 1963) and ^{181}TaSb ($B = 0{\cdot}76\ (03) \times 10^{-5}\ K^{-3/2}$, Jaaffrey *et al* 1982).

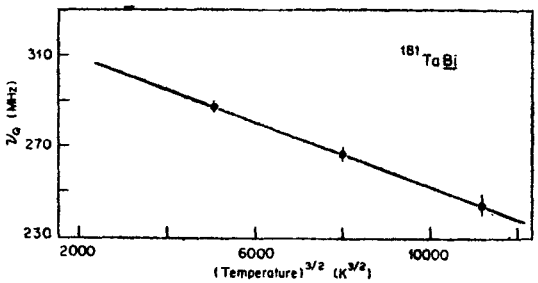

Figure 2. A plot of quadrupole interaction frequency ν_Q as a function of $T^{3/2}$ where T is expressed in K.

The measurements reported here show that the system ^{181}TaBi does not show any anamolous behaviour. With the quoted errors in the values of B for ^{181}TaBi, ^{209}BiBi and ^{112}SbBi systems, it is not possible to look for the effect of the host to impurity force constant (Heubes *et al* 1979).

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