# Fermi Surface of Tungsten from Magnetoacoustic Measurements

JOHN A. RAYNE
*Westinghouse Research Laboratories, Pittsburgh, Pennsylvania*
(Received 18 September 1963)

Magnetoacoustic data at frequencies up to 390 Mc/sec have been obtained for high-purity tungsten. From the observed oscillatory behavior, extremal dimensions of the Fermi surface have been determined as a function of crystallographic direction. The resulting shape of the surface is in qualitative agreement with recent theoretical predictions. Estimates of the extremal areas along symmetry directions are in reasonable accord with those found from high-field de Haas-van Alphen data.

## I. INTRODUCTION

THE band structure of the chromium group of transition metals, and in particular tungsten, is of great theoretical interest. Magnetoresistance[1] and anomalous skin effect studies[2] have shown that the Fermi surface of tungsten is closed and that the effective area is considerably less than that of a sphere containing one electron for atom. Such experiments show unequivocally that the free-electron theory does not provide an adequate description of its band structure.

Lomer[3] has recently proposed a model, based on the calculations of Wood for iron,[4] which seems to be in agreement with the above experimental data. The resulting Fermi surface is compensated in character and consists essentially of electron and hole surfaces, situated at the zone center and the zone corners, respectively, which are degenerate along ⟨100⟩. Additional pockets of holes occur at the centers of the zone faces, together with small pockets of electrons or holes along the cubic axes. Preliminary magnetoacoustic data,[5] using a randomly oriented crystal of relatively low purity, seem to be in qualitative agreement with the model. No precise comparison is possible, however, due to the rather poorly defined oscillatory behavior and the difficulty of aligning the field along a low index crystallographic direction. For this reason the present work was undertaken, using very high purity, oriented single crystals of tungsten and operating at a fairly high frequency; viz., 390 Mc/sec.

In general, quite pronounced oscillatory behavior is obtained, allowing accurate extremal dimensions of the Fermi surface to be obtained. The shape of the Fermi surface is in quite good agreement with the general features of the Lomer model, although the dimensions differ in detail from his estimates. Along symmetry directions, however, the extremal areas estimated from the magnetoacoustic data are in good agreement with those obtained from pulsed-field de Haas-van Alphen measurements. It is thus concluded that the Lomer model provides a reasonably complete picture of the Fermi surface of tungsten.

## II. EXPERIMENTAL TECHNIQUE

Magnetoacoustic measurements were made at 390 Mc/sec using an automatic recording technique similar to that described previously.[6] One-microsecond rf pulses are produced by plate-modulating a JVM triode oscillator, tuning from approximately 390 to 450 Mc/sec. The attenuation is measured by a transmission method, the transmitting and receiving transducers being 30-Mc/sec $X$-cut crystals excited at an odd harmonic. After amplification and rectification, the received pulses pass to a gated amplifier, where a selected echo is integrated by a diode detector to give a dc voltage proportional to its amplitude. This voltage is applied to the $Y$ axis of an $X-Y$ recorder and a voltage proportional to $1/H$, obtained by a Hall probe inverter,[7] is applied to the $X$ axis. Thus by scanning the field at an appropriate rate, it is possible to trace the magnetoacoustic oscillations automatically as a function of $1/H$.

Suitably oriented single crystals of tungsten were grown in an electron beam furnace by H. Sell of the Westinghouse Lamp Division, Bloomfield, New Jersey. These crystals were $\frac{1}{4}$ in. in diameter and were grown with axes directed along [100], [110], and [111],

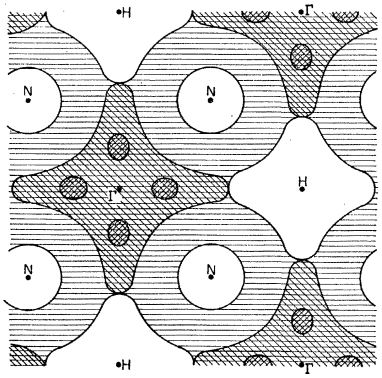


FIG. 1. Extended section in (100) plane of the Fermi surface proposed by Lomer for chromium-group metals.

[1] E. Fawcett, Phys. Rev. **128**, 154 (1962).
[2] E. Fawcett and D. Griffiths, J. Chem. Phys. Solids **23**, 1631 (1962).
[3] D. M. Lomer, Proc. Phys. Soc. (London) **80**, 489 (1962).
[4] J. H. Wood, MIT Quart. Progr. Rept., Solid State and Mol. Theory Group **33**, 20 (1959).
[5] J. A. Rayne and H. Sell, Phys. Rev. Letters **8**, 462 (1962).
[6] J. A. Rayne, Phys. Rev. **129**, 652 (1963).
[7] This device is similar to that described independently by H. H. Wieder, Rev. Sci. Instr. **34**, 422 (1963).

respectively. Each crystal had a resistance ratio of approximately 25 000 to 1. Acoustic specimens, about $\frac{3}{4}$ in. in length, were cut from the ingots by a diamond wheel. The ends of each specimen were polished to be parallel within 0.0001 cm and to be flat within a fringe over their entire area. Using glycerine as a bond, no difficulty was experienced in obtaining good echoes at liquid-helium temperatures. All data were taken at 4.2°K, since the effects of phonon scattering are negligible due to the high Debye temperature of tungsten.

## III. THEORY

### A. Oscillatory Attenuation

From the theory of the magnetoacoustic effect[8] it is known that, for sound propagating in a direction $\mathbf{q}$ with a transverse magnetic field $\mathbf{H}$, the attenuation is periodic in $1/H$. This period $\Delta(1/H)$ is related to some dominant orbit extremum in the direction $\mathbf{q}\times\mathbf{H}$ by the equation

$$k_{\text{ext}}=(e/\hbar c)[\lambda/\Delta(1/H)], \quad (1)$$

where $\lambda$ is the relevant sound wavelength. As is customary in the interpretation of such experiments, we shall assume that the extremum is the extremal dimension of the Fermi surface in the direction $\mathbf{q}\times\mathbf{H}$. It should be noted that, in the following, we consider the wave-number vector $k_{\text{ext}}/2$ rather than the extremal diameters given by Eq. (1).

### B. Fermi Surface of Tungsten

Figure 1 shows an extended section, taken in a (100) plane, of the Fermi surface for chromium group metals proposed by Lomer.[3] Here $\Gamma$ is the zone center and $\Gamma H$ a [100] direction, the square $HNH\cdots$ being the trace, in a (100) plane, of the regular duodecahedron forming the Brillouin zone of a body-centered cubic structure.

The main feature of the proposed model is the existence of a star-shaped electron surface centered at $\Gamma$, which touches a similar hole surface, centered at $H$, along the cube axes. These two surfaces contain approximately equal numbers of carriers. In addition to these surfaces there are additional pockets of holes at $N$, the size and shape of which depends sensitively on the crystal potential. Small groups of either electrons or holes are situated along the ⟨100⟩ axes of reciprocal space. From the estimates of Lomer, the associated extremal dimensions would probably be too small to give easily detected oscillations in the present experiments. Table I gives theoretical estimates of the various dimensions of the Fermi surface for tungsten.

## IV. RESULTS AND DISCUSSION

Representative tracings of the data for $q\|[110]$ are shown in Fig. 2. For all field directions at least two prominent periods are visible, as many as thirty fast oscillations being present. From this figure it is possible to estimate the electronic mean free path in the tungsten used for this work. Thus we have

$$1=\pi(n+\tfrac{1}{2})\lambda, \quad (2)$$

where $n$ is the order of the last oscillation clearly observable. Taking $n\sim30$ one obtains $1\sim1.3$ mm, which value seems to be reasonably consistent with the estimated residual resistance ratio.

A number of interesting features are apparent in the data of Fig. 2. For $H\|[1\bar{1}0]$, a short period, corresponding to a large extremal dimension, is visible for a limited angular range of approximately 12°. Reference to Fig. 3 shows that a corresponding period is obtained for $q\|[100]$, $H\|[010]$ over roughly the same angular region. As $H$ is rotated away from $[1\bar{1}0]$, this period increases and becomes approximately independent of angle. For $q\|[111]$ a similar period is observed for $H\|[2\bar{1}\bar{1}]$, a typical curve being shown in Fig. 4. Another point of

TABLE I. Comparison of theoretical and experimental dimensions[a] for Fermi surface of tungsten.

| Direction | Electrons at Γ | | Holes at $H$ | | Holes at $N$ | |
|---|---|---|---|---|---|---|
| | Theory | Exptl | Theory | Exptl | Theory | Exptl |
| [100] | 1.16 | 1.18 | 0.84 | 0.78 | 0.2 | 0.26<br>0.20<br>0.16 |
| [110] | 0.51 | 0.51 | 0.61 | 0.23 | 0.2 | 0.26<br>0.16<br>0.12 |
| [111] | 0.46 | 0.50 | 0.40 | 0.22 | 0.2 | 0.13 |

[a] It is to be noted that these are extremal *radii*.

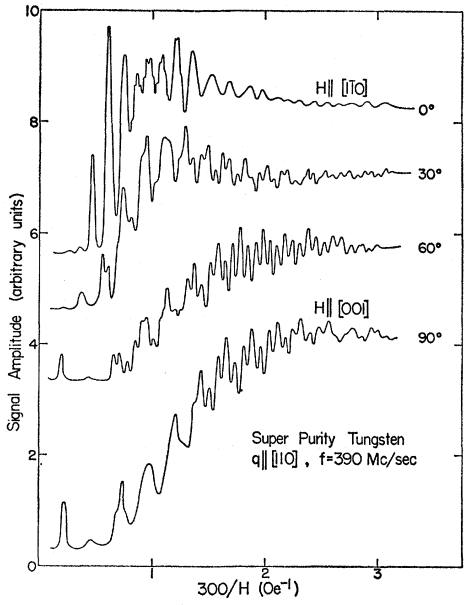


FIG. 2. Representative tracings of data obtained for tungsten with $q\|[110]$. The frequency is 390 Mc/sec.

[8] A. B. Pippard, Proc. Roy. Soc. (London) **A257**, 165 (1960).

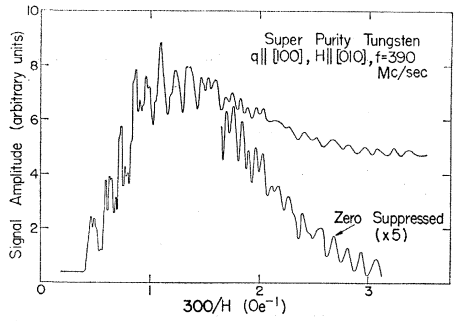


FIG. 3. Tracing of data obtained for tungsten with $q\|[100]$, $H\|[010]$ at a frequency of 390 Mc/sec. The inset shows an expanded part of the curve.

interest is the pronounced beat pattern occurring in the short period oscillation for $q\|[110]$, $H\sim[001]$. When the order of these oscillations increases, the beats disappear and a single short period becomes evident (e.g., $\theta=60°$ for $q\|[110]$). As will shortly become evident, this behavior is all consistent with the main parts of Fermi surfaces proposed by Lomer.

Figure 5 shows the angular dependence of the extremal radii for the Fermi surface of tungsten,[8a] computed from the experimental data using Eq. (1). The close correspondence between these rotation diagrams and the extremal sections of the Lomer model is at once apparent. From Figs. 5(a) and 5(b), it is clear that the shortest period oscillation is associated with those sections of the Fermi surface encompassing the necks of the electron surface centered at $\Gamma$. These oscillations appear only over a limited region, due to difficulty of obtaining an extremal orbit when the magnetic field deviates appreciably from [100] or [110]. The beats which are present in this oscillation (see Fig. 3) are due presumably to the hole surface at $H$. An unequivocal analysis of this beat pattern is not possible, since even in the case of two spherical surfaces the oscillating behavior involves the Bessel function of a double argument. Even in its asymptotic form, the latter is *not* simply the sum of two periodic terms and hence the usual methods of separating the components is not strictly applicable.[9] This fact notwithstanding, the beat pattern has been resolved in the standard manner. The resulting wave vectors, presumably corresponding to the necks of the electron and hole surfaces, are

$$k_{\text{electron}}=1.16\pm0.06, \quad k_{\text{hole}}=0.77\pm0.08,$$

in units of $10^8$ cm$^{-1}$. Now from Fig. 1, it is clear that along [100],

$$\Delta k=k_{\text{electron}}+k_{\text{hole}}=\Gamma H=2\pi/a, \qquad (3)$$

where for tungsten the lattice parameter $a$ at 0°K is approximately 3.14 Å. Substitution of this value in (3) yields $\Delta k=2.0$, which is to be compared to the experimental figure $\Delta k=1.93\pm0.14$. The agreement is within the estimated error and lends definite support to the Lomer model.

From Fig. 5, it is clear that the extremal dimension corresponding to the shortest period is almost constant away from [001]. Thus the electron surface at $\Gamma$ is almost spherical, apart from necks along the cube axes. As has been noted previously, the beat pattern for $q\|[110]$, $H\sim[001]$ is very marked; it is presumably due to the hole surfaces at $H$. The disappearance of the beat pattern for higher order oscillations results from the difference between the electron and hole mobilities, which, according to Fawcett[2], are roughly equal. It would appear from the present work that $\mu_e/\mu_h\sim2$, a not unreasonable value. Although similar beat patterns occur for $q\|[100]$ and $q\|[111]$, they are not very well defined and no attempt has been made to infer a second extremal dimension for them.

In addition to the fast oscillations, a much longer period is observed for all propagation and field directions. Again there are usually well-defined beats, an analysis of which yields the smaller values of $k_{\text{ext}}$ in Fig. 5. These dimensions find a ready interpretation as being due to the holes at $N$ in the Lomer model. In Fig. 1 these pockets of holes appear to be spherical in shape, but this clearly is not a significant feature of the theory. The present data, rather, support the view that the small hole surfaces are ellipsoidal in shape, since the small $k_{\text{ext}}$ of Figs. 5(a) and 5(b) is quite anisotropic. From the observed anisotropy of $k_{\text{ext}}$, it is believed that the ellipsoids are prolate spheroids with their long dimensions along ⟨110⟩ directions. No oscillations, *unequivocally* attributable to the small electron or hole pockets of the Lomer model, have been observed in the present experiments.

In Table I is presented a comparison between the theoretical estimates for the principal dimensions of the Fermi surface and those obtained experimentally. On the whole, there is a surprising agreement between the two, the major discrepancies involving the hole

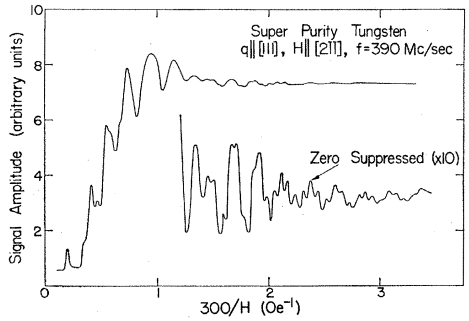


FIG. 4. Tracing of data obtained for tungsten with $q\|[111]$, $H\|[2\bar{1}\bar{1}]$ at a frequency of 390 Mc/sec. The inset shows an expanded part of the curve.

[8a] *Note added in proof.* The relevant wavelength $\lambda$ in Eq. (1) was computed from the elastic data for tungsten extrapolated to 0°K; see D. Bolef and J. de Klerk, J. Appl. Phys. **33**, 2311 (1962).

[9] This point has been discussed by A. Mackintosh, thesis, Cambridge University, 1960 (unpublished).

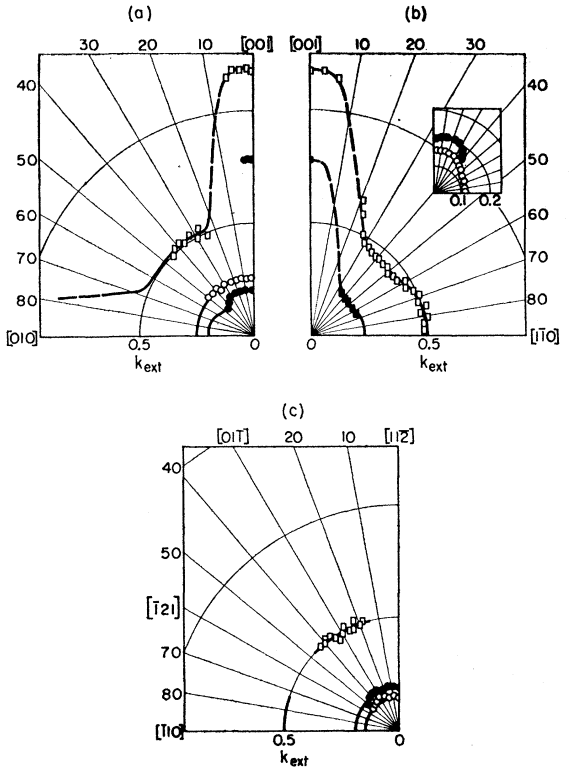


FIG. 5. Angular dependence of extremal wave vectors for tungsten obtained from present experiment using Eq. (1).

surface at $H$. There is, of course, a range of experimental values for the dimensions of the holes at $N$, since these occupy a number of inequivalent sites with respect to the magnetic field. The mean value appears to be in good agreement with theory. A more crucial test is provided by comparing the extremal areas of the various surfaces in Fig. 5 with those obtained from recent pulsed-field de Haas-van Alphen measurements.[10] This comparison is summarized in Table II. It may be seen that there is good agreement for both the main electron and hole surfaces, the discrepancy being within experimental uncertainties. In this connection it should be noted that the value of the extremal area for the electron surface at $\Gamma$, computed from the magnetoacoustic data for $H\|[111]$, is almost certainly too low. This circumstance derives from the fact that the associated orbits certainly pass over the necks of the electron surface, so that the relevant extremal area bulges out along $\langle 211\rangle$. The value quoted in Table II has been calculated on the assumption that the major section of Fig. 5(c) is circular, so that the actual area is certainly higher than this figure. It should be pointed out that the hypothesis of bulges along $\langle 211\rangle$ for the electron surface at $\Gamma$ is supported by the absence of high-frequency oscillatory behavior for $q\|[111]$, $H\|[01\bar{1}]$, since the associated orbits would not have a well-defined extremum in the direction $\mathbf{q}\times\mathbf{H}$, viz., $[2\bar{1}\bar{1}]$. Another check on the dimensions of the electron surface at $\Gamma$ is afforded by a low-field de Haas-van Alphen period in tungsten,[11] which has been ascribed to an extremal neck orbit. This period, which is visible for only a very limited angular region of $H$ about $\langle 100\rangle$, increases very rapidly away from the symmetry direction; the corresponding extremal area is 0.059 Å$^{-2}$. From Figs. 5(a) and 5(b) it would seem that the neck is roughly cylindrical in shape, the average diameter being $\Delta k_{\text{neck}}=0.36\pm0.08\times10^{8}$ cm$^{-1}$. Thus the neck area estimated from the magnetoacoustic data is 0.10 $\pm$0.04 Å$^{-2}$, which agrees with the de Haas-van Alphen data within experimental error. The fact that the area is too large would indicate that the necks are somewhat smaller in diameter than would be inferred from Fig. 5. Correspondingly, the areas estimated from the magnetoacoustic data for $q\|[100]$ and $q\|[110]$ would be too large, as is actually the case.

TABLE II. Comparison of extremal areas for tungsten from de Haas-van Alphen and magnetoacoustic data.

| Field direction | Extremal area[a] (A$^{-2}$) de Haas-van Alphen | Magnetoacoustic |
|---|---|---|
| [100] | 1.45±0.09 | 1.74±0.20 |
| | 0.44±0.06 | 0.67±0.20 |
| | ... | 0.11±0.01 |
| | | 0.20±0.01 |
| [110] | 1.11±0.07 | 1.22±0.10 |
| | 0.47±0.03 | 0.40±0.04 |
| | 0.19±0.01 | 0.08±0.01 |
| | | 0.12±0.01 |
| [111] | 1.04±0.05 | 0.79[b] |
| | ... | 0.40[b] |
| | 0.25[c] | 0.07±0.01 |
| | | 0.11±0.01 |

[a] Note that the order of the areas is electrons at $\Gamma$, holes at $H$ and holes at $N$, respectively.
[b] Lower limits only (see text).
[c] The assignment of this area to the hole surface at $N$ is somewhat uncertain.

The agreement between the two sets of extremal areas for the hole surfaces at $N$ is rather poor. Even more puzzling is the absence of any associated multiple periods in the de Haas-van Alphen data. For this reason, it is felt that more detailed information, on the intermediate periods for the de Haas-van Alphen effect in tungsten, is needed before any definite conclusions can be drawn. It is quite possible that the two smallest areas, computed from the magnetoacoustic data for $H\|[110]$ and $H\|[111]$, belong to the small pockets of carriers along the cube axes. Low-field de Haas-van Alphen data indicates that the maximum area to be expected from these surfaces is 0.09 Å$^{-2}$, which is much larger than that estimated by Lomer but which is the same order as the smaller values in Table II. Thus part of the discrepancy of Table II can be resolved, but the residual disagreement is somewhat disturbing. In

[10] R. F. Girvan and A. V. Gold (private communication).

[11] G. B. Brandt and J. A. Rayne, Phys. Rev. **132**, 1945 (1963); D. Sparlan and J. Marcus, Bull. Am. Phys. Soc. **7**, 548 (1962).

general, however, the agreement between the present data and major features of the Lomer model is quite satisfying.

areas along certain symmetry directions are in reasonable accord with those found from high-field de Haas-van Alphen data.

## V. CONCLUSIONS

High-frequency magnetoacoustic data have been obtained for very pure tungsten. From the observed oscillatory behavior, the extremal dimensions of the Fermi surface have been obtained. The resulting shape of the Fermi surface is in qualitative agreement with the theoretical model of Lomer. Estimates of the extremal

## ACKNOWLEDGMENTS

Thanks are due to H. Sell of the Westinghouse Lamp Division, Bloomfield, New Jersey for providing the high-purity samples of tungsten used in this work. The author would like to express his appreciation to R. Farich for his great care in grinding and polishing the acoustic specimens.

PHYSICAL REVIEW VOLUME 133, NUMBER 4A 17 FEBRUARY 1964

# Spin Temperature in Nuclear Double Resonance*

FRED M. LURIE† AND CHARLES P. SLICHTER
*Department of Physics, University of Illinois, Urbana, Illinois*
(Received 7 October 1963)

A magnetic double resonance technique is described which allows the strong resonance of one nuclear species to be used to detect the much weaker resonance of a second species. Based on the proposal of Hartmann and Hahn, the new technique is experimentally simpler, and involves no critical adjustments of experimental parameters. It involves the method of adiabatic demagnetization in the rotating reference frame. The theoretical interpretation is an adaptation of Redfield's thermodynamic approach, performed in a specially chosen reference system. The technique and theory are verified quantitatively in lithium metal using the strong resonance of the 92.6% abundant $Li^7$ at 15 Mc/sec to detect the much weaker resonance of the 7.4% abundant $Li^6$ at 5.679 Mc/sec.

## I. INTRODUCTION

SEVERAL years ago, Hartmann and Hahn[1] made a brilliant suggestion for a new type of double resonance which promised to provide greatly increased sensitivity in the detection of otherwise weak resonances. The technique enables one to use the strong resonance of one spin system to detect the weak resonance of a second one. If two nuclear species of spin $I$ and $S$ and gyromagnetic ratios $\gamma_I$ and $\gamma_S$ were simultaneously present, acted on by rotating fields $(H_1)_I$ and $(H_1)_S$ tuned to the respective resonances, Hartmann and Hahn's double resonance occurred when

$$\gamma_I(H_1)_I=\gamma_S(H_1)_S. \quad (1)$$

They showed that when this condition was satisfied, the two spin systems were strongly coupled even though the precession frequencies in the static field $H_0$ were at widely different frequencies. The coupling occurs via the dipolar interaction between the $I$ and $S$ spins. Crudely speaking, we may say the precession of the $S$ spins about their $H_1$ causes the component of the dipolar field along the direction of the static field $H_0$ to oscillate at an angular frequency $\gamma_S(H_1)_S$. When the Hahn condition is satisfied, the frequency of alternation is just such as to induce transitions of the $I$ spins relative to their rotating field $(H_1)_I$. Hahn showed that fairly rapid phase changes of the alternating field $(H_1)_S$ would, through this coupling, produce a saturation of the $I$ spins. In this way, even though the $S$ resonance might be hard to observe directly, it could be seen indirectly by its effect on the $I$ spins. Exactly how the method works has been explained in full detail by Hartmann and Hahn.[2] However, the analysis is necessarily rather formidable and cannot, in fact, be carried through completely since an inherent feature of their theory is a calculation of a cross-relaxation time between the two species. In their paper, they also describe the exact sequence of pulses necessary to bring about the double resonance, and they demonstrate the effect.

In our paper, we describe a modification of Hartmann and Hahn's experiment.[3] Our modifications bring about important simplifications in the experimental technique

* This research supported in part by a grant from the U. S. Atomic Energy Commission.
† Present address: the Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania. This paper is based on the Ph.D. thesis presented by Dr. Lurie at the University of Illinois.
[1] S. R. Hartmann and E. L. Hahn, Bull. Am. Phys. Soc. **5**, 498 (1960).
[2] S. R. Hartmann and E. L. Hahn, Phys. Rev. **128**, 2042 (1962).
[3] F. M. Lurie and C. P. Slichter, Phys. Rev. Letters **10**, 403 (1963).