Quantum Oscillations in the Ultrasonic Attenuation and Magnetic Susceptibility of InBi

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The Fermi surface of InBi was investigated using ultrasonic and differential-susceptibility techniques. Quantum oscillations of the de Haas–van Alphen type were observed in both types of measurements and their frequencies were measured in the (001), (010), and (1$\bar{1}$0) planes. Several frequencies which were not observed by previous workers have been discovered. These correspond to new portions of the Fermi surface. In addition, more extensive data on frequencies which had been observed earlier were obtained. The largest portion of the Fermi surface which was observed is approximately a prolate ellipsoid of revolution containing 1.9×10^{20} carriers/cm^3. It was found that, in many cases, the ultrasonic and differential-susceptibility techniques are sensitive to different electron orbits on the Fermi surface and that therefore these two techniques of studying the Fermi surface complement each other.

I. INTRODUCTION

QUANTUM oscillations in the magnetic susceptibility (de Haas–van Alphen effect) and similar oscillatory phenomena in the magnetoresistance, Hall coefficient, temperature and ultrasonic attenuation have yielded important information about the Fermi surfaces of metals, semimetals, and some degenerate semiconductors. More recently the de Haas–van Alphen (dHvA) effect has been used in the investigation of the Fermi surfaces of intermetallic compounds.[1] One of the first of such compounds to be investigated was InBi. This compound has a tetragonal structure, each unit cell containing two atoms of indium and two of bismuth.[2,3] Thorsen and Berlincourt[4] were the first to observe the dHvA effect in InBi. Their experiments were conducted in pulsed magnetic fields, and were confined to one orientation of the magnetic field relative to the crystallographic axes, viz., **H** was 33° from the [100] axis in the basal plane (c plane) of the tetragonal crystal. Subsequently Saito[5] observed three periods along the c axis (tetragonal axis) using the torque method, and studied the variation of these periods with the direction of applied magnetic field; no oscillations were observed when the magnetic field was in or near the basal plane.

In this paper we report on a study of quantum oscillations in the ultrasonic absorption and differential magnetic susceptibility of InBi. The use of both the ultrasonic and the differential-susceptibility techniques combined with the availability of high dc magnetic fields up to ~100 kG made it possible to obtain a more complete set of dHvA data than was obtained by previous investigators, including oscillations observed with the magnetic field in the c plane. In addition, the present study has dramatically pointed out that, at a given magnetic field, the oscillations observed most readily by the ultrasonic technique may arise from different electron orbits on the Fermi surface than those responsible for the oscillations observed in the differential susceptibility.

II. THEORY

According to the theory of the dHvA effect[6] the magnetic moment of a degenerate system of electrons and/or holes may exhibit quantum oscillations as a function of the magnetic-field intensity H. These oscillations are periodic in H^{-1} and the frequency F, defined as the inverse of the period ΔH^{-1}, is given by the Onsager-Lifshitz relation[6–8]

$$F=cS/eh, \qquad (1)$$

where S is the extremal cross-sectional area of the Fermi surface (in $\hbar\mathbf{k}$ space) perpendicular to the magnetic field. In general, more than one series of oscillations may be observed at a given orientation of the magnetic field since more than one extremal area may be present.

The theory of quantum oscillations in the ultrasonic absorption was developed by Gurevich *et al.*,[9] Quinn

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[1] See, A. Beck, J. P. Jan, W. B. Pearson, and I. M. Templeton, Phil. Mag. **8**, 351 (1963); J. P. Jan, W. B. Pearson, and M. Springford, Can. J. Phys. **42**, 2357 (1964).
[2] E. S. Makarov, Doklady Akad. Nauk, SSSR **59**, 899 (1948).
[3] W. P. Binnie, Acta Cryst. **9**, 686 (1956).
[4] A. C. Thorsen and T. G. Berlincourt, Nature **192**, 959 (1961).
[5] Y. Saito, J. Phys. Soc. Japan **17**, 716 (1962); Sci Rept. Res. Inst. Tohoku Univ. **A16**, 42 (1964).
[6] I. M. Lifshitz and A. M. Kosevich, Zh. Eksperim. i Teor. Fiz. **29**, 730 (1955) [English transl.: Soviet Phys.—JETP **2**, 636 (1956)].
[7] L. Onsager, Phil. Mag. 43, 1006 (1952).
[8] In the present work the distinction between B and H is neglected.
[9] V. L. Gurevich, V. G. Skobov, and Yu. A. Firsov, Zh. Eksperim. i Teor. Fiz. **40**, 786 (1961) [English transl.: Soviet Phys.—JETP **13**, 552 (1961)].

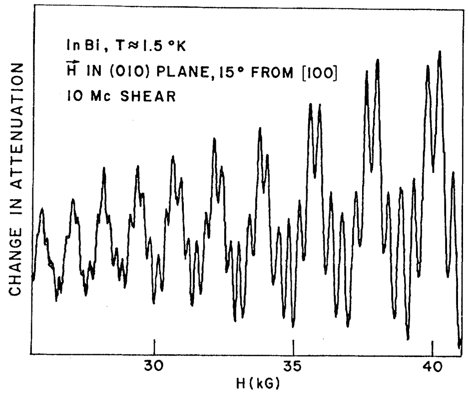

FIG. 1. Recorder tracing of the ultrasonic attenuation of 10-Mc/sec shear waves as a function of magnetic-field intensity. The magnetic field is in the (010) plane, 15° from the [100] axis.

and Rodriguez,[10] and others.[11] According to the theory the attenuation coefficient of ultrasonic waves may exhibit quantum oscillations which are periodic in H^{-1}. These oscillations can be distinguished from other types of oscillations in the ultrasonic absorption by the fact that the period of the former does not depend on the ultrasonic frequency. The frequency of the quantum oscillations is practically identical to the dHvA frequency F. Exceptions to this rule may occur if either (a) the Fermi velocity V_F is comparable to or smaller than the sound velocity V_S, or (b) if the electron mean free path is extremely long and the direction of sound propagation is perpendicular, or nearly perpendicular, to the direction of the magnetic field. Neither of these two situations is expected to occur in the case of InBi. We shall therefore assume that the frequency of the quantum oscillations in the ultrasonic absorption is given by Eq. (1).

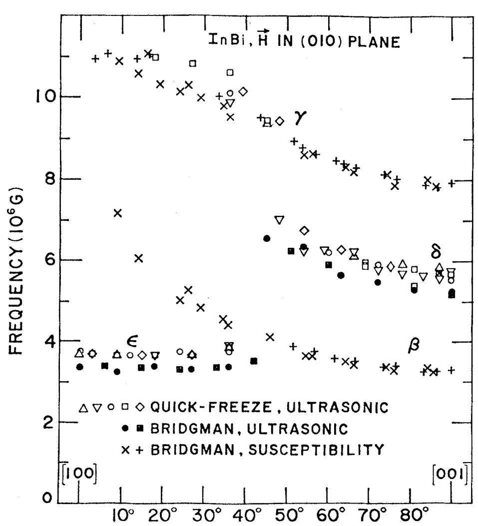

FIG. 2. Observed high dHvA frequencies with **H** in the (010) plane.

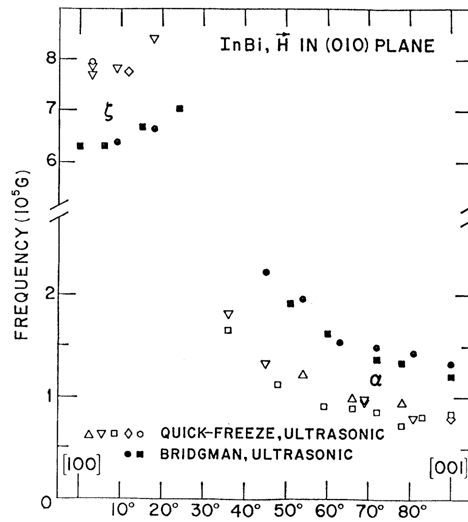

FIG. 3. Observed low dHvA frequencies with **H** in the (010) plane.

III. EXPERIMENTAL TECHNIQUE

Two single crystals of InBi were grown from high purity (99.9999%) indium and bismuth by two different techniques. The first crystal was grown by the "quick-freeze" method which has been described in detail by one of the authors.[12] The second crystal was grown under vacuum by the Bridgman technique. We shall refer to the two crystals as the quick-freeze and Bridgman crystals. Stoichiometric analysis performed on samples which were cut from the quick-freeze and Bridgman crystals indicated that the quick-freeze crystal contained 64.7±0.5 wt.% Bi, while the Bridgman crystal contained 64.2±0.3 wt.% Bi. An ideal sample of InBi contains 64.54 wt.% Bi. Spectroscopic analysis revealed that the impurity content of the quick-freeze crystal was higher than that of the Bridgman crystal. In particular, the quick-freeze crystal contained relatively large impurity concentrations of oxygen and carbon. The existence of these impurities is not surprising since the quick-freeze method of growing InBi involves the use of a graphite boat in which the mixture of indium and bismuth is melted while exposed to air. The ratio of the resistance of the quick-freeze crystal at room temperature to the resistance at 4.2°K was 40, whereas for the Bridgman crystal this ratio was 80. The orientation of the single crystals was determined by standard x-ray techniques.

Specimens for ultrasonic work were prepared in the following way. Long cylinders with their axes parallel to the c axis were spark cut from the two single crystals. Disk-shaped samples a few millimeters thick with parallel and flat c faces were obtained by cleaving the cylinders. A quartz transducer for generating and receiving longitudinal or shear waves was then bonded to one of the c faces. Most bonds were made with Nonaq Stopcock grease, although in some cases Dow Corning

[10] J. J. Quinn and S. Rodriguez, Phys. Rev. **128**, 2487, 2494 (1962).

[11] Cf. Y. Shapira and B. Lax, Phys. Rev. **138**, A1191 (1965) and references therein.

[12] S. Fischler, Trans. Met. Soc. AIME **230**, 340 (1964).

200 silicone fluid of 30 000 centistoke viscosity at 25°C was used. The quartz transducer was excited in its fundamental mode of ~10 Mc/sec or in one of its odd harmonics. The ultrasonic attenuation measurements were carried out using conventional pulse techniques. The details of the ultrasonic equipment have been described previously.[11] The ultrasonic measurements were performed at liquid-helium temperatures, usually at 1.5°K. The magnetic field in these measurements was produced by a $2\frac{1}{8}$-in. bore water-cooled solenoid capable of generating a maximum dc field of 105 kG. The magnetic-field intensity in the solenoid was measured prior to each experimental run with a Newport Type J flux integrator which had been calibrated against NMR. The current through the solenoid was measured during the run and the magnetic field was deduced from the field versus current characteristic of the solenoid. The accuracy of the magnetic-field measurements is estimated to be better than 2%.

The differential magnetic susceptibility was measured by the low-frequency field-modulation technique[13] (hereafter FMT). A small modulation field of 140 cps was superimposed on the large dc field, and the voltage induced by the ac magnetic moment of the sample in a system of suitably arranged pickup coils was synchronously detected at the modulation frequency. For sample dimensions much smaller than the rf skin depth and for modulation amplitudes much smaller than the separation between adjacent dHvA oscillations, the output of the synchronously detected signal is proportional to the differential susceptibility dM/dH.[13] Occasionally the synchronously detected signal was differentiated with respect to time in order to enhance high-frequency dHvA oscillations and/or reduce any non-oscillatory background signal. In some instances the amplitude of the modulation field was made comparable to the interval between two consecutive dHvA oscillations of one frequency in order to reduce the signal due to this frequency and observe a lower frequency more readily.

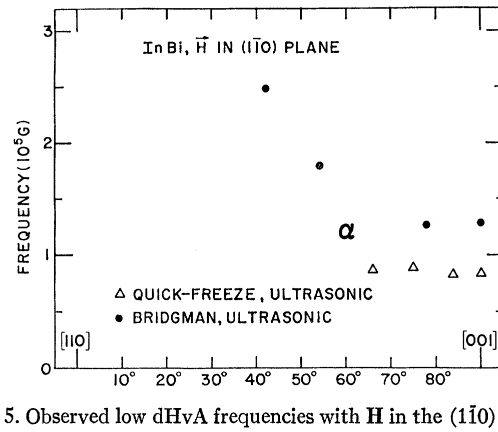

FIG. 5. Observed low dHvA frequencies with **H** in the (1$\bar{1}$0) plane.

Two samples, both spark cut from the Bridgman crystal, were measured by the FMT. These samples were supported by a brass rotation mechanism which allowed variation of the orientation of the sample relative to the magnetic field. The measurements were performed at 1.2°K in 60 kG and 80 kG superconducting solenoids which had been calibrated to better than 1% by a Rawson-Lush rotating coil gaussmeter, and by the EPR of diphenyl picryl hydrazyl (DPPH) at frequencies of 35 and 70 Gc/sec.

IV. RESULTS

The attenuation of 10- to 50-Mc/sec longitudinal and shear ultrasonic waves propagating along the c axis was measured as a function of magnetic-field intensity. The measurements were carried out at liquid-helium temperatures extending down to 1.4°K. Quantum

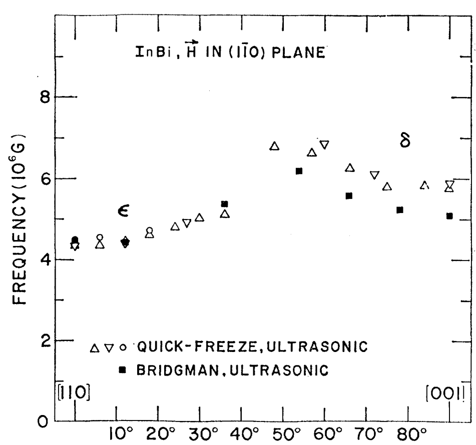

FIG. 4. Observed high dHvA frequencies with **H** in the (1$\bar{1}$0) plane.

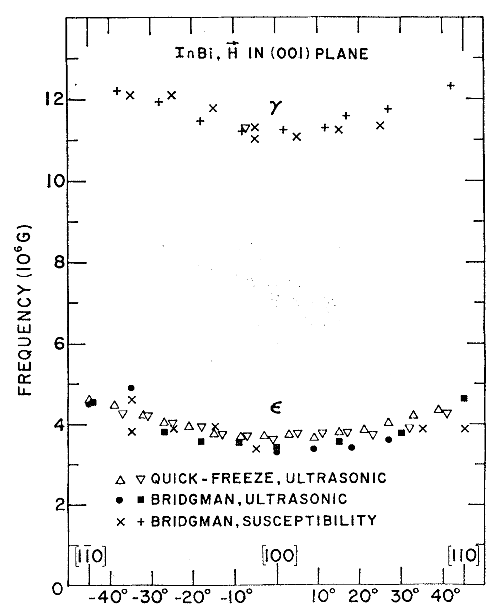

FIG. 6. Observed high dHvA frequencies with **H** in the (001) plane.

[13] A. Goldstein, S. J. Williamson, and S. Foner, Rev. Sci. Instr. **36**, 1356 (1965).

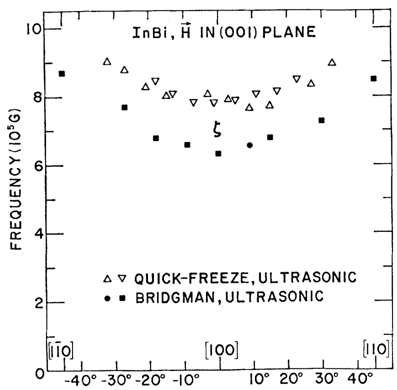

FIG. 7. Observed low dHvA frequencies with **H** in the (001) plane.

oscillations were observed and their frequencies were measured as a function of orientation of the magnetic field **H**. A typical recorder tracing of the attenuation as a function of H is shown in Fig. 1. Five different frequencies, ranging from $\sim 10^5$ to $\sim 10^7$ G were observed in the (010), (1$\bar{1}$0), and (001) planes. The orientation dependence of the observed frequencies is shown in Figs. 2–7. In these figures the crystallographic axes a, b, and c are labelled by [100], [010], and [001], respectively. The [001] axis is the tetragonal axis. For the sake of convenience and clarity, the data for high frequencies ($F > 10^6$ G) have been separated from those of low frequencies ($F < 10^6$ G). The uncertainty in the determination of the frequencies observed by the ultrasonic technique (hereafter UT) is $\pm 3\%$, except for the frequency α measured in the quick-freeze samples with **H** near the [001] direction. In the latter case the error in the frequency can be as large as 10% since only a few broad oscillations were observed. The uncertainty in the angular orientation is $\pm 3°$.

For a given orientation of the magnetic field, the frequencies measured in several samples which were cut from the quick-freeze crystal were in good agreement with each other. The same is true for frequencies measured in several samples which were cut from the Bridgman crystal. However, the frequencies measured in the Bridgman samples differed somewhat from those measured in the quick-freeze samples. This difference was particularly large for the lowest frequencies α and ζ.

The amplitude of the quantum oscillations in the ultrasonic absorption was found to increase as the magnetic-field intensity was increased and the temperature was lowered. At high fields the frequency δ dominated the oscillatory pattern near the [001] direction, while the frequency ϵ was dominant in the (001) plane. The amplitude of the signal from these frequencies was quite large. For example, the amplitude of the oscillations of the δ frequency near the [001] direction in one of the Bridgman samples, measured at $H = 70$ kG, $T = 1.4°$K with a 30-Mc/sec longitudinal wave, was ~ 2 dB/cm. The large amplitudes of the δ and ϵ oscillations made it difficult, at times, to observe other frequencies. Some frequencies were observed more readily with certain ultrasonic frequencies than with others, e.g., the frequency ζ was observed more readily with 10-Mc/sec shear waves than with 30- or 50-Mc/sec shear waves.

The differential magnetic susceptibility of two samples which were spark cut from the Bridgman crystal was measured in the (010) and (001) planes. One of these samples was spark cut from a sample which had been previously studied by the UT. Two dHvA frequencies, labeled β and γ in Figs. 2 and 6, were observed in both samples. An additional frequency of ~ 3.4–3.9×10^6 G was observed in one of the samples in the (001) plane. The uncertainty in the determination of the frequencies is $\pm 2\%$, and the uncertainty in the orientation of the magnetic field relative to the crystallographic axes is $\pm 3°$. The oscillation β was most noticeable at 20–40 kG while the oscillation γ, which appeared in most cases at ~ 20 kG, dominated at high fields ($H \gtrsim 40$ kG). In order to facilitate the observation of the β oscillation, the amplitude of the modulation field was increased in some cases until the amplitude of the dominant γ oscillation was greatly reduced by "overmodulation." An example of the resulting data is shown in Fig. 8. The location of the node in the envelope of the faster oscillation shown in this figure is in good agreement with the theory given in Ref. 13, thus indicating that the modulation field did not vary appreciably throughout the sample. Some beats were observed in the (001) plane. With the magnetic field **H** at an angle of $-35°$ from the [100] axis in the (001) plane the oscillation with the frequency of 3.83×10^6 G showed a beat which was attributed to a subdominant frequency of 4.63×10^6 G. At the equivalent orientation $+35°$ from the [100] axis in the (001) plane, the γ oscillation had a beat node about every 7 oscillations. In the latter case it was not possible, however, to obtain accurate values for the two frequencies responsible for the beat. In particular, it was not clear whether the subdominant frequency was higher or lower than the dominant frequency.

V. DISCUSSION

The six frequencies which were observed in this work are related to the extremal areas of the Fermi surface by Eq. (1). In general there is no simple way of constructing the Fermi surface from the known extermal areas.[14] Consequently one must usually have some prior knowledge of the general features of the Fermi surface (either on the basis of theoretical calculations or, in simple cases, by an inspired guess) before one can determine the Fermi surface from dHvA data. To our knowledge no theoretical calculations of the band structure or Fermi surface of InBi exist at present. As a result, only a few tentative conclusions concerning the Fermi surface of InBi can be stated.

The largest extremal areas of the Fermi surface observed in the present work are those associated with

[14] See, A. B. Pippard, in *Low-Temperature Physics, Lectures delivered at Les Houches*, edited by C. Dewitt, B. Dreyfus, and P. G. de Gennes (Gordon and Breach Science Publishers, Inc., New York, 1962).

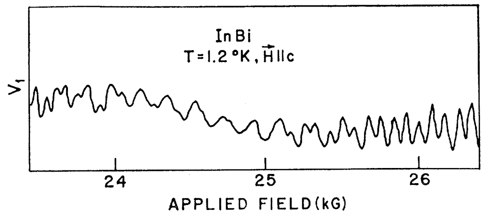

FIG. 8. Recorder tracing of dHvA oscillations observed with the FMT. V_1 is the amplitude of the signal which is synchronously detected at the modulation frequency.

the frequency γ. The anisotropy of this frequency in the (001) plane amounts to only $\sim$10%. Also the square of the period $(1/F)$ in the (010) plane is approximately linear in $\cos^2\theta$, where θ is the angle between $\mathbf{H}$ and the [001] direction. The angular variation of the frequency γ suggests that the portion of the Fermi surface associated with this frequency is approximately (but not exactly) a prolate ellipsoid of revolution, the axis of revolution being parallel to the [001] direction. Using the average frequency 1.17×10^7 G for the γ period in the (001) plane, we deduce that the ratio of the semimajor axis to the semiminor axis of the ellipsoid is 1.5 and that the ellipsoid contains 1.9×10^{20} carriers/cm^3 (2.1×10^{-2} carriers/unit cell). The angular variation of the β frequency is also consistent with that due to a prolate ellipsoid of revolution whose long axis is parallel to the [001] direction. The ratio of semimajor to semiminor axes of this ellipsoid is $\sim$2 and it contains $\sim7\times10^{19}$ carriers/cm^3. The frequencies α, δ, ϵ, and ζ were observed only for a limited range of magnetic-field orientation. The shapes of those portions of the Fermi surface which give rise to these frequencies are unknown. The frequencies of $\sim$3.4–3.9×10^6 G observed by the FMT in the (001) plane are close to the frequencies of the ϵ oscillations observed by the UT. For the field $\mathbf{H}$ at an angle $-35°$ from the [100] axis in the (001) plane a beat was present in the frequency 3.83×10^6 G which was observed by the FMT. The subdominant frequency of 4.63×10^6 G which was deduced in this case is in fair agreement with the frequency 4.9×10^6 G which had been observed by the UT in the same direction. At the same time, the frequency 4.9×10^6 G observed by the UT is higher than that expected from the smooth variation of the ϵ frequency in the (001) plane. These results suggest the existence of several close frequencies in the (001) plane.

The dHvA frequencies observed in the Bridgman samples are somewhat different from those observed in the quick-freeze samples. This difference is particularly noticeable for the α and ζ frequencies. We attribute these differences to slight deviations from ideal stoichiometry and to the presence of impurities which cause a shift in the Fermi level and/or modify the band structure. One expects such differences in the frequencies to be particularly noticeable for frequencies associated with small cross-sectional areas of the Fermi surface, such as the frequencies α and ζ. For large cross-sectional areas of the Fermi surface, the observed frequencies should be reasonably close to those due to an ideal sample. Variations in the frequencies from sample to sample were also observed by Saito.[5] The frequencies labelled α and β in the present work are most likely the α and β frequencies observed by Saito. The frequency which Saito labeled γ is probably the γ frequency observed in the present work, although it is possible that it corresponds to the frequency which we have labelled δ. It should be noted that the frequencies γ and δ are definitely two distinct frequencies since both have been observed in the same sample. Two of the three frequencies observed at one orientation by Thorsen and Berlincourt[4] have also been observed in the present work. The third frequency may be responsible for the beat observed in the present work in the γ oscillation for the field 35° from the [100] axis in the (001) plane.

One interesting feature of the present work is the fact that most of the frequencies observed with the UT were not observed with the FMT and vice versa. Even with the Bridgman sample which was measured both by the UT and FMT at essentially the same temperature and range of magnetic field, the frequencies observed by the UT and FMT were different. The frequencies α, δ, and ζ were not observed by the FMT, while the frequency β was not observed by the UT. The frequency γ which was easily observed by the FMT in the Bridgman samples was not observed in the same samples by the UT, although it was observed by the UT over a limited range of magnetic-field orientation in the quick-freeze samples. Some of the frequencies 3.4–3.9×10^6 G observed by the FMT in the (001) plane are probably the ϵ frequencies observed by the UT. The present results indicate that the FMT and UT are in many cases sensitive to different extremal areas of the Fermi surface. This is not unexpected, since the *amplitude* of the oscillations in the ultrasonic absorption is determined by a different mechanism from the one which determines the amplitude of the oscillations in the magnetic susceptibility. In addition, the FMT tends to enhance high frequencies, because it measures the *derivative* of the magnetic moment with respect to H, and is not as sensitive to low frequencies. The fact that the FMT and UT complement each other in the study of Fermi surfaces has been first noticed by two of the authors in connection with the study of the Fermi surface of arsenic.[15] The present study, however, gives a more striking evidence for this complementary aspect of the two techniques.

ACKNOWLEDGMENTS

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[15] Y. Shapira and S. J. Williamson, Phys. Letters **14**, 73 (1965).