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OSCILLATORY FIELD DEPENDENCE OF THE KNIGHT SHIFT IN A MONOCRYSTAL OF TIN*

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Measurements of the Sn^{119} nuclear-magnetic-resonance (nmr) signal as a function of magnetic field in a monocrystal of white tin at 1.35°K show an oscillatory field dependence of the Knight shift. The existence of oscillations in the nmr frequency in metals superimposed on the normal linear dependence on magnetic field has been predicted by several authors.[1-4] Estimates of the amplitude of these oscillations due to oscillations in the diamagnetic shielding constant vary from $\Delta\sigma/\sigma \approx 10^{-5}$ with no dependence on applied field[2] to $\Delta\sigma/\sigma \approx 1.2\times10^{-4}$ at 10^4 G with the amplitude increasing as $H^{1/2}$.[3,4] Calculations indicate that the paramagnetic contribution to the amplitude of the oscillatory term is of order 10^{-7} to 10^{-6}.[2] A search for the oscillatory Knight shift in Sn in the field region around 10 kG was carried out by Jones and Williams[5]; no reproducible oscillatory effect was observed. In the present investigation the Knight shift was measured in the field range of 11.5 to 12.5 kG, and a definite oscillatory effect was observed. To our knowledge, this is the first direct experimental evidence that the effect is observable.

The tin monocrystal used was first cut from a zone-refined bar by spark erosion into the form of a cube approximately 1 cm on a side. This cube was then cut into 24 slices, each 0.3 mm thick, and reassembled with 0.025-mm sheets of Mylar between adjacent slices. A residual-resistance ratio measurement on a 0.6-mm thick sample cut from the same crystal gave a value of $(R_{300}/R_{4.2}) = 21\,600$. This ratio was measured in the residual field (90 G) of the magnet. Since the mean free path of the carriers is greater than 0.6 mm and magnetoresistance is appreciable at 90 G, the ratio in bulk samples at zero field would be much larger. The nmr measurements were made with a conventional Pound-Knight marginal oscillator and phase-sensitive detector. A recorder trace of the Sn^{119} resonance at 1.35°K is shown in Fig. 1. No attempt has been made to analyze the observed line shape, but it has been checked at each field and found not to change within the experimental error. The accuracy with which the absolute Knight shift could be measured is limited by the unknown position of the true resonant field on the spectrum. However, any position on the line could be determined to ±0.1 G. Since the frequency measurements were accurate to 1 part in 10^5, the total error in determining changes in the Knight shift is not greater than 3 parts in 10^5. The linewidth remains constant at 1.5 G for all fields investigated. The Sn^{119} nmr signal from a saturated solution of $SnCl_2$ in HCl with a 0.1 M addition of $MnCl_2$ was used as a reference to calculate the Knight shifts.

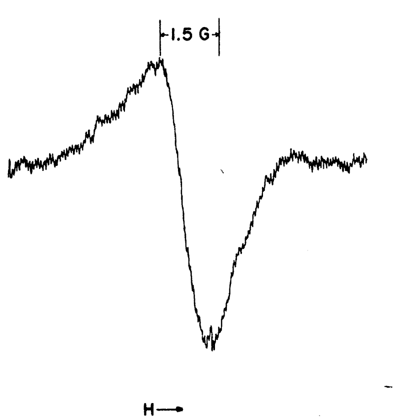

FIG. 1. A recorder trace of the derivative of the nmr signal of Sn^{119} at 1.35°K. This trace was recorded with a 0.1-G peak-to-peak, 295-Hz modulation field. A 3-sec integration time and 10-min total sweep time was used.

In Fig. 2 is shown the results of plotting the Knight shift as a function of reciprocal field for two different directions of applied field. The points of maximum Knight shift are plotted versus integers in Fig. 3. The observed periods are 4×10^{-7} G^{-1} near the (001) direction and 3.5×10^{-7} G^{-1} approximately 15° from the (001) toward the (110) direction. These periods are consistent with those found in the de Haas–van Alphen effect for oscillations due to the third-band holes in these directions.[6] It should be point-

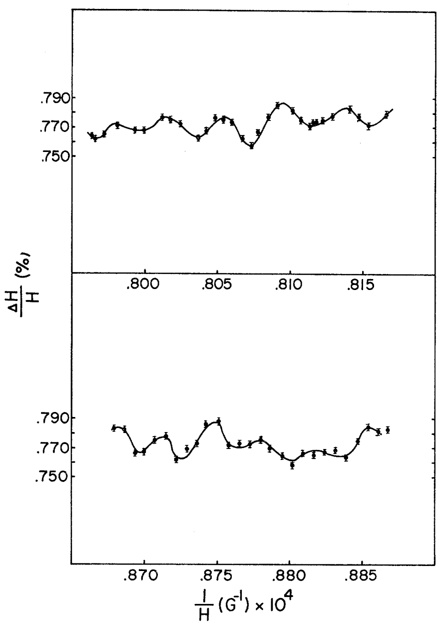

FIG. 2. Plot of measured Knight shift versus reciprocal field for two field directions in a tin monocrystal. The upper plot is for the field near the (001) direction and the lower approximately 15° from the (001) towards the (110). The uncertainty represented by the bars is ±0.003%.

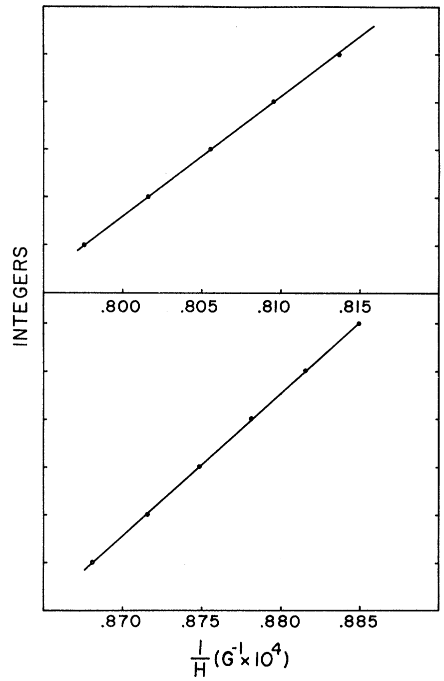

FIG. 3. Reciprocal field values of maximum Knight shift versus integers for two field directions in a tin monocrystal. The upper plot is for the field near the (001) direction and the lower approximately 15° from the (001) towards the (110).

ed out that the observed periods could well be due to a beating of frequencies arising from the third-band holes and fifth-band electrons. A more extended field range would be necessary to separate the two.

The most striking feature of the oscillations is their amplitude. The measured amplitude is $\Delta\sigma/\sigma \approx 6\times10^{-3}$ which is 40 times the largest estimates for either the paramagnetic or diamagnetic component. Over the rather limited field range in which these measurements were made, no estimate can be obtained of the field dependence of this amplitude. More detailed calculations of the oscillatory terms in the shielding factors are required to account for the observed amplitudes. For field directions exactly along the (001) directions one might expect an increase in amplitude due to magnetic breakdown.

Preparations are currently underway in this laboratory to extend the range of these measurements to 20 kG and to measure the detailed angular dependence of both amplitude and period of the oscillations. We are indebted to Professor C. G. Grenier for many helpful discussions.

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