

# Temperature Dependence of the $\beta$ -Tin Isomer Shift\*

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(Received 23 July 1969)

A study of the Mössbauer spectrum of  $\beta$ -tin from 77 to 450°K shows that the isomer shift exhibits an explicit dependence on temperature, and therefore that the electron density at the nucleus depends on temperature even when the volume is held constant. Plausible arguments are presented to show that this effect is related to the explicit temperature dependence of the Knight shift. By combining Knight-shift and Mössbauer results, it is found unambiguously that in  $^{119}\text{Sn}$ ,  $\delta R/R$  is positive and equals  $(1.8 \pm 0.4) \times 10^{-4}$ .

THE Mössbauer spectrum has been studied in  $\beta$ -tin from 77 to 450°K and an explicit temperature dependence of the isomer shift has been found.<sup>1</sup> A similar phenomenon has been observed in the Knight shift in  $\beta$ -tin and the relationship between the two effects will be discussed below.

A white tin source was kept at 77°K at the tip of a Mössbauer drive immersed in liquid nitrogen in a Dewar described previously.<sup>2</sup> The absorber was kept in vacuum in the space below the liquid-nitrogen reservoir. The spectrum was recorded in the pulse-height mode on a 400-channel analyzer. The channel number corresponding to zero velocity was stable to better than 0.2 channels, or 0.005 mm/sec. The position of the centroid of the absorption line was obtained by fitting the data by computer to a single Lorentzian. Fits of four Lorentzian lines to the most accurate data yielded the same centroids as the single line fits. The measurements were repeated with three different combinations of sources (0.8 and 1.5-mCi) and absorbers (each 0.0009 in. thick, and 99.99 and 99.999% purity, respectively).

The position of the Mössbauer absorption line  $\delta(T_a)$  as a function of absorber temperature  $T_a$  is given in velocity units by

$$\begin{aligned} \delta(T_a) = & \delta(77^\circ\text{K}) + \frac{3k}{2Mc}(77^\circ\text{K} - T_a) \\ & + \frac{3k\theta^2}{40Mc} \left( \frac{1}{77^\circ\text{K}} - \frac{1}{T_a} \right) + \int_{77^\circ\text{K}}^{T_a} \left[ \left( \frac{\partial \delta_{IS}}{\partial T_a} \right)_{V_a} \right. \\ & \left. + \left( \frac{\partial \delta_{QS}}{\partial T_a} \right)_{V_a} - \frac{\beta}{K} \left( \frac{\partial \delta}{\partial P_a} \right)_{T_a} \right] dT_a, \end{aligned}$$

where  $\delta(77^\circ\text{K})$  is the residual shift when both source

and absorber are at the same temperature. The next two terms represent the second-order Doppler shift at constant volume, where the characteristic Debye temperature  $\Theta$  for this case should be the high-temperature limit of the specific-heat Debye temperature, 170°K in  $\beta$ -tin.<sup>3</sup> The last term in the integral gives the correction that has to be applied because of volume expansion;  $\beta(T)$  is the coefficient of thermal expansion,<sup>4,5</sup>  $K(T)$  is the isothermal compressibility,<sup>6</sup> and  $(\partial \delta / \partial P_a)_{T_a} = -(1.8 \pm 0.2) \times 10^{-6}$  mm/sec-atm is an average of two independent experimental results<sup>7</sup> and was assumed to be temperature-independent. The second term in the integral represents the constant-volume temperature dependence of the line shift resulting from quadrupole interactions in the source and absorber. The first term in the integral represents an actual temperature dependence of the constant-volume isomer shift<sup>8</sup>:

$$\delta_{IS} = (4\pi Ze^2 R^2 c / 5E_0) S'(Z) (\delta R/R) [\psi_a^2(0) - \psi_s^2(0)].$$

Here,  $E_0$  is the energy of the transition,  $R$  is the radius of the nucleus in its ground state, and  $\psi^2(0)$  is the total nonrelativistic electron density at either source ( $s$ ) or absorber ( $a$ ) nucleus. The factor  $S'(Z)$  is a relativistic correction and equals 2.31 in tin. The difference  $\delta R$  between the charge radius of the nucleus in its excited and ground states is taken to be positive if the excited radius is larger than the ground-state radius. Thus, the coefficient  $4\pi Ze^2 R^2 c S'(Z) / 5E_0 = 1.23 \times 10^3$  if  $\delta_{IS}$  is expressed in mm/sec and  $\psi^2(0)$  in units of  $a_0^{-3}$ , where  $a_0$  is the Bohr radius.

<sup>3</sup> A. A. Maradudin, S. Ruby, and P. A. Flinn, *Phys. Rev.* **126**, 9 (1962); J. L. Feldman and G. K. Horton, *ibid.* **132**, 644 (1963).

<sup>4</sup> H. D. Erling, *Ann. Phys. (Leipzig)* **34**, 136 (1939).

<sup>5</sup> B. G. Childs and S. Weintraub, *Proc. Phys. Soc. (London)* **B63**, 267 (1950).

<sup>6</sup> D. G. House and E. V. Vernon, *Brit. J. Appl. Phys.* **11**, 254 (1960).

<sup>7</sup> V. N. Panyushkin and F. F. Voronov, *Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu* **2**, 153 (1965) [English transl.: *Soviet Phys.—JETP Letters* **2**, 97 (1965)]; H. S. Moeller and R. L. Mössbauer, *Phys. Letters* **24A**, 416 (1967); N. Panyushkin, *Fiz. Tverd. Tela* **10**, 1915 (1968) [English transl.: *Soviet Phys.—Solid State* **10**, 1515 (1968)].

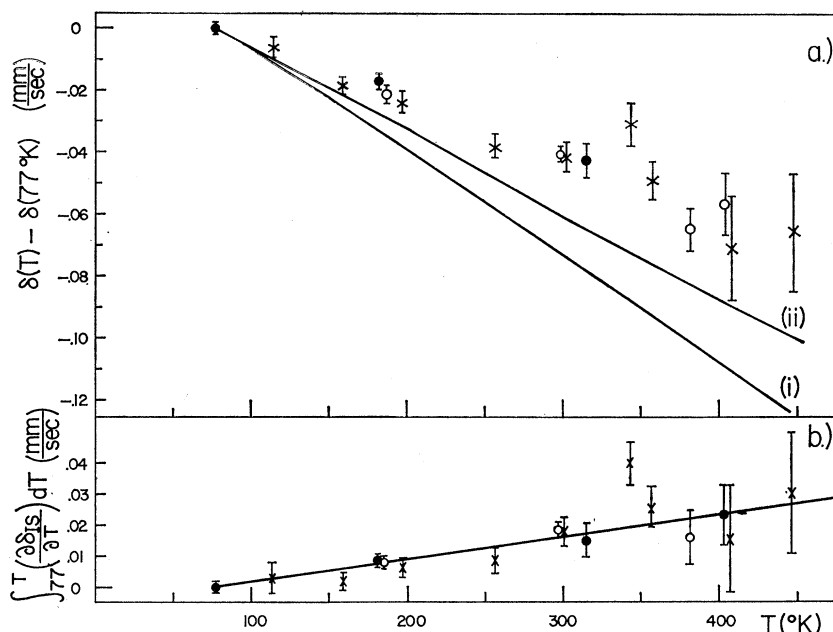
<sup>8</sup> D. A. Shirley, *Rev. Mod. Phys.* **36**, 339 (1964). As in this paper, we use  $R = 1.2 A^{1/3}$  fm.

\* Work supported by the National Science Foundation.

<sup>1</sup> A similar study was carried out in the temperature range of  $3.96^\circ < T < 77.4^\circ\text{K}$  by N. S. Snyder [*Phys. Rev.* **178**, 537 (1969)] in which no conclusion could be reached concerning the temperature dependence of the isomer shift because of uncertainties in the quadrupole shift.

<sup>2</sup> J. R. Harris, N. Benczer-Koller, and G. M. Rothberg, *Phys. Rev.* **137**, A1101 (1965).

FIG. 1. (a) Experimental line shift as a function of absorber temperature. Curve (i) shows the predicted second-order Doppler shift at constant volume; curve (ii) incorporates the volume correction. (b) The solid curve represents the best linear fit to the difference between the experimental data corrected for the quadrupole shift and curve (ii). The different symbols correspond to different source and absorber combinations.



The residual shifts  $\delta(77^{\circ}\text{K})$  for the three source-absorber combinations were  $+0.0134 \pm 0.0014$ ,  $-0.0042 \pm 0.0004$ , and  $-0.0134 \pm 0.0010$  mm/sec. Most, if not all, of  $\delta(77^{\circ}\text{K})$  can be accounted for by the combination of quadrupole splitting and the existence of preferred orientations in the rolled sources and absorbers. The x-ray studies of the samples and the calculations of  $\delta(77^{\circ}\text{K})$  will be described in detail in a subsequent publication. The shifts due to impurities in the samples are negligible.<sup>9</sup> These calculations also provide an estimate of  $(\partial\delta_{QS}/\partial T_a)_{V_a} = (1 \pm 1) \times 10^{-5}$  mm/sec  $^{\circ}\text{K}$ , approximately the same for the three cases measured, even though the residual shifts are different. Experimentally, the shift of the Mössbauer-line position with temperature was the same in all three cases, and the average of the three sets of runs will be analyzed below. The linewidths observed in the three cases were consistent with each other; the temperature dependence of the linewidth and of the Mössbauer fraction will be discussed in a separate paper.

In Fig. 1(a), the data points represent the measured line position as a function of temperature minus the residual shift at  $77^{\circ}\text{K}$ . The lower curve (i) shows the predicted second-order Doppler shift at constant volume. The upper curve (ii) incorporates the volume correction. The data are not fit by this second curve which shows that there is in fact a temperature-dependent isomer shift. Figure 1(b) shows the difference between the experimental data and curve (ii) after subtraction of the quadrupole shift. The solid line is the

best linear fit to this difference and yields

$$(\partial\delta_{IS}/\partial T_a)_{V_a} = (7.2 \pm 0.5) \times 10^{-5} \text{ (mm/sec } ^{\circ}\text{K)}.$$

A simple explanation of the origin of the observed effect which yields the correct order of magnitude with reasonable assumptions, and predicts the observed explicit temperature dependence of the Knight shift will be outlined. The explicit temperature dependence of the isomer shift is given by

$$(\partial\delta_{IS}/\partial T)_{V_a} = 1.23 \times 10^3 (\delta R/R) [\partial\psi_a^2(0)/\partial T]_{V_a}.$$

In a rigid, perfect lattice the  $s$  character of the electron wave function varies with the position of the electron state in the Brillouin zone. In a real vibrating lattice, however, the electron-phonon interaction will produce admixtures of states within an energy range of about  $kT$  of the original state. All states lying below the Fermi energy by more than about  $kT$  remain occupied, while states near the Fermi energy mix with higher states and change  $\psi_a^2(0)$ . Muto *et al.*<sup>10</sup> have shown that this change depends linearly on temperature. The core electrons may contribute indirectly insofar as their density at the nucleus is affected through screening by the conduction electrons.<sup>11,12</sup> In the calculations that follow, we have used the Hartree-Fock electron densities given by Ruby *et al.*<sup>13</sup> which include core effects. The conduction-electron configuration is taken to be

<sup>10</sup> T. Muto, S. Kobayasi, M. Watanabe, and H. Kozima, J. Phys. Chem. Solids **23**, 1303 (1962).

<sup>11</sup> M. F. Crawford and A. W. Shawlow, Phys. Rev. **76**, 1310 (1949).

<sup>12</sup> W. Humbach, Z. Physik **141**, 59 (1955).

<sup>13</sup> S. L. Ruby, G. M. Kalvius, G. B. Beard, and R. E. Snyder, Phys. Rev. **159**, 239 (1967); G. K. Shenoy and S. L. Ruby (private communication).

<sup>9</sup> B. I. Verkin, V. V. Chekin, and A. P. Vinnikov, Zh. Eksperim. i Teor. Fiz. **51**, 1870 (1966) [English transl.: Soviet Phys.—JETP **24**, 16 (1966)].

$5s^{1+m}p^{3-m}$ . The total density at the nucleus  $\psi_{5s^{1+m}p^{3-m}}^2(0)$  can be expressed in terms of the density at the nucleus of an atom in the configuration  $5s^1p^0$ ,  $\psi_{5s^2}^2(0)$ , by

$$\psi_{5s^{1+m}p^{3-m}}^2(0) = (1+m)(1-mx)(1+my)\psi_{5s^2}^2(0),$$

where  $x$  is the fraction by which the contribution of a single  $5s$  electron is reduced by the presence of another  $5s$  electron due to mutual screening and  $y$  is the effect of a  $5p$  electron. The screening factors  $x=0.15\pm0.03$  and  $y=0.13\pm0.03$  and the parameter<sup>14</sup>  $m=0.25$  were determined from Ruby *et al.*<sup>13</sup> The resulting density is insensitive to  $m$  because increasing the number of  $s$  electrons while decreasing the number of  $p$  electrons by the same amount, produces cancelling effects in the screening. Thus

$$\begin{aligned} \left(\frac{\partial\psi_a^2(0)}{\partial T}\right)_{v_a} &= \frac{\partial\psi_{5s^{1+m}p^{3-m}}^2(0)}{\partial m} \left(\frac{\partial m}{\partial T}\right)_v \\ &= 0.95\psi_{5s^2}^2(0) \left(\frac{\partial m}{\partial T}\right)_v. \end{aligned}$$

The order of magnitude of  $(\partial m/\partial T)_v$  can be estimated by assuming that the variation of the  $s$  character of the wave function with electron energy across the conduction band (about 10 eV) is roughly equivalent to the change of one  $p$  electron into one  $s$  electron. Thus

$$\left(\frac{\partial m}{\partial T}\right)_v = \left(\frac{\partial m}{\partial E}\right)_v \left(\frac{\partial E}{\partial T}\right)_v \approx \left(\frac{1}{10 \text{ eV}}\right) \frac{\partial}{\partial T} (kT) \approx 10^{-5} \text{ } ^\circ\text{K}^{-1}.$$

With  $\psi_{5s^2}^2(0)=19a_0^{-3}$  (Ref. 13) and  $\delta R/R \approx 10^{-4}$  (Ref. 15), we obtain  $\partial\delta_{\text{IS}}/\partial T \approx 2 \times 10^{-5}$  (mm/sec  $^\circ\text{K}$ ) in order-of-magnitude agreement with experiment.

A quantitative estimate of  $(\partial m/\partial T)_v$  can be obtained from measurements of the temperature dependence of the Knight shift. In general, the isomer shift and the Knight shift bear no direct relationship to each other because the isomer shift depends on the density and the nucleus of all  $s$  electrons, while the Knight shift depends on the density at the nucleus of  $s$  electrons at the Fermi surface only, and moreover on the difference between the numbers of electrons with spin up and spin down. However, the explicit temperature dependence of the isomer shift and of the Knight shift both depend only on the change in electron density at the nucleus due to changes in the wave functions of electrons at the Fermi surface. For want of quantitative information we assume that the effect of core polarization on the Knight shift is negligible compared with other considered uncertainties.

The Knight shift is ordinarily given by<sup>16</sup>

$$\begin{aligned} K &= (8\pi/3)(\chi_p\Omega)P_F' \\ &= (8\pi/3)(\chi_p\Omega)F_r(\tfrac{1}{2},Z)(1-\delta)(1-\epsilon)P_F, \end{aligned}$$

where  $P_F$  represents the density at the nucleus, averaged over the Fermi surface of electrons with the Fermi energy;  $\chi_p$  is the Pauli susceptibility per unit volume;  $\Omega$  is the atomic volume;  $F_r(\tfrac{1}{2},Z)=1.31$  is the correction which changes the nonrelativistic electron density into a relativistic density for a point nucleus;  $1-\delta=0.98$  and accounts for finite nuclear size; and  $1-\epsilon \approx 1$  corrects for a uniform distribution of nuclear magnetization. The value for  $\chi_p=3.95 \times 10^{-29}$  cm<sup>3</sup>/atom was obtained from specific-heat measurements,<sup>17</sup> and  $(\partial K/\partial T)_v = [(9.0 \pm 2.3) \times 10^{-7}]^\circ\text{K}^{-1}$ .<sup>18</sup> Since the explicit temperature dependence of  $\chi_p\Omega$  is negligible, then

$$(\partial P_F/\partial T)_v = (3.1 \pm 0.8) \times 10^{-4} a_0^{-3} \text{ } ^\circ\text{K}^{-1}.$$

Because  $P_F$  does not include the core electron densities,  $(\partial P_F/\partial T)_v$  is related to  $(\partial m/\partial T)_v$  by  $(\partial P_F/\partial T)_v = 0.9\psi_{5s^2}^2(0)(\partial m/\partial T)_v$ . Finally,

$$(\partial\delta_{\text{IS}}/\partial T)_{v_a} = (1.23 \times 10^3)(1.05)(\partial P/\partial T)_v \delta R/R,$$

and  $\delta R/R = (1.8 \pm 0.4) \times 10^{-4}$ , where the error is statistical only.

This analysis yields an unambiguous determination for the sign of  $\delta R/R$ . The magnitude lies between  $\delta R/R = (3.3 \pm 1.1) \times 10^{-4}$  obtained from Mössbauer measurements combined with measurements of internal conversion,<sup>19</sup> and  $\delta R/R \approx (1.2 \pm 0.4) \times 10^{-4}$  which covers most of those results<sup>15</sup> obtained from Mössbauer measurements combined with chemical calculations. Greenwood *et al.*<sup>20</sup> with a somewhat different chemical calculation obtain  $\delta R/R = 3.6 \times 10^{-4}$ .

The consistency of  $\delta R/R$  values obtained by the three different methods confirms the relation between the temperature dependence of isomer shift and that of the Knight shift. In fact, if one adopts a value of  $\delta R/R$  from Mössbauer chemical experiments, the temperature dependence of the Knight shift may be predicted on the basis of this model. It is interesting to note that over the range of 77 to 450°K the total increase in  $s$ -electron density at the nucleus is equivalent to only  $6 \times 10^{-3}$   $s$  electrons.

*Note added in proof.* G. T. Emery and M. L. Perlman (private communication) have recalculated  $\delta R/R$  in Ref. 19 and find  $\delta R/R = (1.84 \pm 0.37) \times 10^{-4}$  in excellent agreement with the present results.

<sup>16</sup> H. Kopferman, *Nuclear Moments*, translated by E. E. Schneider (Academic Press Inc., New York, 1959).

<sup>17</sup> W. D. Knight, A. G. Berger, and V. Heine, *Ann. Phys. (N. Y.)* **8**, 173 (1959).

<sup>18</sup> G. A. Matzkanin and T. A. Scott, *Phys. Rev.* **151**, 360 (1966).

<sup>19</sup> J. P. Bocquet, Y. Y. Chu, O. C. Kistner, M. L. Perlman, and G. T. Emery *Phys. Rev. Letters* **17**, 809 (1966).

<sup>20</sup> N. N. Greenwood, P. G. Perkins, and D. H. Wall, *Phys. Letters* **28A**, 339 (1968).

<sup>14</sup> In Ref. 12 the parameter  $m$  refers to the *total* number of electrons and therefore corresponds to  $(1+m)$  in this paper.

<sup>15</sup> S. L. Ruby *et al.* Ref. 13; J. K. Lees and P. A. Flinn, *J. Chem. Phys.* **48**, 882 (1968); A. J. F. Boyle, D. St. P. Bunbury and C. Edwards, *Proc. Phys. Soc. (London)* **79**, 416 (1964); M. Cordey-Hayes, *J. Inorg. Nucl. Chem.* **26**, 915 (1964).