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Shubnikov–de Haas Effect and Cyclotron Resonance in a Dilute Bi-Sb Alloy

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Magnetoresistance oscillations (Shubnikov–de Haas effect) and Azbel-Kaner cyclotron resonance were studied in a dilute Bi-Sb alloy (Sb concentration of 0.96 wt. %) at 4.2°K for various orientations of the magnetic field. It was found that the electron cyclotron masses, and the extremal cross-sectional areas of the electron Fermi surface, decrease to approximately 80 and 62%, respectively, of the corresponding values in pure Bi. The observed changes in cyclotron masses and Shubnikov–de Haas frequencies in the alloys are consistent with the nonparabolic model and the assumption of rigid motion of the conduction band, and the valence band just beneath it, with respect to the hole band. Effective masses at the bottom of the conduction band were calculated. The electron Fermi energy and concentration in the alloy were determined. The band overlap deduced from this result is in agreement with other work.

I. INTRODUCTION

THE Shubnikov–de Haas effect and Azbel-Kaner cyclotron resonance have been used to investigate the electronic band structures of pure Bi and Sb. These are semimetals characterized by low Fermi energies and charge carriers (electrons and holes in equal number) of small momentum. It is plausible, because of the long de Broglie wavelength of the charge carriers at the Fermi energy in Bi, that the local perturbation produced by alloying a small amount of Sb in Bi will not be resolved and the mean free path of the charge carriers will not be substantially decreased. This argument, as well as the results of Esaki and Heer,[1] suggest that it will be feasible to observe the Shubnikov–de Haas effect and cyclotron resonance in dilute Bi-Sb alloys, and to study their electronic band structure by these effects. The present work reports the observation of these effects in a 1% alloy and gives information on the band structure of dilute Bi-Sb alloys. To the best of our knowledge, the Shubnikov–de Haas effect and Azbel-Kaner cyclotron resonance have not been observed in Bi-Sb alloys in the past.

Bi and Sb are group V elements and have very similar crystalline structure. X-ray studies[2] have shown that alloying Bi and Sb results in changes in the lattice parameters. The addition of (neutral) Sb to a Bi crystal can then be expected to alter the energy band structure and change the electron and hole concentrations by equal amounts. De Haas–van Alphen studies[3,4] reveal that the extremal cross-sectional areas of the electron Fermi surface and the Fermi energy in pure Bi decrease with increasing Sb concentration; i.e., that the overlap of the conduction and valence band decreases with alloying.

Theoretical and experimental studies[5–7] have shown that the conduction band in Bi is nonparabolic. According to this model, the cyclotron masses change when the Fermi energy is decreased by alloying with Sb. In our experiments, we observed this change of cyclotron masses of electrons directly. These data, together with the Shubnikov–de Haas data, are consistent with the nonparabolicity to be associated with a gap between the conduction band and the (lower) valence band of ~15 meV and a rigid motion, upon alloying, of these bands with respect to the hole band. It should be

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[1] L. Esaki and J. Heer, J. Appl. Phys. **34**, 234 (1963).
[2] P. Cucka and C. S. Barrett, Acta Cryst. **15**, 865 (1962).
[3] D. Shoenberg and M. Zakki Uddin, Proc. Roy. Soc. (London) **A156**, 687 (1936).
[4] N. B. Brandt and V. V. Shchekochikhina, Zh. Eksperim. i Teor. Fiz. **41**, 1412 (1961) [English transl.: Soviet Phys.—JETP **14**, 1008 (1962)].
[5] B. Lax, Bull. Am. Phys. Soc. **5**, 167 (1960); B. Lax, J. G. Mavroides, H. J. Zeiger, and R. J. Keyes, Phys. Rev. Letters **5**, 214 (1960).
[6] M. H. Cohen, Phys. Rev. **121**, 387 (1961).
[7] R. N. Brown, J. G. Mavroides, and B. Lax, Phys. Rev. **129**, 2055 (1963).

pointed out that in Ref. 4 Fermi energies versus Sb concentrations were derived from the de Haas–van Alphen data and the conclusion drawn that the effective masses in dilute Bi-Sb alloys are unchanged. This interpretation should be modified when the nonparabolic band structure is considered. Further discussion on this aspect will be taken up in Sec. IV.

II. EXPERIMENTAL

A. Preparation of Samples

Bi and Sb of 99.9999% purity were purchased from the Consolidated Mining and Smelting Company of Canada, Ltd. Appropriate amounts of Bi and Sb were zone leveled in a 10-in. quartz boat twenty times in a high vacuum. Single crystals were cut from the central portion of the ingots by a Servomet spark cutter and etched in *aqua regia*. The Sb concentration was determined by measuring the density of the specimens. The crystallographic orientation of the sample was determined both by cleaving in liquid nitrogen and by x-ray studies. Specimens used for cyclotron resonance were electrolytically polished by the same method and solution used for polishing pure Bi.[8]

B. Shubnikov–de Haas Effect

The Shubnikov–de Haas measurements were made using a technique to be described elsewhere,[9] which subtracts out the monotonically increasing part of the magnetoresistance, and allows for greater sensitivity than the traditional methods. The Bi-Sb alloy samples, approximately $2\times0.2\times0.2$ cm, were mounted in a standard helium Dewar. The current was along the bisectrix axis. The magnetic field, in the bisectrix plane, was measured with a Bell 120 gaussmeter. A typical X-Y plotter trace of the oscillatory part of the magnetoresistance versus magnetic field is shown in Fig. 1.

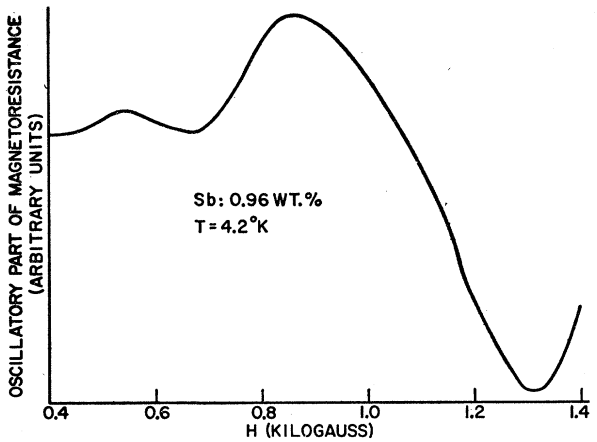

FIG. 1. A typical trace of the oscillatory part of the magnetoresistance in a Bi-Sb alloy. The monotonic part has been bucked out. H is in the bisectrix plane, 25° from the binary axis.

[8] W. J. Tegart, *The Electrolytic and Chemical Polishing of Metals in Research and Industry* (Pergamon Press, Inc., London, 1959).

[9] R. D. Brown, Bull. Am. Phys. Soc. **9**, 264 (1964).

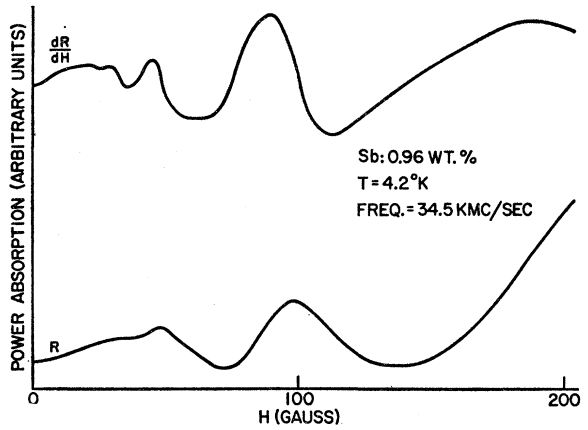

FIG. 2. Power absorption versus magnetic field with H directed along the bisectrix axis and perpendicular to the microwave electric field.

C. Cyclotron Resonance

Electrolytically polished Bi-Sb alloy samples of sizes approximately $1\times1\times0.3$ cm were mounted at the bottom of a resonant cavity in a standard microwave spectrometer tuned at 34.5 kMc/sec. The measurements were carried out in a standard procedure described elsewhere.[10] The magnetic field was in the plane of the sample and perpendicular to the trigonal axis of the crystals. Both surface resistance R and its field derivative dR/dH were measured as the magnetic field was varied. In the latter case, a small magnetic field, modulated at 105 cps, was added and the signal from the crystal detector was fed into a lock-in amplifier. Typical X-Y plotter traces are shown in Fig. 2.

III. RESULTS

The measured electron cyclotron resonance masses m^* for H in the trigonal plane are tabulated in Table I. These results are shown in Fig. 3; the observed m^* values are indicated by points. Their angular variation can be fitted by the solid curves which are obtained from the angular variation curves of m^* for pure Bi[10] reduced by a scale factor of 0.8. The agreement is

TABLE I. Cyclotron masses with H in the trigonal plane. θ = angle between H and bisectrix axis.

θ (deg)	m_I^*/m_0	m_{II}^*/m_0	m_{III}^*/m_0
0	0.0158(±5%)	0.0158 (±5%)	0.00807(±5%)
5	0.0181(±5%)	0.0128 (±5%)	0.00832(±5%)
10		0.0118 (±5%)	0.00815(±5%)
15		0.0108 (±5%)	
20	0.0428(±5%)		0.00808(±5%)
25	0.0704(±5%)		0.00832(±5%)
30	0.111 (±5%)	0.00832(±5%)	0.00832(±5%)

[10] Y.-H. Kao, Phys. Rev. **129**, 1122 (1963).

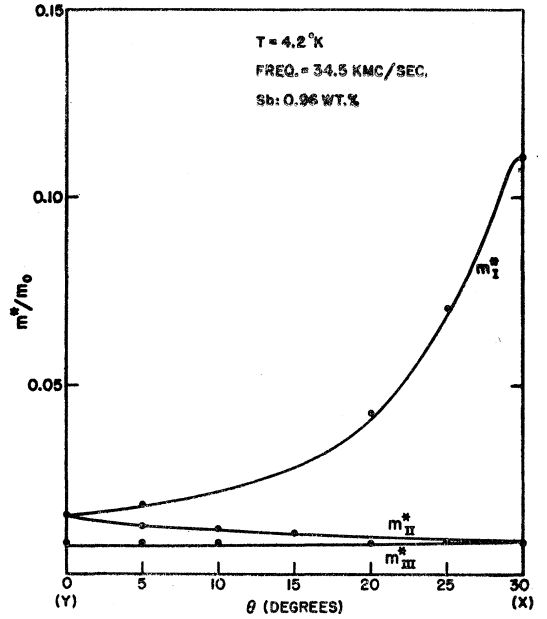

FIG. 3. Angular variation of the electron cyclotron masses with H in the trigonal plane. θ is the angle between H and the bisectrix axis. The observed values are shown by points. The solid curves are the angular variations of electron cyclotron masses in pure Bi but reduced by a constant scale factor 0.8.

reasonably good. From the number of observed subharmonics of the resonance frequency, we estimate the relaxation time of electrons in the Bi-Sb alloy to be $\sim$0.1 nsec. No cyclotron resonance of holes was observed. Spin resonance was not observed, presumably due to insufficient sensitivity of our spectrometer.

The observed Shubnikov–de Haas effect frequencies f for H in the bisectrix plane are tabulated in Table II. These results are shown as points in Fig. 4. The solid curves are the angular variations of electron cyclotron masses for pure Bi all reduced by a scale factor of 0.8. Within the experimental error, f is proportional to m^*. The angular variation of m^* and f for H in the binary plane was measured by Brandt and Shchekochikhina[4] using the de Haas–van Alphen effect.

From the results shown in Figs. 3 and 4, combined with the de Haas–van Alphen data,[4] we come to the conclusion that within the experimental uncertainties both m^* and f in dilute Bi-Sb alloys are decreased isotropically with increased Sb concentration. Using the values of m^* in pure Bi determined by Kao[10] and Fig. 3, we find

$$m^*/m_{\mathrm{Bi}}{}^*=0.8\pm0.08. \quad (1)$$

Using the values of f in pure Bi determined by Shoenberg[11] and Fig. 4, we find

$$f/f_{\mathrm{Bi}}=0.62\pm0.07. \quad (2)$$

For a given H, we obtain from Fig. 4

$$f/(m^*/m_0)=1.0\times10^6(\pm15\%)\mathrm{Oe}$$

or the "parabolic" Fermi energy E_F in the alloy is

$$E_F=S/2\pi m^*|_{0.96\ \mathrm{wt.\ \%\ Sb}}=11.6\ \mathrm{meV}(\pm15\%), \quad (3)$$

where $S=ehf/c$ is the extremal cross-sectional area of the Fermi surface perpendicular to H.

TABLE II. Shubnikov–de Haas frequencies with H in the bisectrix plane. θ=angle between H and trigonal axis.

θ(deg)	$f\times10^4$(Oe) Sample No. 1	Sample No. 2
0	5.23 (±5%)	
2.5	4.63 (±5%)	
10	2.62 (±5%)	2.7 (±5%)
20		1.92 (±5%)
30	1.59 (±5%)	1.78 (±5%)
40		1.52, 1.16 (±5%)
50	1.31 (±5%)	0.99 (±5%)
60		1.0 (±5%)
65	0.952 (±5%)	
70		0.847 (±5%)
75	0.855 (±5%)	
80	0.938 (±5%)	0.833 (±5%)
85	0.891 (±5%)	
90	0.857 (±5%)	0.833 (±5%)

IV. DISCUSSION

A. Model and Approximation

Theoretical and experimental studies have shown that the conduction band in Bi is nonellipsoidal-nonparabolic (NENP). In Cohen's NENP model,[6] for the

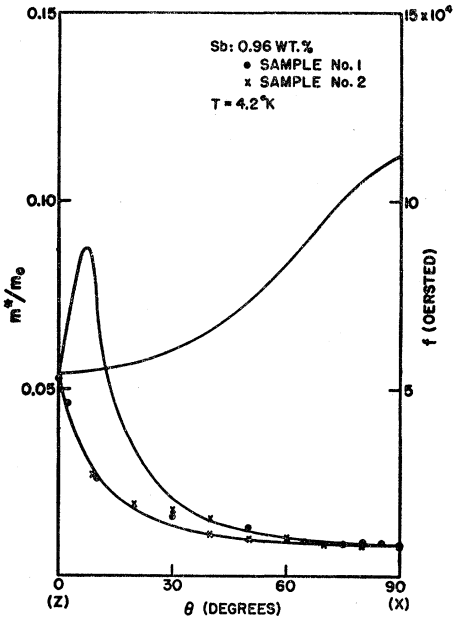

FIG. 4. Angular variation of the Shubnikov–de Haas frequency f and the electron cyclotron masses m^* with H in the bisectrix plane. θ is the angle between H and the trigonal axis. The observed values of f are shown by points. The solid curves are the angular variation of electron cyclotron masses in pure Bi but reduced by a constant scale factor 0.8. Agreement in the angular variation indicates that f is proportional to m^*.

[11] J. S. Dhillon and D. Shoenberg, Phil. Trans. Roy. Soc. (London) A248, 1 (1955).

electron Fermi surface located at points L, one of the electron Fermi surfaces can be expressed by

$$\frac{p_1^2}{2m_1}+\frac{p_2^2}{2m_2}+\frac{p_3^2}{2m_3}=E\left(1+\frac{E}{E_g}\right)-\frac{1}{E_g}\left(\frac{p_2^2}{2m_2}\right)^2, \quad (4)$$

where 1, 2, 3 refer to the principal axis system of the surface, the m's are the effective masses at the bottom of the conduction band, E_g is the energy gap, and E is the Fermi energy. This model differs from Lax's nonparabolic model by the presence of the last term in (4). Including this term in the Fermi surface thus takes into account the fact that $m_2 \gg m_1, m_3$ and makes the band nonellipsoidal but parabolic in the 2 direction.

Calculation of the extremal cross-sectional area S and cyclotron mass m^* for an arbitrary direction of applied field H from (4) is very complicated. To interpret our data in terms of Cohen's model, we shall make a simplifying approximation as follows: In calculating S and m^* for a given H, the nonellipsoidicity of (4) will be neglected with S approximated by the area of an ellipse with lengths of semimajor and semiminor axes determined by the extremal values of the momenta in (4). This approximation will make the Fermi surface essentially ellipsoidal and nonparabolic (ENP). As an example, we consider the case of $H \| 3$ axis.

$$S_{\mathrm{ENP}}=2\pi(m_1m_2)^{1/2}E(1+E/E_g)^{1/2} \quad (5)$$

$$m^*_{\mathrm{ENP}}=(m_1m_2)^{1/2}(1+3E/2E_g)/(1+E/E_g)^{1/2}. \quad (6)$$

The NENP expressions for S and m^* are given in the Appendix of Ref. 10 [Eqs. (A6) and (A8)]. For $E/E_g=1$, we find $S_{\mathrm{ENP}}/S_{\mathrm{NENP}}=1.41/1.50$, $m^*_{\mathrm{ENP}}/m^*_{\mathrm{NENP}}=1.77/1.91$, indicating an error from this approximation of only $\sim 6\%$. Corrections for the nonellipsoidicity are well within our experimental errors.

For $H \| 2$ axis,

$$S=2\pi(m_1m_3)^{1/2}E(1+E/E_g), \quad (7)$$

$$m^*=(m_1m_3)^{1/2}(1+2E/E_g). \quad (8)$$

Combining Eqs. (5)–(8), we obtain

$$H\|3: \quad S/2\pi m^*=E(1+E/E_g)/[1+\tfrac{3}{2}(E/E_g)], \quad (9)$$

$$H\|2: \quad S/2\pi m^*=E(1+E/E_g)/(1+2E/E_g). \quad (10)$$

For $E/E_g=1$, the value of $S/2\pi m^*$ changes by $\lesssim 20\%$ from $H\|3$ to $H\|2$. The angular dependence of S and m^* upon the direction of H is too complicated to be used for analyzing our data, which were taken with reference to the crystallographic axes which are somewhat tilted from the principal axes. In studying the quantity $S/2\pi m^*$, we shall, therefore, make the further approximation of considering only the average of the two extremal values as given by (9) and (10) and disregarding its angular dependence on the direction of H. The error introduced this way should be $\lesssim 10\%$, which is comparable with our experimental uncertainties. Similarly, in studying m^*/m^*_{Bi} and S/S_{Bi}, we shall also neglect the angular dependence on the direction of H and consider the average values obtained from (6) and (8) for m^*, and from (5) and (7) for S.

B. Band Parameters

With no information on the values of E_g as a function of Sb concentration in Bi at the present time, there is no unique way to determine both the Fermi energy and the effective masses of electrons in these alloys. Cyclotron resonance and Shubnikov–de Haas effect and/or de Haas–van Alphen effect in alloys give only two sets of equations for the three sets of unknowns. There is, therefore, not enough evidence existing to show how the band structure changes in dilute Bi-Sb alloys. Measurements of E_g in these alloys, for example, by infrared magnetoreflection or magnetoabsorption experiments, will provide us with the necessary data to determine all the unknown parameters in the conduction bands.

However, we may attempt to interpret the change of band parameters in dilute alloys on a qualitative basis. Consider two interpenetrating fcc sublattices in a simple cubic lattice. If we now displace the sublattices relative to each other along the body diagonal of the cube and carry out a slight deformation, the resulting lattice is that of Bi.[12] The body diagonal in the direction of the displacement becomes the trigonal axis in Bi; the lattice now has rhombohedral symmetry. Comparison with the crystallographic structure and energy bands in Pb-Te suggests that the energy gap in Bi and its alloys may be associated with the displacement of the sublattices; while the overlap of the hole and electron bands may be associated with the rhombohedral distortion and spin-orbit interaction.[13,14] Crystal structure studies[2] have shown that in dilute Bi-Sb alloys (Sb concentration <10 at. %) the displacement of the two sublattices is essentially unchanged. Employing the argument given above, we shall anticipate the energy gap in our alloys to be the same as that in pure Bi. Henceforth, we shall consider only the case of fixed E_g and m's in the dilute alloys.

From (9), we obtain

$$E/E_g=\tfrac{1}{2}[\tfrac{3}{2}\alpha-1\pm(1+\alpha+9\alpha^2/4)^{1/2}]. \quad (11)$$

From (10), we obtain

$$E/E_g=\tfrac{1}{2}[2\alpha-1\pm(1+\alpha^2)^{1/2}], \quad (12)$$

where $\alpha=S/(2\pi m^*E_g)$.

There are three sets of experimental values of E_g and E_{Bi} in the literature which are tabulated in Table III. From (3), (11), (12), and E_g we calculate E/E_g and E; from (6), (8), and E_{Bi} we calculate m^*/m^*_{Bi} and from (5) and (7) we calculate f/f_{Bi}. These results are listed

[12] E. I. Blount and M. H. Cohen [quoted by A. L. Jain, Phys. Rev. 114, 1518 (1959)].

[13] J. J. Hall and S. H. Koenig, IBM J. Res. Develop. 8, 241 (1964).

[14] M. H. Cohen, L. M. Falicov, and S. Golin, IBM J. Res. Develop. 8, 215 (1964).

TABLE III. Measured values of E_g and E_{Bi} and calculated values of E/E_g, E, m^*/m^*_{Bi}, and f/f_{Bi}.

E_g(meV)	E_{Bi}(meV)	E/E_g	E(meV)	$m^*/m_{Bi}{}^*$	f/f_{Bi}
15 [a]	25 [a]	1.1 ±15%	16.5±15%	0.8±10%	0.55±10%
15.3[b]	27.6[b]				
24 [c]	22 [c]	0.57±15%	13.7±15%	0.8±10%	0.54±10%

[a] Reference 7. [b] Reference 15. [c] W. E. Engeler, Phys. Rev. 129, 1509 (1963).

in Table III. The agreement between these results and our measured values of m^*/m^*_{Bi} and f/f_{Bi} [(1) and (2)] is consistent with the assumption of fixed E_g and m's in the alloys, though the results are insensitive to the particular value of E_g and E_{Bi} used.

C. Effective Masses

Taking the value of $E_{Bi}/E_g=25/15$, we calculate the effective masses at the bottom of the conduction band by using the NENP model and the cyclotron masses determined in Ref. 10. The following values were obtained (method of computation in Ref. 10):

$$m_1=0.00163\,m_0,$$
$$m_2=1.35\,m_0, \tag{13}$$
$$m_3=0.00264\,m_0.$$

D. Carrier Concentrations

In the NENP model, the electron concentration is given by

$$n_e=(16\pi/3h^3)(2m_1m_2m_3)^{1/2}E^{3/2}(1+6E/5E_g). \tag{14}$$

Using values of $E_{Bi}=25$ meV and $E_g=15$ meV, we obtain the electron concentration per "ellipsoid" in pure Bi:

$$(n_e)_{Bi}=1.30\times10^{17}/\text{cm}^3. \tag{15}$$

Assuming fixed E_g and m's in dilute alloys, the electron concentration n_e in alloys is given by

$$n_e/(n_e)_{Bi}=(E/E_{Bi})^{3/2}(1+6E/5E_g)/(1+6E_{Bi}/5E_g). \tag{16}$$

Using $E/E_g=1.1$, $E_{Bi}/E_g=5/3$, and (15), we find for a Bi-Sb alloy with 0.96 wt.% of Sb, the ratio $n_e/(n_e)_{Bi}=0.42$. The number $(n_e)_{Bi}$ is ~30% greater than the now accepted value.[13,15] The ratio is presumably more accurate.

E. Band Overlap

Assuming charge neutrality in Bi and Bi-Sb alloys, we set $n_e=n_h$. Taking the ellipsoidal-parabolic model of the holes, we calculate the hole Fermi energy E_h in the alloys from

$$E_h/(E_h)_{Bi}=[n_e/(n_e)_{Bi}]^{2/3}. \tag{17}$$

Assuming the ratio $n_e/(n_e)_{Bi}$ to be correctly given by the preceding and using $(E_h)_{Bi}=12.0$ meV,[10] we obtain

$$E_h=6.67\text{ meV}. \tag{18}$$

From Table III and (18), the overlap energy in the alloy of 0.96 wt. % Sb is 6.67+16.5=23.2 meV in comparison with the value of 12+25=37 meV in pure Bi. Assuming a linear decrease in overlap with increasing Sb concentration, we find by extrapolation that at a value of 2.6 wt. % of Sb the bands uncross. This value (~4.3 at. % of Sb) is in agreement with some earlier work,[16] but in disagreement with Smith.[17]

ACKNOWLEDGMENT

We would like to thank Dr. S. H. Koenig for his interest in this research and for valuable discussions of the work.

[15] G. E. Smith, G. A. Baraff, and J. M. Rowell, IBM J. Res. Develop. 8, 228 (1964).
[16] V. Heine, Proc. Phys. Soc. (London) A69, 513 (1956); A. L. Jain, Phys. Rev. 114, 1518 (1959).
[17] G. E. Smith, Phys. Rev. Letters 9, 487 (1962).