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On the Anisotropic Knight Shift of Nuclear Magnetic Resonance in Metallic Tin

by

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I. Introduction

It is well known that the Knight shift in single crystal of white tin shows an anisotropy which depends on the orientation of the external magnetic field with respect to the crystallographic axis. It has been observed by Bloembergen and Rowland in powder specimen and recorded as asymmetric resonance curve.

Hamiltonian for the nuclear spin interaction with the conduction electrons is

$$\mathcal{H} = \frac{8\pi}{3}\beta\gamma\hbar I \cdot S(r)\cdot\delta(r) - \beta\gamma_N\hbar I\left(\frac{S}{v^3} - \frac{3(S\cdot r)}{v^5}\right)$$

where the terms for the electron orbits and for the quadrupole interaction are not included.

We find from equation (1) for the shift

$$\Delta H/H_0 = K + \tfrac{1}{2}K'(3\cos^2\theta - 1) \qquad (1)$$

where H_0 is the external field, K is the shift due to the s-wave character electrons and K' is the anisotropic shift due to the p-wave character electrons.

The shift which is represented above, however, has not been measured directly in powder specimen, for the crystallographic axes are distributed over all directions and line shap of resonance is asymmetric which represent a superposing of all angles resonance shifts. The analysis for this curve gave for the anisotropy

$$(\Delta H_\perp - \Delta H_{11})/H_0 = 0.05\%. \qquad (2)$$

We intend to measure this anisotropy directly by means of the single crystal of foils of metallic tin for specimen. It performs us to orient a crystallographic axis to desired direction and if it is thiner enough than the skin depth of this metal, this effect can be avoided.

The equipment which we used here consist of a PKW type of radio-frequency spectrometer and a magnet with a field near 15000 gauss in max. in a 6 cm gap. The inhomogenity in the volume occupied by the samples is negligible compared to the width of resonance lines in this experiment.

The single crystal foil specimen which will explain about it in subsequent section, is set in the coil between the poles of magnet, and the magnet is turned from direction parallel to [001] to direction [100].

II. The Method of Producing Single Crystal Foils

It is necessary for us first to prepare the specimen formed from many single crystal foils of tin. To produce single crystal foils from metallic tin melted, the method of zone melting is adopted by reason of its greater adequacy.

1. Equipment

The equipment consists of two parts. The one is an electric furnace and the other is a glass

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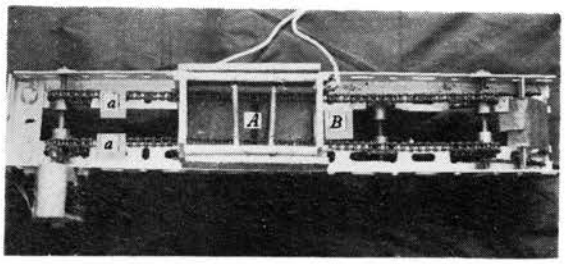

In Fig. 1. (a) S are the chain conveyors which carry a glass mould, A and B are the points where the temperature gradient is measured.

mould. The structure of the adopted furnace is shown in Fig. 1. Its heater room is covered with asbestos when in use. The glass mould consists of two sheets of quartz glass (25 cm × 3 cm × 0.2 cm in dimensions) between which a tin foil will be set, and several tools to tighten them, as shown in Fig. 2.

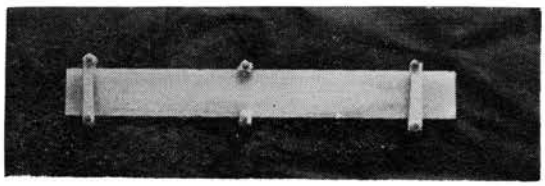

Fig. 2.

2. Procedure

A single crystal seed with a desired crystallographic orientation as illustrated in Fig. 3 and a tin foil with a wedge-shaped end must be reserved. After welding the seed to the end of tin foil, they are set in the glass mould and put on the conveyors of the furnace, and then polycrystals in the foil are allowed to grow into single crystal of which the axis is identified with crystallographic axis of seed by the method of zone melting in the air. The conditions of growth are as below.

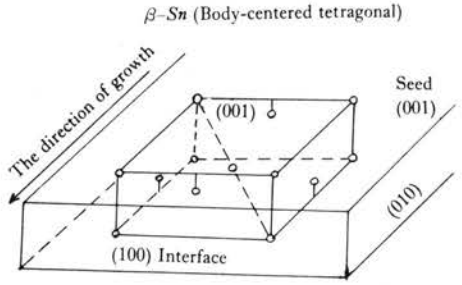

Fig. 3. The crystallographic arrangement of the seed used.

Conditions of growth

the purity of the tin foils used	99.7%
the thickness of them	$(50\pm5)\times10^{-4}$ cm *
the growth speed	1.5 cm/min
the temperature gradient	25 ± 2 °c/cm

* This value was decided after consideration of the skin effect. The skin depth for 10 Mc/s radio wave is about 30μ.

3. Specimen

A single crystal foil produced is shown in Fig. 4 in which the direction of growth is designated with an arrow, and the photographs (negative images) of the electron microscope of seed and grown crystal are given in Figs. 5 and 6 respectively.

After cutting down with care a large number of fragments from the adoptable grown crystal foils of which [001]-directions are less than 10° from their verical axes, their directions are put as uniformly as possible and they accumulated by inserting isolated papers between them, and made into such a column of nearly single crystal of tin as in Fig. 7 by means of an adhesive agent.

It is investigated by means of the megohm meter that the isolation of the resulting single cyrstal is perfect. On examining the cut fragment by the metallurgical microscope, damages of their borders are found to be very slight.

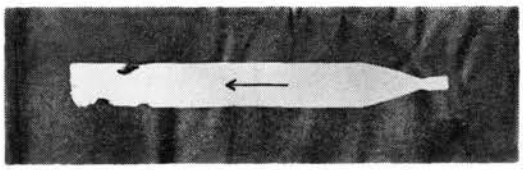

Fig. 4.

Fig. 5. The seed crystal magnified by 4300 times.

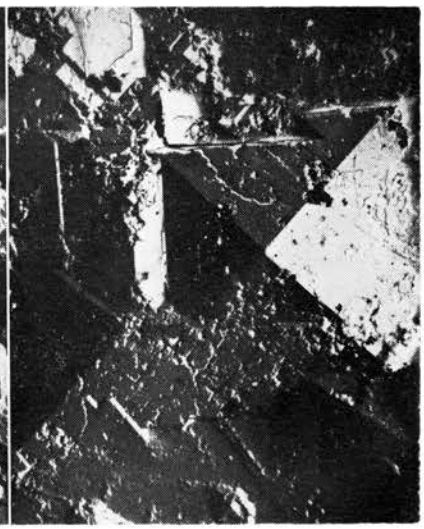

Fig. 6. Grown crystal magnified by 2750 times.

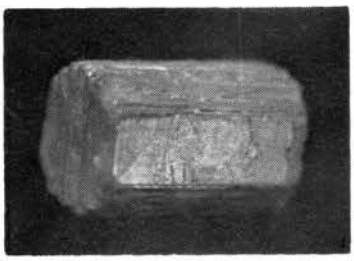

Fig. 7. The dimensions of the column of nearly single crystal of tin are 10 mm and 15 mm in diameter and length respectively.

III Experimental Results

The experimental data are given in Table I, and shown in Fig. 8. It is compared with Fig. 9 which shows asymmetric resonance in powder specimen of white tin.

Table 1. Are the angles between H and [001], shifts are measured from arbitral fixed point.

Angle from [001]	shift (gauss)	Angle from [001]	shift (gauss)
−15	16.3	45	14.1
−10	16.3	50	13.5
− 5	16.5	55	13.3
0	16.8	60	12.9
5	16.8	65	12.5
10	16.5	70	12.4
15	16.3	75	12.1
20	16.1	80	13.1
25	15.4	85	11.9
30	15.3	90	11.6
35	15.0	95	12.1
40	14.7	100	12.3

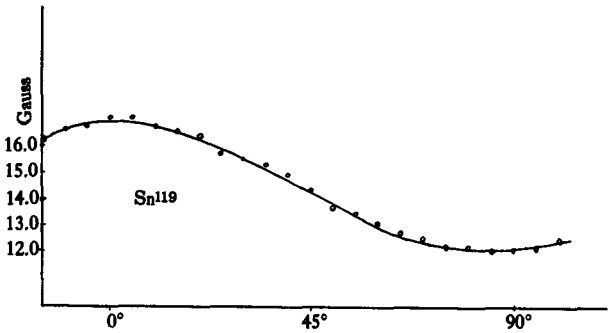

Fig. 8. Anisotropy as a function of orientation of the external fiedl with respect to the crystal axis [001], at room temp. $\nu=10$ Mc/s, H_0 is about 6300 gauss

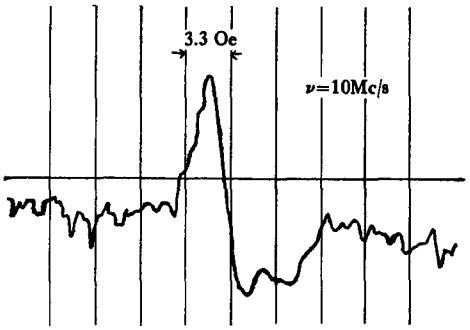

Fig. 9. Resonance curve of Sn_{119} at 77°K in powder specimen

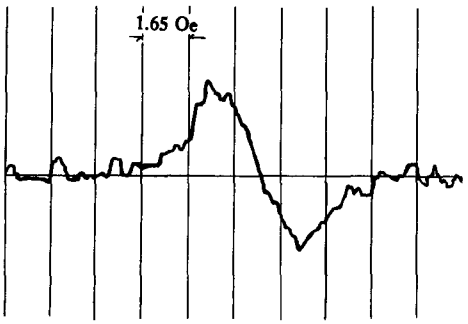

Fig. 10. Resonance curve in Sn of foil specimen., in direction 45° from [001], $H=6300$ gauss at room temp.

The Knight shift which is measured from the referance SnCl is 0.723% in the direction [100] and 0.808% in [001], so the ansotropy is 0.083%, 5.28 gauss. And $K=75.3\times10^{-4}$ $K=5.5\times10^{-4}$ in the equation (2).

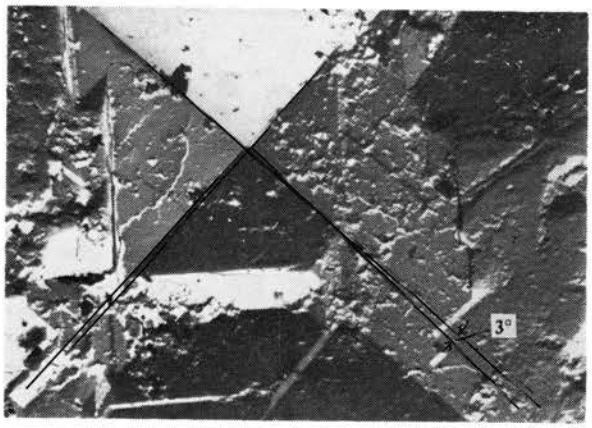

Fig. 11. The electron microscopic. ×3600

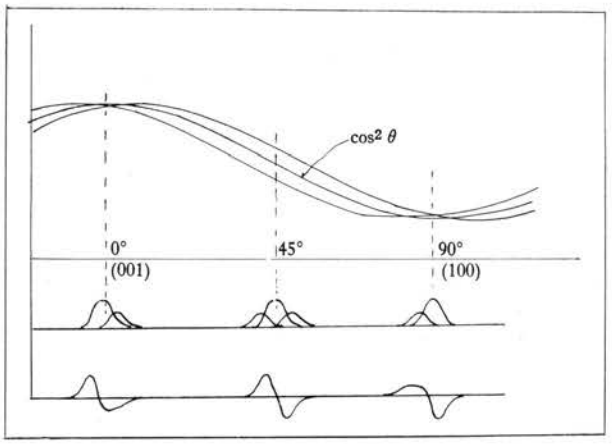

Fig. 12.

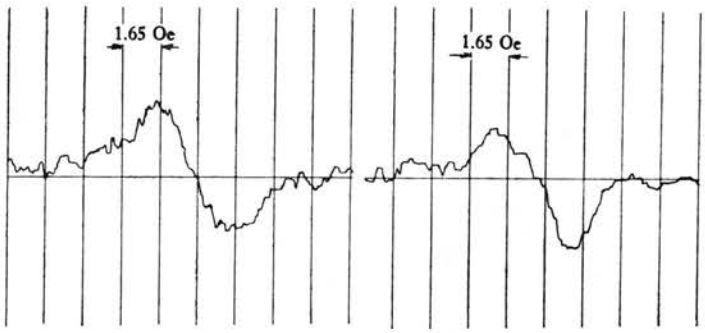

Fig. 13. The line shape in [001]. 0°

Fig. 14. The line shape in [100]. 90°

About the line width, it should be 1.54 gauss from calcuration from crystal size and magnetic moment of Sn, but in this experiment it is about 3.1 gauss as shown in Fig. 10. This difference can be explained by considering fluctuation of the direction of crystal axes in our specimen.

The distribution in the direction of axes is therefore about 1.5 gauss in shift, and calcurated $\pm 8°$ in angle at 45° from [001]. And it agree with the value of fluctuation which measured from the microscope photograph as shown in Fig. 11. The angle between two edges is about 3° on the photograph, therefore the deviation of [001] axis from vertical would be about $\pm 6°$.

The line shapes in the direction 0° and 90° from [0001], therefore, whould be asymmetric as shown in Fig. 12, and agreed as shown in Figs. 13, 14, so we can easily find the both terminal points of anisotrpic shift.

IV Acknowledgement

This work was intiated by the encouragement and interest of Dr. F. E. Fujita to whom the authers wish to express their gratitude, and they are thankfull to Dr. J. Ito and Dr. K. Asayama for their helpfull advice, and to Mr. T. Kaneshiro for his cooperation in this experiment.

V References

1) Knight, W.D.: *Phys. Rev.* 76 1259 (1949)
2) Bloembergen, N. and Rowland, T.J.: *Acta Metallurgica*, **1**, 731 (1955)