PHYSICAL REVIEW VOLUME 178, NUMBER 2 10 FEBRUARY 1969

Mössbauer-Effect Measurements of the Thermal Shift of Sn^{119} in β-Sn below 90°K†

N. S. SNYDER*
Lyman Laboratory, Harvard University, Cambridge, Massachusetts 01451
(Received 26 August 1968)

The shift in the resonant absorption energy of the 23.9-keV transition of Sn^{119} was observed as the temperature of a β-tin Mössbauer absorber was varied between 90 and 3.6°K. The metallic Sn^{119m} source was kept at constant temperature. A continuously calibrated slope-detection method was employed. The standard deviations of the fractional energy shifts observed were about 0.8 parts in 10^{15}, or 3% of the total thermal shift of approximately 26×10^{-15} measured between 77 and 4°K. Earlier measurements of the thermal shift in metallic tin had a statistical accuracy of about 40% over 100°K, and were not extended below 77°K. Such observations were interpreted on the basis of the relativistic time-dilation effect. Because of the improved accuracy of the present measurements, it has been necessary to consider also the temperature variation of the isomer shift and of the quadrupole asymmetry of a preferentially aligned sample in assessing the agreement with theory. The recrystallization texture of the 27-μ absorber foil was analyzed by x-ray methods. A search for a possible small shift in energy at the superconducting transition in tin was also made, using the same apparatus. Measurements were made by alternating the absorber temperature above and below the transition temperature every few minutes. The results indicated no change in the absorption energy within the limits of 0.8 parts in 10^{15}, in accord with previous studies.

1. INTRODUCTION

THE term "thermal shift" refers to the energy change of a nuclear γ-ray transition caused by a temperature change of the lattice environment. Since the size of such shifts even at high temperatures is limited to a few parts in 10^{15} per °K, the techniques of nuclear resonant absorption (Mössbauer effect) are required for observation. At present thermal shifts are thought to originate chiefly from two sources: the relativistic time-dilation shift,[1,2] which is proportional to $\langle v^2\rangle$, the mean-squared velocity of the emitter or absorber, and the isomer shift,[3] which originates in the finite volume of the nucleus and depends upon the electron density at the nucleus and the difference in charge radius between the ground and excited states. As discussed in Sec. 2, the volume-dependent part of the change of the isomer shift with temperature can be obtained to a good accuracy from measurements of the pressure coefficient of the transition energy if results for the compressibility and thermal expansion are available. However, there are at present no detailed theories which would give predictions for the explicit temperature variation of the isomer shift, and experimental data on the problem have so far not established any general principles. For Fe^{57} in metallic iron at room temperature,[4] the volume-independent shift was interpreted to fall between values of about -0.1 and $+0.02\times10^{-15}$/°K, while for studies of Fe^{57} in various host lattices,[5] an explicit shift of equal magnitude and opposite sign to the volume-dependent shift was postulated to explain the results. A reinterpretation of these and other Fe^{57} data, using a new approach for the subtraction of the time-dilation shift[6] has, however, indicated the presence of an explicit temperature dependence of the isomer shift, although the magnitude of about 0.1×10^{-15}/°K found is close to the statistical uncertainty in the data.

Early measurements of the thermal shift of the 23.9-keV line of Sn^{119} in β-tin[7] were not of sufficient accuracy to reveal the presence of even the volume-dependent isomer shift, although this shift is expected to be a sizable fraction of the larger relativistic shift. The measurements of the β-tin thermal shift discussed in this paper were undertaken to investigate further the existence of an explicit temperature dependence of the isomer shift and the completeness of present interpretations of the thermal shift. A Sn^{119m} source of isotopically enriched β-tin was kept at a constant temperature while measurements were made with a β-tin absorber at a series of temperatures between 90 and 3.6°K. The shifts were observed by a continuously calibrated method of slope detection, described further in Sec. 3.

The thermal shift of tin is of interest because measurements of the pressure coefficient of the transition energy $(1/\nu)(\partial\nu/\partial P)_T$ at room temperature are available,[8,9] and the compressibility and thermal expansion are large enough that the volume dependence of the isomer shift is not overshadowed by the larger time-dilation shift.

---

† This paper is based on a thesis submitted to Harvard University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Supported in part by the Office of Naval Research under Contract No. Nonr 1866 (56).

* Present address: National Bureau of Standards, Boulder, Colo.

[1] R. V. Pound and G. A. Rebka, Jr., Phys. Rev. Letters 4, 274 (1960).

[2] B. D. Josephson, Phys. Rev. Letters 4, 341 (1960).

[3] O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters 4, 412 (1960); D. A. Shirley, Rev. Mod. Phys. 36, 339 (1964).

[4] R. V. Pound, G. B. Benedek, and R. Drever, Phys. Rev. Letters 7, 405 (1961).

[5] W. A. Steyert and R. D. Taylor, Phys. Rev. 134, A716 (1964).

[6] R. M. Housley and F. Hess, Phys. Rev. 164, 340 (1967).

[7] A. J. F. Boyle, D. St. P. Bunbury, C. Edwards, and H. E. Hall, Proc. Phys. Soc. (London) 76, 165 (1960).

[8] V. N. Panyushkin and F. F. Voronov, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu 2, 153 (1965) [English transl.: JETP Letters 2, 97 (1965)].

[9] H. S. Möller and R. L. Mössbauer, Phys. Letters 24A, 416 (1967); H. S. Möller, Z. Physik 212, 107 (1968).

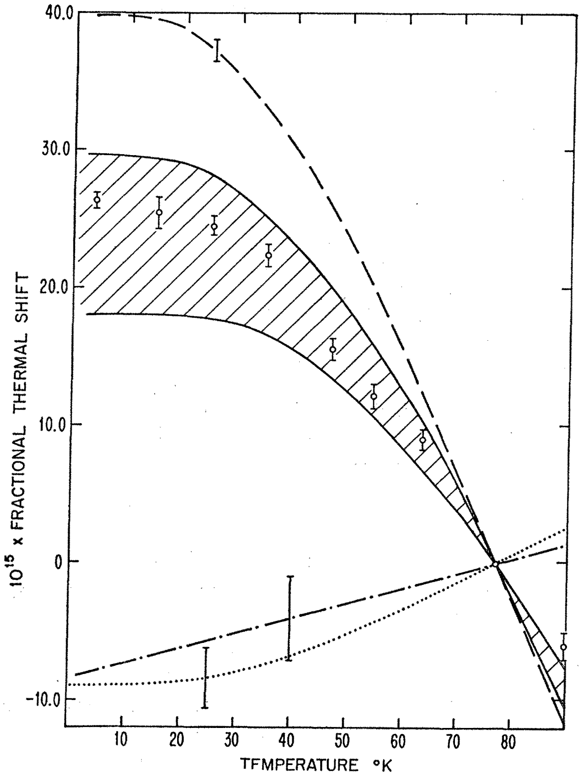

FIG. 1. Prediction for the thermal shift of β-tin. The dashed line represents the time-dilation contribution, the dotted line the volume-dependent isomer shift, and the broken line the quadrupole asymmetry. Bars indicate the error associated with each curve. The indicated experimental points are discussed in the text.

Furthermore, this latter effect can be predicted from specific-heat measurements[10,11] below 100°K, where the resonant fraction f is large. However, because the β-tin lattice is tetragonal, a complication results from the temperature dependence of the asymmetry in intensity of the quadrupole-doublet components of the excited state. This effect is discussed further in Sec. 2, and the results of an x-ray examination to determine the extent of preferential alignment of the polycrystalline sample are presented in the Appendix.

In addition to the thermal shift, a possible shift of the γ-ray energy at the superconducting transition in tin was sought. The same continuously calibrated slope-detection apparatus was used, with the temperature alternately switched between 3.65 and 3.80°K every few minutes to eliminate the influence of long-term drifts.

2. THERMAL SHIFT

A. Relativistic Time-Dilation Shift

In the harmonic-potential approximation, the temperature coefficient of the time-dilation shift for a monatomic lattice with one atom per unit cell is

$$(1/\nu)(\partial\nu_{\rm rel}/\partial T)_P=-C_{LV}/2mc^2. \qquad (1)$$

C_{LV} is the specific heat of the lattice at constant volume. Measurements of the specific heat of β-tin made by Lange[10] between 10 and 100°K agree with other results[11] at the lower end of this temperature region. The specific heat of α-tin in this temperature range was also measured by Lange with the same apparatus, and the values agree very well with more recent data.[12] The predicted contribution to the thermal shift is shown by the dashed line in Fig. 1, in which 77.4°K is arbitrarily chosen to have zero shift. The bar indicates the error of about 2% in the specific-heat measurements. In comparison to this error and that expected from the thermal shift measurements, the corrections for the electronic specific-heat contribution and the conversion of the data to constant volume are negligible and were not included. A Debye-model estimate[4] for tin indicates that the relativistic volume-dependent contribution to the thermal shift is small compared to the explicit term in Eq. (1). Possible anharmonic corrections to Eq. (1) will also be neglected here, since a three-dimensional calculation for lead[13] gave a correction of only about 0.5%.

B. Isomer Shift

In the approximation that the volume and temperature are adequate parameters to describe the isomer shift at constant pressure, one may write

$$\frac{1}{\nu}\left(\frac{\partial\nu_{\rm isom}}{\partial T}\right)_P=\frac{1}{\nu}\left(\frac{\partial\nu_{\rm isom}}{\partial P}\right)_T\left(\frac{\partial P}{\partial \ln V}\right)_T\left(\frac{\partial \ln V}{\partial T}\right)_P+\frac{1}{\nu}\left(\frac{\partial\nu_{\rm isom}}{\partial T}\right)_V. \qquad (2)$$

Two room-temperature measurements of $(1/\nu)(1\nu/1P)_T$ for β-tin are available, both based upon finding the center of the line traced out by a velocity spectrometer rather than upon the more sensitive slope-detection method. The measurements of Panyushkin and Voronov[8] give about $(-8.3\pm3.0)\times10^{-18}$ bar^{-1}, while the maximum value of the coefficient measured by Möller and Mössbauer[9] is about 4.7×10^{-18} bar^{-1}. The high-pressure points (around 100 kbar) in the published graphs were not included in obtaining the above quantities because a phase transition occurs near this pressure[14] and the authors did not give an estimate of possible pressure variation over their samples. Because both SnO and SnO_2 have a much higher resonant

---

[10] F. Lange, Z. Physik. Chem. (Leipzig) **110**, 343 (1924).

[11] W. H. Keesom and J. van der Ende, Proc. Acad. Sci. Amsterdam **35**, 143 (1932).

[12] R. W. Hill and D. H. Parkinson, Phil. Mag. **43**, 309 (1952).

[13] E. M. Iolin, Fiz. Tverd. Tela **5**, 1194 (1963) [English transl.: Soviet Phys.—Solid State **5**, 872 (1963)].

[14] J. C. Jamieson, Geol. Soc. Am. Spec. Papers **73**, 178 (1963). R. A. Stager, A. S. Balchan, and H. G. Drickamer, J. Chem. Phys. **37**, 1154 (1962); J. D. Barnett, V. E. Bean, and H. T. Hall, J. Appl. Phys. **37**, 875 (1966).

fraction f at room temperature than β-tin does, and these impurities have been found in some sources,[15] more accurate low-temperature measurements of the pressure coefficient would be useful. However, the coefficient is not expected to vary much with temperature since the isomer shift makes the dominant contribution.

Rayne and Chandrasekhar[16] have made low-temperature measurements of all the elastic coefficients of β-tin which are needed for the calculation of the volume compressibility at 300, 77, and 4°K. There is evidently no significant change in the compressibility below 77°K, where the value 1.72×10^{-6} bar^{-1} is found. At room temperature, the calculated comparessibility is 1.82×10^{-6} bar^{-1}, which agrees with the direct measurements of compressibility by Bridgman and others.[17] However, the room-temperature elastic constants of Rayne and Chandrasekhar are not in complete agreement with recent measurements of other authors,[18] and such differences could affect the calculated compressibility by as much as 25%. A direct measurement of the compressibility at 77°K was made in connection with another investigation,[19] but the result of 3.1×10^{-6} bar^{-1} seems too large in comparison with the room-temperature value to be probable. From a measurement of the Young's modulus[20] at 93°K a value for the compressibility which agrees with the Rayne and Chandrasekhar coefficients can be obtained.

The dotted line in Fig. 1 shows the contribution to the thermal shift from the volume dependence of the isomer shift. The value used for the pressure coefficient was $(-8.3\pm3.0)\times10^{-18}$ bar^{-1}, the compressibility was taken as 1.72×10^{-6} bar^{-1}, and the low-temperature thermal-expansion data of White[21] was employed. The uncertainty indicated by the bar is due mainly to the pressure-coefficient measurements. For tin, there seem to be no theoretical considerations at present that can be applied to predict the size of a possible explicit temperature dependence of the isomer shift as can be essayed for the case of Fe^{57} in several hosts.[6,22]

C. QUADRUPOLE ASYMMETRY

The spin-$\frac{3}{2}$ excited state of the Sn^{119} transition is split by the quadrupole interaction in β-tin, but the splitting Δ is not large enough compared to the linewidth to be resolved.[23,24] If θ is the angle between the direction of γ-ray transmission and the axis of symmetry of a tin microcrystal, the angular dependence of the transition intensities may be denoted by $I_{|m|}(\theta)$, and the variation of the resonant fraction with angle by $f(\theta)$. The extent of the preferential alignment of the individual crystals in the sample may be represented by a distribution factor $a(\theta)$. Then if $G_{|m|}=\int a(\theta)f(\theta)\times I_{|m|}(\theta)d\theta$, the shift in the centroid of the line is given simply by

$$\delta\nu_{\mathrm{quad}}=\tfrac{1}{2}\Delta\frac{G_{1/2}-G_{3/2}}{G_{1/2}+G_{3/2}},\qquad(3)$$

for the case of these studies in which only Δ of the absorber is a variable. The lineshape asymmetry exhibited by even a randomly oriented polycrystalline sample was first considered by Karyagin.[25] (See, also, Goldanskii *et al.*[26]) Using in Eq. (3) the approximation of Kündig *et al.*[27] for $f(\theta)$ when f is known for directions parallel and perpendicular to the axis of symmetry, and substituting the f-anisotropy measurements of Alekseevskii *et al.*,[28] one obtains for the total shift from 77 to 4°K due to this effect about $-|\Delta|\times(2.7\times10^{-3})$, or -3×10^{-15} in fractional units.

On the other hand, if the microcrystals of the sample are mainly aligned in one direction, f cancels out of Eq. (3), and the dependence on Δ can be much stronger. Details of an x-ray study of the absorber are given in the Appendix, since a search of the literature did not lead to any relevant references. The result was a contribution to the thermal shift of $(-0.20\pm0.04)\delta|\Delta|$ from the quadrupole asymmetry. There have been no determinations of the change in Δ below 77°K to an accuracy adequate for the present purposes, although one author reported an upper limit of ±0.03 mm/sec.[28] However, two different methods,[23,24] both employing the Mössbauer effect, have given similar results for the change in the splitting between 300 and 77°K. The more accurate of these two determinations gives

$$\begin{aligned}\delta\Delta=(0.07\pm0.028)\ \mathrm{mm/sec\ or}\ (1/\Delta)(d\Delta/dT)\\=(-1.1\pm0.4)\times10^{-3}/^{\circ}\mathrm{K}.\end{aligned}$$

This rate of change of Δ is also consistent with the rate reported[29] just above the superconducting transition of

---

[15] C. Lamborizio and I. Ortalli, Nuovo Cimento **36**, 1059 (1965).

[16] J. A. Rayne and B. S. Chandrasekhar, Phys. Rev. **120**, 1658 (1960).

[17] S. C. Prasad and W. A. Wooster, Acta Cryst. **8**, 682 (1955).

[18] W. P. Mason and H. E. Bömmel, J. Acoust. Soc. Am. **28**, 930 (1956); D. G. House and E. V. Vernon, Brit. J. Appl. Phys. **11**, 254 (1960).

[19] A. J. Darnell and W. F. Libby, Phys. Rev. **135**, A1453 (1964).

[20] W. Köster, Z. Metallk. **39**, 1 (1948).

[21] G. K. White, Phys. Letters **8**, 294 (1964).

[22] G. B. Benedek and J. Armstrong, J. Appl. Phys. Suppl. **32**, 106S (1961); W. M. Walsh, Jr., J. Jeener, and N. Bloembergen, Phys. Rev. **139**, A1338 (1965); E. Šimánek and R. Ohrbach, Phys. Rev. **145**, 191 (1966).

[23] K. P. Mitrofanov, M. V. Plotnikova, and V. S. Shpinel', Zh. Eksperim. i Teor. Fiz. **48**, 791 (1965) [English trans.: Soviet Phys.—JETP **21**, 524 (1965)].

[24] B. A. Komissarova, A. A. Sorokin, and V. S. Shpinel', Zh. Eksperim. i Teor. Fiz. **50**, 1205 (1966) [English transl.: Soviet Phys.—JETP **23**, 800 (1966)].

[25] S. V. Karyagin, Dokl. Akad. Nauk SSSR **148**, 1102 (1963) [English transl.: Proc. Acad. Sci. USSR, Phys. Chem. Sec. **148**, 110 (1964)].

[26] V. I. Gol'danskii, E. F. Makarov, and V. V. Khrapov, Phys. Letters **3**, 344 (1963).

[27] W. Kündig, K. Ando, and H. Bömmel, Phys. Rev. **139**, A889 (1965).

[28] N. E. Alekseevskii, A. P. Kir'yanov, V. I. Nizhankouskii, and Yu. A. Samarskii, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu **2**, 269 (1965) [English transl.: JETP Letters **2**, 171 (1965)].

[29] F. Pobell, Z. Physik **188**, 57 (1965).

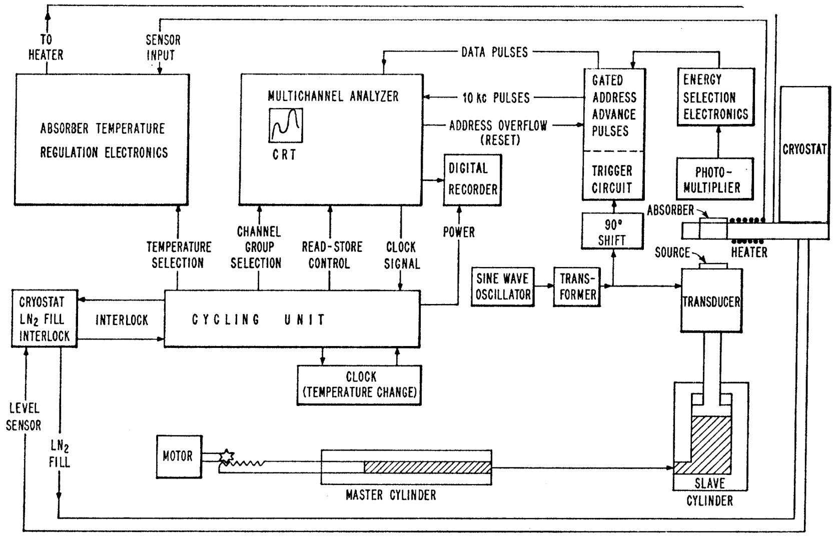

FIG. 2. Schematic diagram of the experimental arrangements.

3.72°K. The sign and magnitude of the field gradient in β-tin indicates that the conduction electrons are its main source.[30] Nuclear magnetic resonance studies have shown similar temperature variation for the quadrupole splitting in indium[31] and antimony,[32] the periodic table neighbors of tin, with one and three $5p$ electrons, respectively. In these two metals, the rate of change of the quadrupole splittings decreases somewhat below 77°K. On the basis of this decrease and the higher-temperature results for tin mentioned above, the change in Δ between 77 and 4°K has been estimated as $\delta\Delta = (0.012\pm0.008)$ mm/sec, with a liberal allowance for the uncertainty involved. The resulting fractional shift is $(-8.0\pm5.7)\times10^{-15}$, more than twice that for a randomly oriented sample. In Fig. 1, this shift is prorated linearly over the temperature interval, as shown by the broken line. The bar indicates the uncertainties discussed above. The resultant of the three contributions of the relativistic time-dilation shift, the volume-dependent isomer shift, and the quadrupole asymmetry should fall within the area bounded by the two solid lines. These solid lines represent the expected range of error when the independent uncertainties of the three components are combined to give the rms value.

If the change of Δ with temperature is volume-dependent to a significant extent, part of the correction discussed above would already be included in the term involving the experimentally determined pressure coefficient. Observations of the linewidth with pressure[8] are not accurate enough to answer this question. Measurements of the anisotropic Knight shift[33] which gives the volume dependence of the average quadrupole moment per electron at the Fermi surface are available, however, and may be used to set a rough upper limit. This procedure indicates that only a fraction of the observed change of Δ with temperature may be ascribed to volume effects, and that the contribution by the mechanism of Eq. (3) is only a fraction of the pressure coefficient. Since the total effect of the temperature variation of Δ makes a contribution of the same order of magnitude as that of the volume dependence, it would seem that the correct procedure was followed above.

3. EXPERIMENTAL PROCEDURE

A. Source and Absorber

The 2-mCi source of Sn^{119m} obtained from New England Nuclear Corporation was prepared from tin enriched to about 96% in the mass-118 isotope. The source was rolled after it was received to a thickness of about 10 μ. The absorber was rolled to a thickness of 27 μ from natural tin of 99.9999% purity supplied by A. D. Mackay, Inc. No heat treatment was needed for the rolling, of course, but it should be noted that the absorber was heated to about 60°C when it was attached to the cryogenic sample holder. The recrystallization texture of the absorber is described in the Appendix. Rolling and heating took place more than two years before this x-ray examination was made. The full linewidth for this source-absorber combination was found to be about 1.20 mm/sec at liquid-nitrogen temperatures, using Fe^{57} calibration.

B. Shift Detection

The slope-detection method for measuring shifts small compared with the linewidth was used; the procedure was employed in measurements of the gravitational red

---

[30] F. Borsa and R. G. Barnes, Phys. Rev. Letters **12**, 281 (1964).

[31] W. W. Simmons and C. P. Slichter, Phys. Rev. **121**, 1580 (1961); R. R. Hewitt and T. T. Taylor, Phys. Rev. **125**, 524 (1962).

[32] R. R. Hewitt and B. F. Williams, Phys. Rev. **129**, 1188 (1963).

[33] G. A. Matzkanin and T. A. Scott, Phys. Rev. **151**, 360 (1966).

shift.[34] The measured shifts are calibrated by introducing a known Doppler displacement velocity which again is small compared with the linewidth. A schematic diagram of the automated experimental arrangement is given in Fig. 2, and a more detailed description than that given below may be found in the author's dissertation.[35] The source is mounted on an electromagnetic transducer driven by a sine wave at 100 Hz. The transducer is situated in a cryogenic environment at liquid-nitrogen temperatures. A hydraulic slave cylinder moves the transducer and its nitrogen Dewar towards and away from the stationary absorber at the constant velocity of 24.05×10^{-3} mm/sec. A geared-down synchronous motor which is reversed every 6 min powers the master hydraulic cylinder. Data pulses are directed to a Radiation Instrument and Development Lab. 400-channel analyzer (Model 34-12) operated in the time mode and synchronized to the transducer waveform.

C. Temperature Control

The transducer is enclosed in a radiation shield. Copper magnet wire is used for a resistance thermometer at the source holder. Fluctuations of source temperature during data accumulation were kept below ±0.5°K by controlling the level of liquid nitrogen in the Dewar. The absorber is mounted on a horizontal "cold finger" with heater coil which was added to the bath of a conventional metal cryostat. A radiation shield at cryostat bath temperature was provided for the absorber. A carbon resistor was cemented into a hole in the copper bar to provide a signal for electrical temperature control at liquid-helium temperatures. The resistor was calibrated before and during each run by a helium vapor-pressure thermometer. To monitor higher temperatures, a miniature platinum temperature sensor (Rosemount 146 L2) was also cemented into a position near the absorber. Fine control of absorber temperature is effected by an error signal to the heater using electronics based on designs by Blake *et al.*[36] Control was maintained within ±5 m°K at liquid-helium temperatures.

For temperatures in the range between liquid helium and nitrogen, a system which delivered cold helium gas from a separate supply Dewar to the bottom of the cryostat was developed. This permitted the same geometrical setup to be used for these temperatures so that any systematic shift due to relative vibration between source and absorber should cancel out of the measurements. Temperature drift over a 24-h period was typically less than 0.25°K, well within the stability required for the experiments.

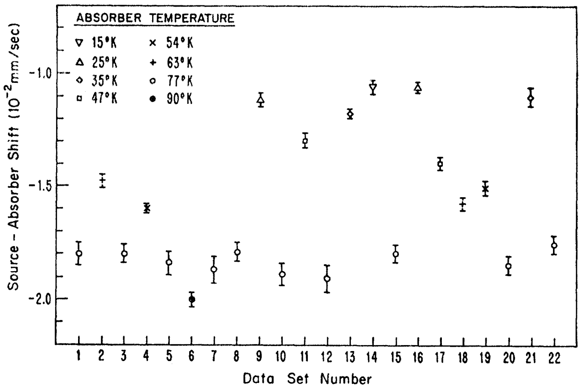

FIG. 3. Source-absorber thermal shifts for β-tin. Measurements extended over a six-month period.

4. EXPERIMENTAL RESULTS

A. Thermal Shift

Data from all runs are shown in Fig. 3, which is presented to give an indication of the shift reproducibility over a six-month period. The errors shown are the statistical standard deviations. Data with the absorber at 77.4°K were taken at the beginning of most of the runs, and the stability of these points over the period of data taking is within the statistical uncertainty. However, some of the runs repeated at other temperatures do not show such good agreement, although the deviations seem to be random rather than systematically in one direction. It is unlikely that errors due to the platinum temperature sensor occurred, because the reproducibility at liquid-nitrogen temperatures was better than that claimed by the manufacturer. Other possibilities are recrystallization changes in the source, which was rolled just before the measurements started, or a change in the second harmonic response of the transducer or the oscillator output, which could cause a small instrumental shift. Since these small discrepancies are only slightly larger than the statistical uncertainty, it was not feasible to investigate them further with the existing apparatus. A better procedure would be to take simultaneous measurements at the standard temperature (77.4°K here), and regard only the difference as significant.

The averaged results for the thermal shift are shown in Fig. 1. The error bars represent the statistical uncertainty associated with each temperature and, also, the much smaller contribution from the statistical uncertainty of the 77.4°K shift which was subtracted to obtain each point. The point at 3.7°K was obtained by averaging the measurements at the superconducting transition discussed in Sec. 4B. The agreement between the measured thermal shift and the prediction is reasonably good, but the lattitude permitted by the experimental errors in the components that make up the theoretical curve is considerable, as discussed in Sec. 2. On the basis of the present agreement, there

---

[34] R. V. Pound and G. A. Rebka, Jr., Phys. Rev. Letters **4**, 337 (1960); R. V. Pound and J. L. Snider, Phys. Rev. **140**, B788 (1965).

[35] N. S. Snyder, thesis, Harvard University, 1968 (unpublished).

[36] C. Blake, C. E. Chase, and E. Maxwell, Rev. Sci. Instr. **29**, 715 (1958); C. Blake and C. E. Chase, *ibid.* **34**, 984 (1963).

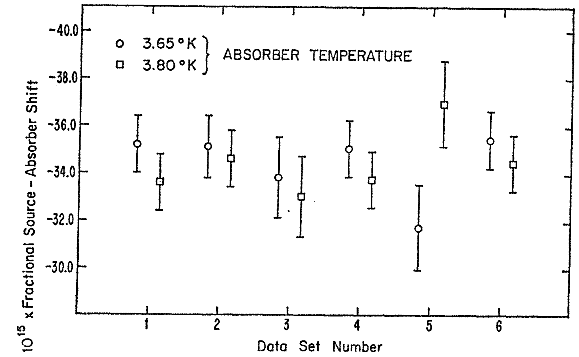

FIG. 4. Source-absorber shifts measured above and below the 3.72°K superconducting transition temperature.

seems to be no necessity of postulating an explicit temperature dependence of the isomer shift. However, the uncertainties in the predicted curve would allow an explicit term of as much as $\pm 0.14 \times 10^{-15}/°\mathrm{K}$ around 70°K. According to the conclusions of Ruby *et al.*,[37] the atomic 5*s* electron density is chiefly responsible for the observed isomer shifts between various compounds of tin. Using this analysis, one obtains roughly $(\partial \ln\psi_{5s}^2(0)/\partial T)_V \approx \pm 20 \times 10^{-6}/°\mathrm{K}$. It is interesting to compare this to some recent measurements of the temperature and pressure dependence of the isotropic Knight shift of β-tin,[33,38] although the average of $\psi^2(0)$ is taken over the Fermi surface in the latter case. The explicit temperature dependence deduced for the Knight shift was $(-0.12 \pm 0.03) \times 10^{-3}/°\mathrm{K}$ at room temperature, and the magnitude at lower temperatures would evidently be about the same.[38] Matzkanin and Scott[33] have attempted to explain their results in accord with the hypothesis that the temperature dependence is due to variations of the electron density, but their calculation for this temperature dependence is about an order of magnitude smaller than their results. The present estimates of $(\partial\psi_{5s}^2(0)/\partial T)_V$ are also about an order of magnitude smaller.

B. Superconducting Transition

The transition temperature of a sample of the tin used for the absorber was measured by a resistive method in a separate experiment and found to be in accord with the presently accepted value of 3.72°K. Results of individual runs are shown in Fig. 4 where the bars represent statistical standard deviations. The weighted average over all runs gives

$$(1/\nu)[\nu(3.65°\mathrm{K}) - \nu(3.80°\mathrm{K})] = (-0.38 \pm 0.77) \times 10^{-15}.$$

In terms of *s* electron density, using the same analysis as above, $\delta\psi_{5s}^2(0)/\psi_{5s}^2(0) \approx (-50 \pm 110) \times 10^{-6}$. It is apparent from Fig. 4 that the fifth run looks slightly anomalous, and its contribution is significant in terms of decreasing the magnitude of the weighted average. But even if this run is excluded for reasons of possible instrumental malfunction, the revised average still does not give a shift larger than the statistical uncertainty. Furthermore, the probability that an individual run could fall two standard deviations from the mean is small (about 5%) but not negligible. Hence, it is concluded that no shift has been observed within about 0.8 parts in 10^{15}. This is in agreement with previous measurements by Pobell[29] which did not, however, employ a continuously calibrated method of measurement as did the present measurements. Most effects which could give rise to a superconducting transition shift such as the volume change[39] are expected to be several orders of magnitude below the present limits of accuracy, with the possible exception of a significant change of the quadrupole splitting.[29,31]

ACKNOWLEDGMENTS

The author would like to thank Professor R. V. Pound for suggesting this investigation and for many useful discussions during the course of the work. Velocity-synchronization electronics for the time-mode operation of the multichannel analyzer were designed by Dr. Rufus F. Walker. Professor B. Roessler of the Brown University Division of Engineering was most helpful in arranging for x-ray films of the sample. The author was a National Science Foundation Graduate Fellow.

APPENDIX

Previous work on the recrystallization texture of tin[40,41] was not directly applicable to the present case. The grains of the sample described here were about 1 mm wide at the surface, too large to permit the usual pole-figure determination with an x-ray diffractometer. Hence, it was decided to take a series of Laue exposures with a 1-mm collimated beam at several positions on the foil. Because the surface area is about 600 mm², these exposures can only be regarded as a sampling. Radiation from a Mo target with a 35-keV energy cutoff was used; this should have penetrated the 27 μ sample rather well.

Except for two very faint films in which the beam was evidently misaligned, all the films gave a clear indication of an oriented crystal. No portions of Debye arcs were seen; the back-reflection spots were confined to angular regions which had about a one-degree spread. The [100] and [010] zone hyperbolas were visible, as was their intersection point, the (001) spot. Series of planes of other zones also appeared and were used to verify the

---

[37] S. L. Ruby, G. M. Kalvius, G. B. Beard, and R. E. Snyder, Phys. Rev. **159**, 239 (1967).

[38] F. Borsa and R. G. Barnes, J. Phys. Chem. Solids **27**, 567 (1966).

[39] G. D. Cody, Phys. Rev. **111**, 1078 (1958); K. Andres, J. L. Olsen, and H. Rohrer, IBM Journal **6**, 84 (1962).

[40] J. Prins, Z. Krist. **86**, 301 (1933).

[41] K. Toman and M. Simerská, Czech. J. Phys. **8**, 101 (1958).

analysis, using published tables of angles for β-tin.[42] The four-fold symmetry of the pattern served to eliminate the (100) and (010) orientations, which would, if present, make a contribution to the shift of opposite sign from the (001) orientation. In the eight films examined, the (001) pole was always found between 6 and 30° from the normal to the foil, with some clustering at about 20°. The average value was $\theta=21°$ with an rms deviation of 7.4°. This indicates that the (001) plane is nearly the plane of the foil, but the possibility that some nearby plane, such as the (112) plane, is actually the preferred plane would have to be examined in a definitive study. For the purposes of the present experiments, the quadrupole asymmetry was calculated from the angular distribution to be $-|\Delta|(0.20\pm0.04)$, using also Eq. (3) and the angular intensity ratios for $|m|$ of $\frac{1}{2}$ and $\frac{3}{2}$. The uncertainty given is somewhat larger than the observed rms deviation in view of the fact that it was impractical to sample the entire area of the foil.

---

[42] S. A. Bradford and R. W. Vieth, Trans. Met Soc. AIME **236**, 232 (1966), and references cited therein.

PHYSICAL REVIEW VOLUME 178, NUMBER 2 10 FEBRUARY 1969

Zeeman Effect in the Absorption Spectra of Trivalent Ytterbium Ions in Different Site Symmetries in Calcium Fluoride

J. Kirton and A. M. White
Royal Radar Establishment, Malvern, Worcestershire, England

(Received 30 September 1968)

The Zeeman effect has been observed in the optical spectra of Yb^{3+} ions in different sites in CaF_2. All but one of the correlations between ESR and optical spectra, reported by Kirton and McLaughlan, have been checked and confirmed, and the upper-state g values have been determined. Ambiguity in the interpretation of the rhombic spectra has been eliminated, and we have shown with 90% confidence that the upper-state splitting of Yb^{3+} in cubic sites is greater than 18.3 cm^{-1}.

1. INTRODUCTION

A RECENT study[1] of the CaF_2:Yb^{3+} system resulted in an attempted correlation between the optical and electron-spin-resonance (ESR) absorption spectra of Yb^{3+} ions in different site symmetries. This correlation was based on a number of measurements of specially prepared samples containing different relative concentrations of the various sites. It was not found possible to distinguish between two of the rhombic spectra (labelled R_1 and R_2) and, in every case, it was necessary to assume that sites giving observable ESR signals also gave observable optical absorption and vice versa. A much more satisfactory method of correlation is to compare the g values of the ESR lines with those of the optical lines measured in a Zeeman effect experiment. Using the latter technique, we have confirmed all but one (R_5) of the correlations made in Ref. 1, have obtained excited state g values, and have removed the ambiguity about the rhombic spectra, R_1 and R_2.

2. APPARATUS

All the Zeeman patterns described in this work were observed with the Poynting vector of the incident light normal to the steady magnetic field. The absorption of the samples was examined using a tungsten filament source and a single-beam Jarrell Ash 3.4-m spectrograph operating mainly in first order. During initial surveys, a liquid-nitrogen-cooled Mullard 150 CVP photomultiplier was used for detection and the signals, after dc amplification, were recorded on a strip chart.

For precise wavelength measurements, the spectra were photographed on Kodak Type 1-M plates. Although maximum sensitivity in the region between 9200 Å and 9800 Å was obtained by using ammonia hypersensitization as recommended by the makers, it was found that the loss in sensitivity resulting from hypersensitization with triethanolamine was less important than the improvement in signal-to-noise ratio which was a consequence of the reduction in background. The spectra were photographed using an input spectral slit width of 0.25 cm^{-1}, the half widths of the sharpest absorption lines being about 0.5 cm^{-1}. The samples were usually cooled by mounting them on the cold fingers of either liquid-nitrogen or liquid-helium Dewars, although in selected cases, the samples were immersed in liquid helium. Samples were oriented in the magnetic field using the {111} cleavage planes of CaF_2 and a 70.6° vee groove cut in a copper attachment to the Dewar cold finger. Magnetic fields were obtained from a Varian 15-in. electromagnet with 'Fieldial' control. The dimensions of the liquid-helium Dewar imposed a minimum pole gap of 2½ in. for which the maximum field was about 22 kG. Fields up to about 32 kG were obtained across a 1-in. gap when liquid-nitrogen sample cooling was employed. Although the

---

[1] J. Kirton and S. D. McLaughlan, Phys. Rev. **155**, 279 (1967).