Gamma-ray Compton profiles of copper and nickel

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(Received 6 August 1973)

Te^{123m} 160-keV γ rays were used to measure the Compton profiles of fcc copper and nickel single crystals in the [100], [110], and [111] directions. The differences in the profiles in the various directions are only on the order of 1% but still clearly show the presence of d-type bonds in the [110] directions. Comparison of copper and nickel shows that the d bonding is quite similar in that the high-momentum anisotropy is the same in both systems. The reduction in the s-d band separation in going from copper to nickel is expected to explain the differences in the low-momentum anisotropy (free-electron contribution). Although our experimental resolution is too poor to clearly resolve details as sharp as the necks, our data for copper have the trend expected from such necks. The profiles and the anisotropy are expected to provide the first stringent test for d-like wave functions in these systems.

I. INTRODUCTION

In recent years the number of solid-state systems studied by Compton scattering has grown considerably.[1-9] From the few instances where a comparison between theory and experiment has been made, it is found that a better understanding of the interactions of the outer electrons in solids is possible if an accuracy of about 1% or better is achieved. Four examples of such comparisons are the studies of LiH,[1,10] Li and Na,[2] vanadium,[6,11] and diamond, Si, and Ge.[3,12]

The latter study illustrates quite clearly the sensitivity the anisotropy of the Compton profiles to the nature of the bonding in solids. Numerous studies of the anisotropy in transition metals have been reported[13-16] but a comparison of accurate data and comprehensive calculations is yet to be made. In choosing copper and nickel we expect that such a comparison is forthcoming.[17] Since copper and nickel both have the fcc crystal structure, roughly the same density and lattice constant, and similar type of electrons participating in the bonding it is not too surprising that the anisotropy of the Compton profiles are similar. The presence of the d bands at the Fermi surface in nickel may explain the difference observed in anisotropy in the low-momentum region. The total profiles, however, differ by much more than the anisotropy effects since the atomic potential that the electrons experience in copper and nickel differ by a sizeable amount. In some sense the anisotropy differences between copper and nickel are a second-order effect of the different magnitude of potentials in an equivalent environment.

In Sec. II we will give a synopsis of Compton-scattering theory. In Sec. III we give the experimental details, while in Sec. IV we will present the data. Finally, in Sec. V we will briefly discuss our results.

II. THEORY

The theory of the Compton-scattering cross section and the validity of the impulse approximation have been described previously.[18,19] Here we simply list some of the important relations for the convenience of the reader.

Simplifying the expression for the relativistic Compton cross section given in Ref. 19, we find

$$\left(\frac{d\sigma}{d\omega\, d\Omega}\right)_{\rm rel} = \frac{r_0^2 m_0 c \omega_2 B J(q)}{2\omega_1[(\omega_1^2+\omega_2^2-2\omega_1\omega_2\cos\theta)^{1/2}+(q/m_0c)(\omega_1-\omega_2)]},$$

where

$$B=\omega_1 A_1/\omega_2 A_2+\omega_2 A_2/\omega_1 A_1,$$

$$A_1=1+q/m_0c,\quad A_2=1-q/m_0c,$$

$$\omega=\omega_1-\omega_2,\quad \cos\theta=\vec{k}_1\cdot\vec{k}_2/|\vec{k}_1||\vec{k}_2|,$$

$$J(q)=\int\int n(p_0)\,dp_\alpha\,dp_\beta,$$

and the relationship between the energy (eV) of the scattered photon and q (a.u.) is given by

$$q=\frac{k\cdot p_0}{|k|}=\frac{-137[\omega_1-\omega_2-\omega_1\omega_2(1-\cos\theta)/m_0c^2]}{(\omega_1^2+\omega_2^2-2\omega_1\omega_2\cos\theta)^{1/2}}.$$

The integration for $J(q)$ is over a series of planes in momentum space perpendicular to $\vec{k}$ and the limits of p_α and p_β are functions of q. Here we denote the energy and wave vector of the incident and scattered photon by ω_1, $\vec{k}_1$ and ω_2, $\vec{k}_2$, respectively; $\hbar=1$ and $n(\vec{p}_0)$ is the probability that an electron in the ground state of the system will have a momentum $\vec{p}_0$. We also use the condition

$$\int_{-\infty}^{\infty} J(q)\,dq=1 \text{ (per electron)}$$

to normalize our data.

How anisotropy in $n(\vec{p}_0)$ reveals itself in the Compton profile was briefly discussed in Ref. 3.

III. EXPERIMENTAL DETAILS

The experimental apparatus and experimental technique is basically identical to that previously described.[3] We will therefore only discuss the features which were different in these experiments.

A. Samples

Samples of Cu and Ni used in the anisotropy measurements were prepared by cutting slices 0.236 in. thick from large single crystals such that the planes of the slices were normal to a ⟨100⟩, ⟨110⟩, or ⟨111⟩ axis. To ensure that the scattering volume was constant the samples were placed behind a Pb mask with a 0.75-in.-diam hole in the center. The samples used for the Compton-profile measurements had a ⟨100⟩ axis normal to the slices which were 0.023 in. thick. These were also placed behind a Pb mask with a 0.75-in.-diam hole.

B. Data collection and analysis

Since the anisotropies, especially in Cu, were smaller than in diamond, Si, and Ge, more counts were taken in this study. Specifically for ⟨100⟩ Cu more than 250 000 counts were accumulated in four separate runs, for ⟨111⟩ Cu over 120 000 counts, and in ⟨110⟩ Cu 63 000. For the three directions in nickel over 85 000 counts were accumulated. For the thin 0.023-in. ⟨100⟩ Cu and Ni 23 000 counts were accumulated.

Two modifications of our data processing techniques were used in this study. They were originally initiated because of the small size of the anisotropies but in retrospect warrant inclusion in all future anisotropy studies.

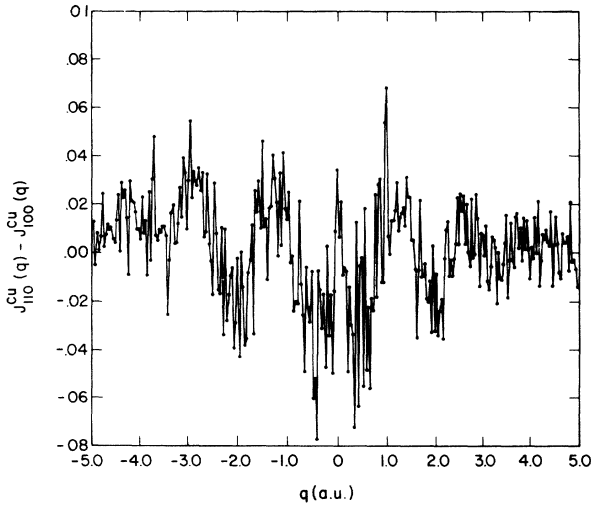

FIG. 1. Copper $J(q)_{110}-J(q)_{100}$ anisotropy on a point-by-point basis. The final experimental results given in Fig. 2 are smoothed and $\pm q$ averaged.

The data for each sample was first corrected for background, detector efficiency, sample absorption, Compton cross section, and then integrated and normalized to the prescribed number of electrons. The corrected data for two different samples was then subtracted channel by channel and the difference inspected. To increase statistical accuracy the data for plus and minus q were then averaged, smoothed and again inspected. This procedure allows one to not only evaluate the accuracy of the data but to also evaluate the effect of the smoothing procedure. A typical anisotropy curve on which no averaging and no smoothing has been performed is shown in Fig. 1.

We have also decided to present the anisotropy data without correcting for the effect of the finite resolution of the spectrometer. This is done because in attempting to remove the resolution effects, the signal-to-noise ratio is found to decrease significantly. Any procedure used to deconvolute the resolution function from data which is composed of both signal and noise suffers from the result that the noise is enhanced relative to the signal. Computer simulations reveal that for a tolerable increase in noise (factor of 2) only 80% of the finite resolution effects were removed. We, therefore, feel that a more accurate comparison of experiment and theory is possible by smearing the theoretical calculation with the experimental resolution function and then comparing that to the unconcaluted data. For our spectrometer the resolution function, which includes effects of both energy and angular resolution,[3] is given by

$$R(q) = (1/\sigma\sqrt{2\pi})e^{-q^2/2\sigma^2},$$

where $\sigma = 0.195$ a.u. The small, long tail previously described[3] has been ignored since its effect is well below our noise. Thus the anisotropy data (e.g., Fig. 1) has only been smoothed by a low-pass filter such that the observed anisotropies are not sensitive to the exact value of the filter's cutoff.[3]

The thin-crystal data were processed in exactly the same manner as described previously[3] including the removal of resolution effects. Multiple-scattering[3] effects are estimated to be +0.8% at $q = 0$ based on the Ge work as well as a study of 0.040- and 0.023-in.-thick Ni samples. For the anisotropy data a rough estimate of the effects of multiple scattering is provided by the ratio of $J(0)$ for the thick crystals to its value for the thin crystals. For the samples used in this study the ratio was 1.08 and thus the data shown in Fig. 2 has been increased by 8%.

IV. DATA

The measured thin crystals results for Cu and Ni after subtraction of the $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$ atomic

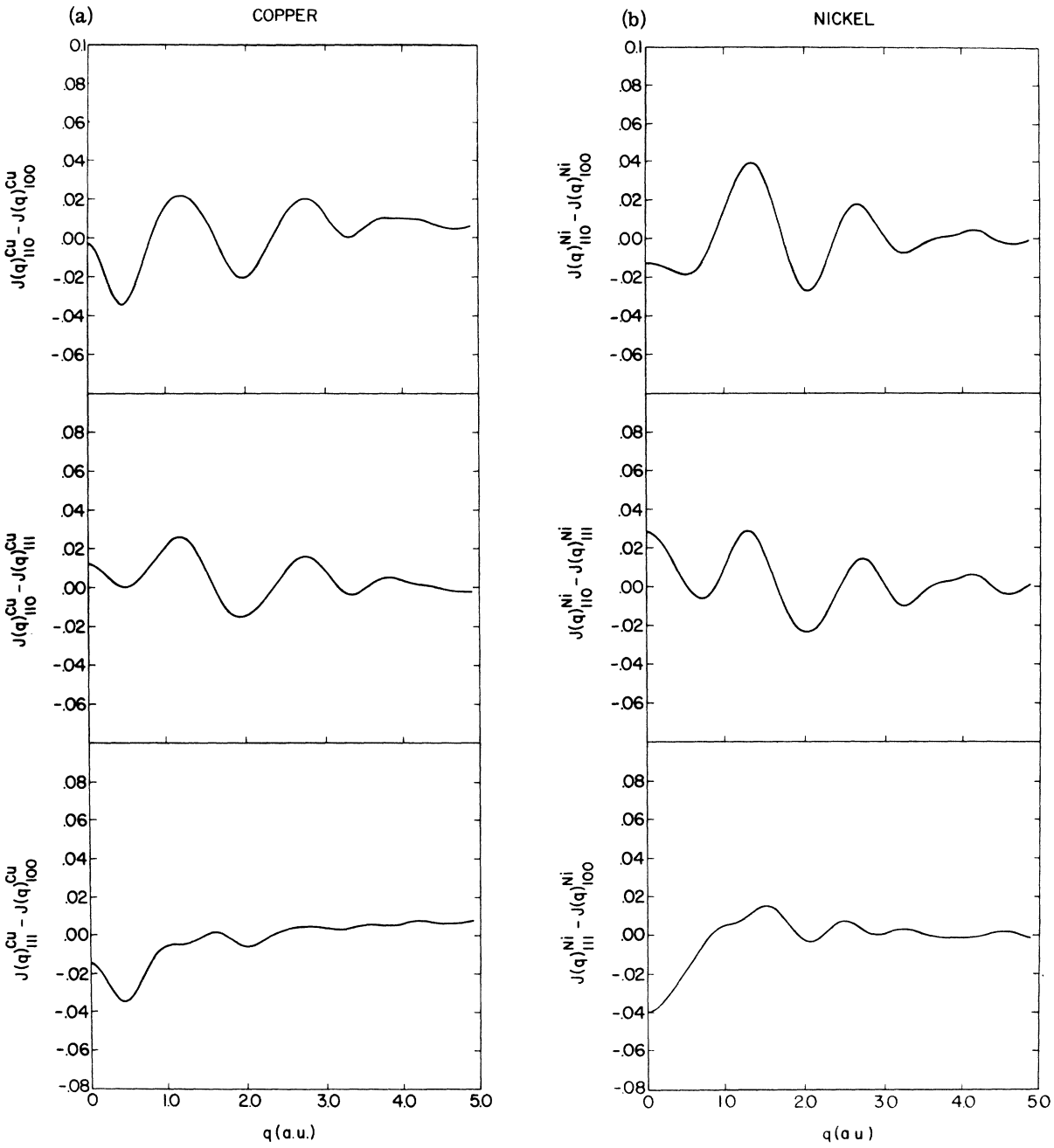

FIG. 2. Measured anisotropies in copper and nickel. Finite-resolution effects have not been removed.

core contribution is given in Table I. Calculations of the atomic-valence Compton profile are also included for comparison.[20] The resolution-uncorrected anisotropies in Cu and Ni for the three directions are given in Fig. 2. The striking high-momentum anisotropy and its similarity in Cu and Ni is very obvious. Performing resolution corrections in the previously described manner[3] yields an anisotropy which is illustrated in Fig. 3 (i.e., compare with Fig. 2).

An experimental estimate of the noise in these measurements is provided by the results of comparing two sets of ⟨100⟩-Cu data each set comprised of two independent runs of 60 000 counts each. The result of that comparison is shown in Fig. 4. By comparing Fig. 2 and Fig. 4 one finds that in these

TABLE I. Measured thin crystals results after subtraction of the atomic core contribution.

	Nickel $J(q)$			Copper $J(q)$		
9	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6$ Core[b]	$3d^8 4s^2$ Valence[b]	Expt.[a] Valence	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6$ Core[b]	$3d^{10}\,4s^1$ Valence[b]	Expt.[a] Valence
0	2.513	4.389	2.680	2.432	3.583	2.782
0.1	2.510	4.144	2.663	2.429	3.387	2.760
0.2	2.500	3.540	2.626	2.420	2.936	2.709
0.3	2.484	2.847	2.566	2.405	2.487	2.628
0.4	2.461	2.270	2.475	2.384	2.176	2.517
0.5	2.432	1.880	2.351	2.357	2.000	2.376
0.6	2.396	1.652	2.200	2.323	1.909	2.215
0.7	2.353	1.532	2.038	2.283	1.856	2.048
0.8	2.303	1.471	1.880	2.237	1.817	1.895
0.9	2.247	1.435	1.740	2.185	1.778	1.767
1.0	2.185	1.405	1.641	2.127	1.735	1.671
1.2	2.047	1.338	1.442	1.998	1.629	1.531
1.4	1.895	1.250	1.293	1.856	1.502	1.411
1.6	1.736	1.148	1.170	1.708	1.366	1.299
1.8	1.577	1.040	1.057	1.559	1.230	1.184
2.0	1.424	0.933	0.946	1.416	1.102	1.065
2.2	1.283	0.830	0.838	1.281	0.982	0.955
2.5	1.096	0.690	0.701	1.102	0.820	0.815
3.0	0.860	0.498	0.526	0.869	0.601	0.625
3.5	0.701	0.356	0.379	0.708	0.436	0.464
4.0	0.596	0.253	0.269	0.599	0.315	0.339
5.0	0.466	0.129	0.136	0.467	0.164	0.179
6.0	0.380	0.066	0.068	0.382	0.086	0.088
7.0	0.311	0.034	0.031	0.316	0.046	0.042
8.0	0.253	0.018	0.016	0.260	0.025	0.019
9.0	0.205	0.010	0.009	0.212	0.014	0.018
10.0	0.166	0.005	0.001	0.174	0.008	0.010
15.0	0.063			0.068		
20.0	0.029			0.031		
25.0	0.014			0.016		
30.0	0.008			0.008		

[a]Statictical errors: at $q=0$, $\pm 1\%$; $q=1$, $\pm 2\%$; $q=2$, $\pm 5\%$; $q=4$, $\pm 7\%$; multiple-scattering error at $q=0$, $+1\%$.

[b]Calculated from Clementi wave functions, Ref. 20.

experiments we were able to measure an anisotropy of 0.5% to 1% with a signal-to-noise ratio of better than 4.

V. DISCUSSION

Before giving a brief qualitative interpretation of the data it is worth placing the experimental results presented here in perspective to information obtained by other techniques. Copper has been studied extensively by positron annihilation[21–25] and indeed anisotropies have been observed which have been attributed both to the necks of the Fermi surface as well as the core. However, due to the large anisotropies of the positron wave function itself in copper no direct comparison with our results is possible.[17] The greater annihilation rate with the outer electrons also gives a distorted view of the relative sizes of core to Fermi-surface anisotropies as well as preventing one from obtain-

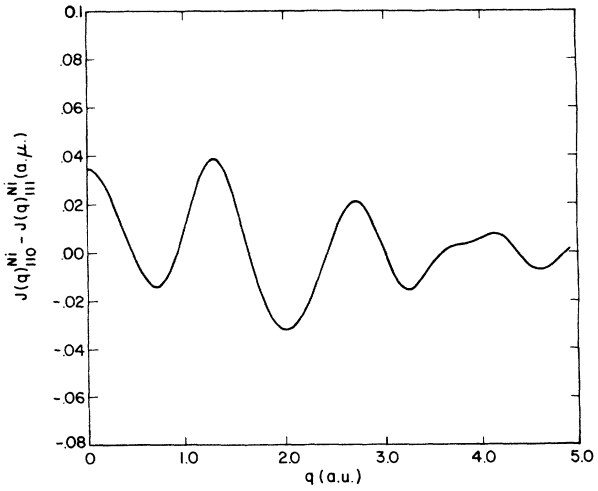

FIG. 3. Nickel $J(q)_{110}$-$J(q)_{111}$ anisotropy for which approximately 80% of the effects of finite resolution have been removed.

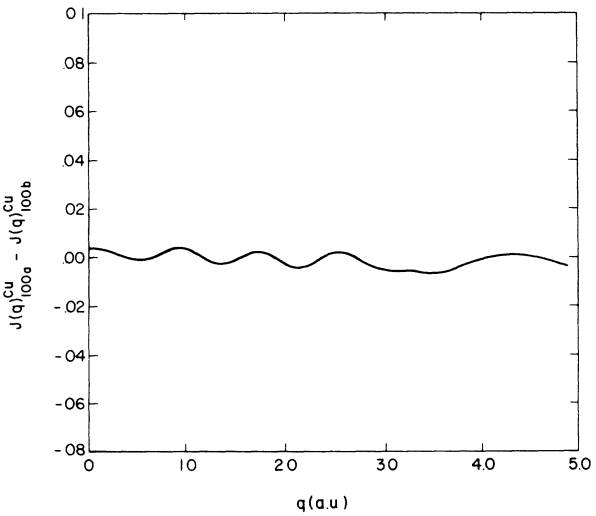

FIG. 4. Difference between two sets of Cu ⟨100⟩ measurements. Resolution corrections have not been performed on the data.

ing a momentum distribution for the d electrons without calculating first the role of the positron wave function. It is expected that the positron measurements will give good Fermi-surface data because of their higher resolution but that the Compton measurements will tell us more about the d electrons and their role in bonding in the transition metals.

The other measurement technique which gives comparable information is elastic scattering structure factor studies. An accurate study has been performed on Ni[26] but it was unable to give quantitative information about the small anisotropy of the charge distribution nor could it even speculate as to its d- or s-type character. The comparison adds support to the view that Compton scattering, which is an easier measurement to perform, enables one to get more quantitative information about solid state effects.

It was briefly discussed in the introduction that the observed high-momentum anisotropy in both Cu and Ni is a strong indication of d-electron bonding in those systems. Figure 2 clearly shows it is the ⟨110⟩ direction which is unique. The ⟨110⟩ direction is not only the nearest-neighbor direction but in addition the t_{2g} orbitals have lobes along the ⟨110⟩ axes. Thus any d bonding present would be along that direction. The fact that the ⟨111⟩–⟨100⟩ anisotropy is very small in the high-momentum region is because both directions cut the ⟨110⟩ bond at roughly the same angle (45° and 35°) and thus to first order the bond looks the same. In the study of diamond, Si, and Ge[3] it was found that the ⟨111⟩ direction is sensitive to the solid-state effects but there is still significant ⟨100⟩–⟨110⟩ anisotropy. As is shown in that work the anisotropy is very similar to the geometrical anisotropy of the Jones zone. The absence of such geometrical anisotropy for d bonds in Cu and Ni is a natural consequence of their essential tight binding (i.e., atomic character). To first order the observed anisotropy for d electrons will be due to small deviations produced by bonding on an otherwise isotropic distribution.

The anisotropy observed in the low-momentum region ($q < 1$) is essentially a reflection of the Fermi surface. The neck diameters in Cu and Ni are 0.14 and 0.05 a.u., respectively, so that with a spectrometer resolution of 0.22 a.u. [full width at half-maximum (FWHM)] we will certainly not resolve clearly the sharp details of the necks. However, the ordering of the profiles at $J(0)$ is qualitatively correct for Cu.

These qualitative speculations, while reasonable, certainly must await detailed confirmation. It is our expectation that detailed calculations will shortly be published.[17]

We would like to thank K. Bachmann for growing the nickel single crystals used in these experiments.

[1]W. C. Phillips and R. J. Weiss, Phys. Rev. 171, 790 (1966).
[2]P. Eisenberger, L. Lam, P. M. Platzman, and P. Schmidt, Phys. Rev. B 6, 3671 (1972).
[3]W. A. Reed and P. Eisenberger, Phys. Rev. B 6, 4569 (1972).
[4]S. Manninen, J. Phys. F 1, 60(L) (1971).
[5]R. J. Weiss, Phys. Rev. Lett. 24, 883 (1971).
[6]T. Paakkari, S. Manninen, O. Inkinen, and E. Liukkonen, Phys. Rev. B 6, 351 (1972).
[7]J. Felsteiner, R. Fox, and S. Kahane, Solid State Commun. 9, 457 (1971).
[8]T. Fukamachi and S. Hosoya, J. Phys. Soc. Jap. 3, 736 (1970).
[9]R. Currat, P. D. DeCicco, and R. Kaplow, Phys. Rev. B 3, 243 (1971).
[10]W. Brandt, Phys. Rev. 132, 521 (1970).
[11]K. F. Beggren, Phys. Rev. B 6, 2156 (1972).
[12]K. Pandy (unpublished).
[13]W. C. Phillips and R. J. Weiss, Phys. Rev. B 6, 4213 (1972).
[14]T. Paakkari, S. Mannien, O. Inkinen, and E. Linkkoner, Phys. Rev. B 6, 351 (1972).
[15]O. Terasaki, T. Fukamachi, S. Hosoya, and D. Watanabe (private communication).
[16]R. J. Weiss, Phys. Rev. B (to be published).
[17]F. Mueller and A. Freeman (private communication).
[18]P. Eisenberger and P. M. Platzman, Phys. Rev. 172, 415 (1970).
[19]P. Eisenberger and W. A. Reed, preceding paper, Phys. Rev. B 9, 3237 (1974).
[20]E. Clemente, IBM J. Res. Develop. Suppl. 9, 2 (1965).
[21]S. Cushner, J. C. Ershine, and S. Berko, Phys. Rev. B 1, 2852 (1970).

[22]D. L. Williams, E. H. Becker, P. Petijench, and G. Jones, Phys. Rev. Lett. 20, 448 (1968).
[23]S. Berko and J. Plaskett, Phys. Rev. 112, 1877 (1958).
[24]P. E. Mijnarends, Phys. Rev. 178, 622 (1969).
[25]K. Fujiwara and O. Sueoka, J. Phys. Soc. Jap. 21, 1947 (1966).
[26]M. Diana, G. Mazzone, and J. J. DeMarco, Phys. Rev. 187, 973 (1969).