Low-energy electron-diffraction determination of the structure of successively deposited ordered layers of Cd on Ti(0001). II. Second, third, and fourth layers

H. D. Shih and F. Jona

Department of Materials Science, State University of New York, Stony Brook, New York 11794

D. W. Jepsen and P. M. Marcus

IBM Research Center, P.O. Box 218, Yorktown Heights, New York 10598

(Received 3 August 1976)

The study of the structural aspects of the initial stages of epitaxial growth of Cd on Ti(0001) by LEED (low-energy electron-diffraction) analysis is carried out for two, three, and four deposited layers of Cd. A structure analysis of the 2nd (1×1) phase confirms it to consist of two complete close-packed atomic layers of Cd, separated by the interlayer spacing along $\langle 0001 \rangle$ in bulk Cd (2.81 Å). The interplanar Ti-Cd distance at the interface (2.63 Å) has increased slightly with respect to its value when only a single layer of Cd was adsorbed on the Ti(0001) surface (2.57 Å). The second-layer Cd atoms lie in the sites which continue hexagonal close packing of the first Cd layer and the first Ti layer. The structure of the third atomic layer, although essentially known, cannot be directly proven by model calculations because of limitations of the computer program available at this time. However, a four-layer-thick Cd film is shown to give the same LEED spectra as a semi-infinite Cd(0001) crystal.

I. INTRODUCTION

In part I of this study,[1] we discussed the details of experiments involving the slow vacuum deposition of Cd onto a Ti(0001) substrate. We showed how careful monitoring of Auger electron spectroscopy (AES) and low-energy electron-diffraction (LEED) intensity spectra revealed the formation of stable phases, which we labeled 1st (1×1), 2nd (1×1), 3rd (1×1), and 4th (1×1), and which we tentatively identified with the completion of the first, second, third, and fourth Cd layer, respectively. This identification was proven to be correct for the 1st (1×1) phase by a quantitative analysis of LEED intensities based on 10 beams at two angles of incidence. The results of that analysis can be summarized as follows: (i) The 1st (1×1) phase consists of a close-packed full monoatomic layer of Cd oriented epitaxially on the Ti(0001) surface; (ii) the Cd atoms are located on the threefold-symmetrical hollows of the Ti(0001) surface that correspond to face-centered-cubic (fcc) stacking of the Cd layer and the first two Ti layers (i.e., the sequence of close-packed planes is $...A_{Ti}B_{Ti}C_{Cd}$); and (iii) the interplanar spacing between the Cd overlayer and the first Ti layer is 2.57 Å (larger than the interlayer spacing along $\langle 0001 \rangle$ in bulk Ti, 2.34 Å, but smaller than the analogous quantity in bulk Cd, 2.81 Å).

In this part of the study, we show that the epitaxial growth can be followed layer by layer to a four-layer case which is identical to crystalline Cd(0001). In the case of two Cd layers, the model is extended to allow variation of two interlayer spacings to fit experiment. Section II discusses

the analysis of the two-layer phase; Sec. III discusses the three-layer phase; Sec. IV discusses the four-layer phase; and Sec. V gives our conclusions.

II. STRUCTURE ANALYSIS OF THE 2nd (1×1) PHASE

Details about the collection of intensity spectra, indexing of beams, identification of incidence angles, etc., were given in paper I and will not be repeated here. The same applies to the details of the calculation procedure.

Presently, we discuss the structural models that apply in particular to the 2nd (1×1) phase. Since the Cd atoms in the first monolayer occupy the C positions in the usual $ABCABC...$ type of sequence that characterizes fcc stacking [the structure of the 1st (1×1) was labeled $...A_{Ti}B_{Ti}C_{Cd}$], the Cd atoms in the second layer have the usual choice between two positions: those which correspond to continuation of the fcc stacking initiated with the 1st (1×1) phase (we label this model $...A_{Ti}B_{Ti}C_{Cd}A_{Cd}$); and those which continue the (hexagonal-close-packed) (hcp) stacking of the last *two* atomic layers (we label this model $...A_{Ti}B_{Ti}C_{Cd}B_{Cd}$). We will see below that the latter model will indeed prove to be correct. Another possibility, in principle, is that the registry of the 1st (1×1) Cd layer might change *as a consequence* of the adsorption of the second layer, thereby preserving, even at the interface, the hcp stacking that prevails in both bulk Ti and bulk Cd. These models are labeled, in our notation, $...A_{Ti}B_{Ti}A_{Cd}B_{Cd}$ and $...A_{Ti}B_{Ti}A_{Cd}C_{Cd}$.

Figures 1–3 present the comparison of three experimental spectra from the 2nd (1×1) phase
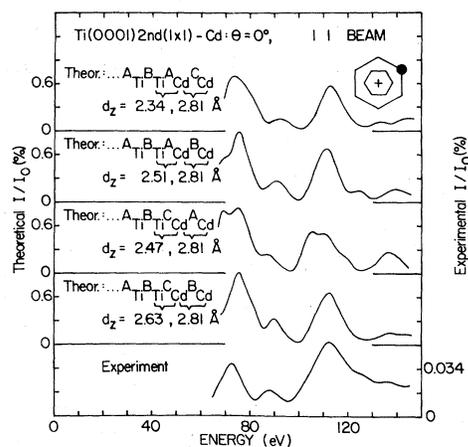
FIG. 1. Comparison between experiment (bottom curve) and calculations for four structural models (see text) for the Ti(0001) 2nd (1×1)-Cd phase: 11 beam.

FIG. 3. Comparison between experiment (bottom curve) and calculations for four structural models (see text) for the Ti(0001) 2nd (1×1)-Cd phase: 20 beam.

with those calculated for all four models described above. It is immediately obvious that the general appearances of all calculated spectra are similar to one another (and to the corresponding experimental curves). The interlayer distances with which the spectra were calculated are given in Fig. 1 and represent the "best" values found for each model. We will have more to say about these distances below. We note, here, however, that careful scrutiny of the correspondence in curve shapes, peak positions, and relative intensities speaks *against* the two models that require change in the registry of the first Cd layer (i.e., $\ldots A_{Ti}B_{Ti}A_{Cd}B_{Cd}$ and $\ldots A_{Ti}B_{Ti}A_{Cd}C_{Cd}$). The preferred model is clearly the one with the second-layer Cd atoms in hcp positions $(\ldots A_{Ti}B_{Ti}C_{Cd}B_{Cd})$, a preference that is continued

and confirmed by the study of five more spectra as presented in Figs. 4 and 5. In these figures, we present also the spectra calculated with the other overlayer model considered $(\ldots A_{Ti}B_{Ti}C_{Cd}A_{Cd})$, which show strong similarities with the observed curves but must nevertheless be discarded on account of a number of non-negligible details in practically all beams.

The search for the correct model was complicated in this case by the fact that there are *two* structural parameters to be fixed in the direction normal to the surface, rather than only one, as is usually the case in almost all surface structure analyses done so far. We call these two param-

FIG. 2. Comparison between experiment (bottom curve) and calculations for four structural models (see text) for the Ti(0001) 2nd (1×1)-Cd phase: 10 beam.
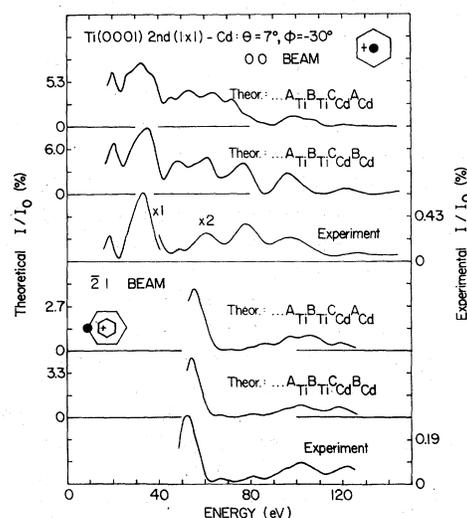
FIG. 4. Comparison between experiment (bottom curves in each panel) and calculations for two models for the Ti(0001) 2nd (1×1)-Cd phase: 00 and $\bar{2}1$ beams at $\theta = 7°$, $\phi = -30°$.
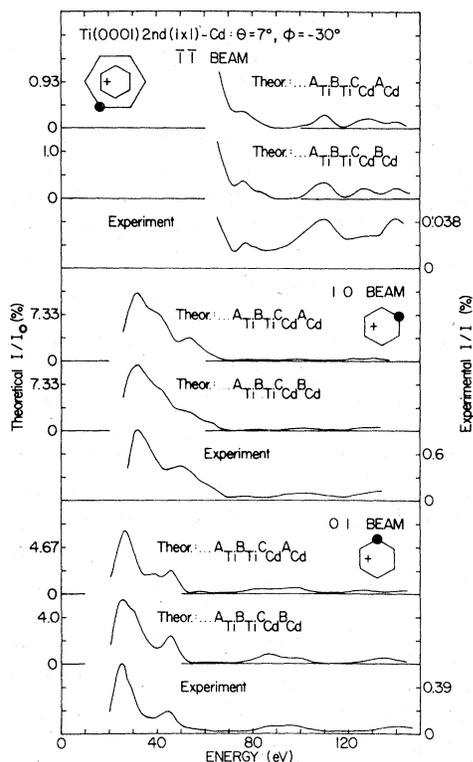
FIG. 5. Comparison between experiment (bottom curves in each panel) and calculations for two models for the Ti(0001) 2nd (1×1)-Cd phase: $\overline{1}\overline{1}$, 10, and 01 beams at $\theta = 7°$, $\phi = -30°$.

FIG. 6. Effect of variations of the distances d_1 and d_2 (defined in the legend) upon the calculated 11 spectrum at normal incidence. Dashed curve: experimental.

eters d_1 and d_2: d_1 is the distance between the planes of the two Cd layers, d_2 is the distance between the planes of Ti and Cd layers at the interface. When there was only *one* Cd layer on the substrate we found (see paper I) that the latter distance was 2.57 Å. Hence, this value may be a reasonable choice for d_2 at the beginning of our search. For d_1, on the other hand, a reasonable starting choice may be 2.81 Å—the interlayer spacing along $\langle 0001 \rangle$ in bulk Cd. We have varied d_1 by about ±0.5 Å and d_2 by about ±1 Å around the respective starting values. We show in Fig. 6 several representative spectra calculated with different pairs of d_1 and d_2 values for the 11 beam. Good correspondence with experiment (dashed curve in the figure) was found for the second, third, and seventh curves from the bottom, i.e., for different values of the d_1 and d_2 parameters. Fortunately, this kind of ambiguity does not persist equally in other beams. In Fig. 7, for example, we see that for the 20 beam, the set producing the second curve from the bottom must be discarded. Similarly, we see that the set producing the third curve from the top, while acceptable for the 20 beam (Fig. 7), is not acceptable for the 11 beam (Fig. 6). When we draw all available beams

into account we conclude that the best set of d_1, d_2 parameters is the one producing the seventh curve in both Figs. 6 and 7. Hence, d_2 is 2.63 Å (slightly enlarged with respect to the value it had when there was a single layer of Cd on the substrate), whereas d_1 is 2.81 Å (i.e., equal to the interlayer spacing along $\langle 0001 \rangle$ in bulk Cd). As far as the nonstructural parameters are concerned, their values remained the same as reported in paper I, with the sole exception of V_0 which is now 9 eV.

III. 3rd (1 × 1) PHASE

The determinations of the atomic arrangements in the first and the second adsorbed Cd layers leave little doubt about the position and the structure of the third layer. We expect that this layer will continue the hcp stacking just begun by the first two Cd layers so that the model describing the three-layer thick Cd film would be $...A_{Ti}B_{Ti}C_{Cd}B_{Cd}C_{Cd}$. As for the interlayer spacings, since the perpendicular distance between the first *two* Cd layers adsorbed was found to be al-
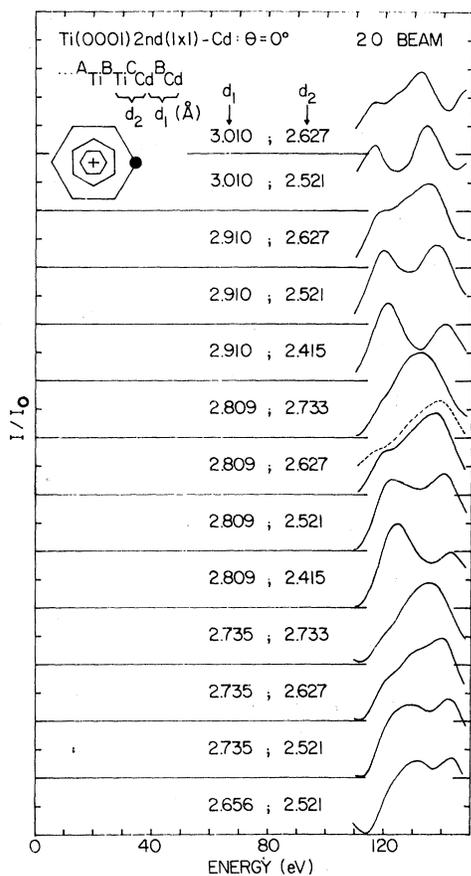
FIG. 7. Effect of variations of the distances d_1 and d_2 (defined in the legend) upon the calculated 20 spectrum at normal incidence. Dashed curve: experimental.
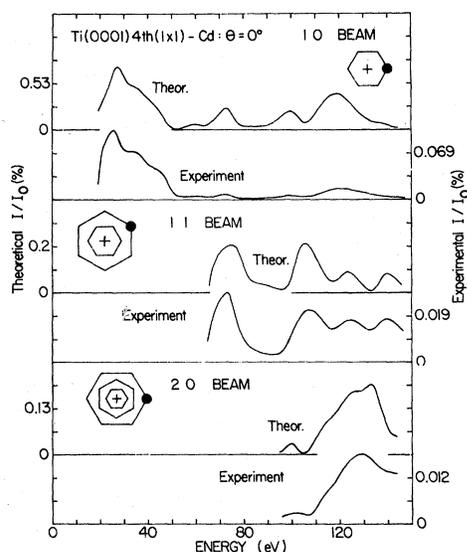
FIG. 8. Theory [calculated for Cd(0001) on a semi-infinite crystal] and experiment [measured on the Ti(0001) 4th (1×1)-Cd phase] for the 10, 11, and 20 beams at normal incidence.

ready the bulk distance, there is hardly any reason to expect a different value for the third adsorbed layer. Unfortunately, we cannot prove that these expectations are correct at the present moment, nor can we determine the interlayer spacing between Ti and Cd layers, because the available computer program does not allow us to handle structural models with more than two surface layers different from the bulk. However, an indirect confirmation is possible in that the fourth-layer spectra agree well with the theory for a semi-infinite Cd crystal (Sec. IV), hence the third layer must have the proper registry and interlayer spacing, at least after the fourth layer is added. It is plausible that the addition of the fourth layer does not disturb the third layer because, as we have shown above, the addition of the second layer does not disturb the registry of the first layer.

IV. STRUCTURE ANALYSIS OF THE 4th (1 × 1) PHASE

The experimental study of the 4th (1×1) phase revealed two important facts (see paper I): (i) The LEED pattern and the intensity spectra of the diffracted beams no longer changed with increasing Cd deposition after formation of the so-called 4th (1×1) phase; (ii) the AES spectrum of this phase was practically indistinguishable from that of a semi-infinite Cd crystal. These observations seem to indicate that the 4th (1×1) phase [which is believed to consist of four atomic layers of Cd on the Ti(0001) substrate] is wholly equivalent to a semi-infinite Cd crystal, as far as the low-energy electrons ($\lesssim 500$ eV) are concerned that are used in LEED or examined in AES. The point could be proven, or at least tested, of course, by comparing the LEED intensity spectra measured on the 4th (1×1) structure with those measured on a bulk Cd(0001) surface. As the latter are not available, we followed the indirect approach of carrying out a quantitative intensity analysis of several beams from the 4th (1×1) phase.

The pertinent structural model is, of course, the one of a semi-infinite "bulklike" Cd(0001) surface in which the only adjustable structural parameter is the spacing d_z^S between the first two atomic layers. In Figs. 8–10 we compare with experiment [i.e., with the curves measured on the 4th (1×1) structure] the spectra calculated for several beams on the basis of such a model. We find excellent agreement between the two sets. For all the calculated curves the value of d_z^S was chosen to be equal to the interlayer spacing along $\langle 0001 \rangle$ in bulk Cd (2.81 Å), because this value was indeed found to produce the best correspondence between
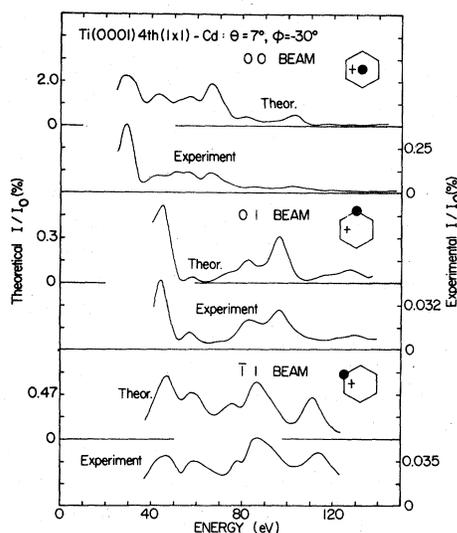
FIG. 9. Theory [calculated for Cd(0001) on a semi-infinite crystal] and experiment [measured on the Ti(0001) 4th (1×1)-Cd phase] for the 00, 01, and $\bar{1}1$ beams at $\theta = 7°$, $\phi = -30°$.

calculations and observations. Figure 11 shows, as an example, the effect of changes in the value of d_z^S upon the intensity spectrum of the 11 beam.

In conclusion, the agreement displayed in Figs. 8–10 proves two points: (i) That the assumption made in paper I about the 4th (1×1) phase being an ordered Cd film with thickness of four or more atomic layer was indeed correct; (ii) that the equivalence claimed for LEED by earlier calculations on Al(001) between a four-layer-thick and a semi-infinite crystal[2] is indeed true. Direct experimental confirmation of this equivalence—the fact that the 00 spectrum of the 4th (1×1) structure is invariant with respect to increased deposition of Cd, was already given in Fig. 2 of Ref. 3.
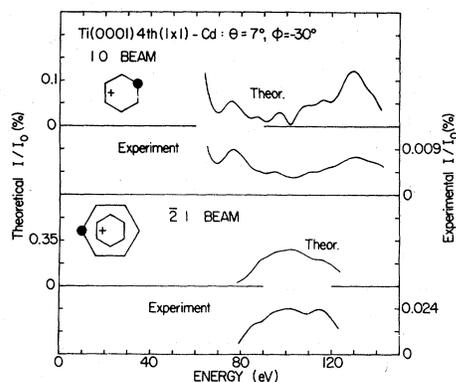
FIG. 10. Theory [calculated for Cd(0001) on a semi-infinite crystal] and experiment [measured on the Ti(0001) 4th (1×1)-Cd phase] for the 10 and $\bar{2}1$ beams at $\theta = 7°$, $\phi = -30°$.
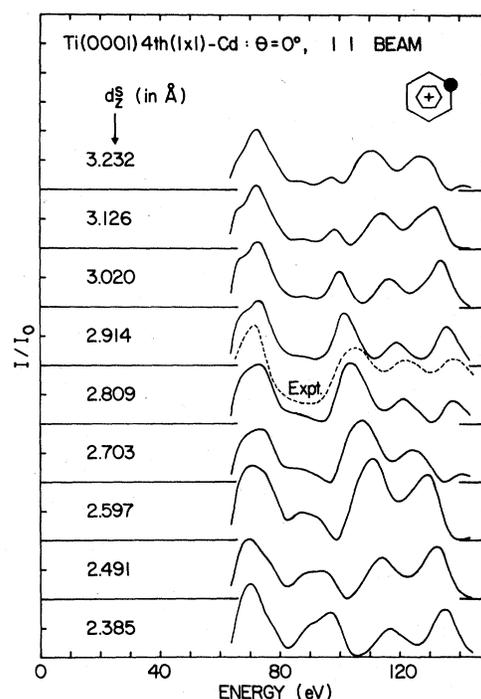
FIG. 11. Effect of variations in the first interlayer spacing d_z^S upon the 11 beam at normal incidence for Cd(0001) on a semi-infinite crystal. Dashed curve: experimental 11 spectrum from the Ti(0001) 4th (1×1)-Cd phase.

V. CONCLUSIONS

The work discussed in paper I and in the present report proves that LEED structure analysis, when supported by ancillary qualitative information such as that provided, e.g., by AES, can be a unique tool in the study of very complex surface phenomena, such as the growth of epitaxial films. In the particular case chosen for this study, this tool enabled us: to recognize the completion of the first full monolayer; to establish that the atoms in such layer are *not* in the positions that the substrate's atom would occupy; to determine the elevation of the adsorbate layer over the substrate; to recognize the completion of the second full atomic layer; to identify the positions of the atoms in such second layer with respect to those in the first; to establish that the interplanar distance between first and second deposited layers is already equal, within the accuracy of the method, to the corresponding spacing in the bulk material; to recognize the completion of the third full atomic layer of the growing epitaxial film; to do the same about the fourth atomic layer; to establish that the LEED response is insensitive to further growth beyond the fourth layer of the epitaxial film; and to establish that a four-layer-thick Cd film is equivalent,
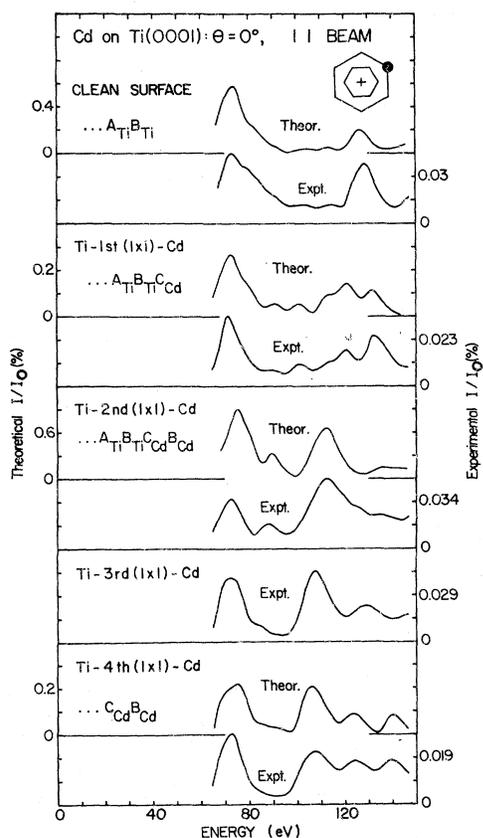
FIG. 12. Progressive changes in experimental LEED intensities, as exemplified by the 11 beam at normal incidence, and in their model-theoretical counterparts, from the clean Ti(0001) surface (top panel) through the 1st (1×1), the 2nd (1×1), the 3rd (1×1), and the 4th (1×1) phases.

as far as LEED is concerned, to a semi-infinite Cd crystal. We believe that this is the first documented quantitative structure determination of the growth sequence of an epitaxial film layer by layer.

The information obtained from this study about the growth mechanism may be only partially new, as the principle of layer-by-layer growth was hypothesized a long time ago, although its quantitative proof and the details about interatomic distances have never been offered before. The most important aspect of this work, however, is the

fact that LEED structure analysis has matured to the point of being able to provide quantitative information of this sort. The achievement may be succinctly summarized in Fig. 12 by means of the example of the 11 beam at normal incidence. The spectrum of this beam from the clean substrate surface was matched by a model calculation in the structure analysis[4] of Ti(0001) (top panel in Fig. 12); the spectrum of the same beam from the first full Cd monolayer was matched by a corresponding calculation in the structure analysis of the 1st (1×1) phase (second panel from the top in Fig. 12); similar success was obtained for the second full layer of Cd atoms (third panel from the top in Fig. 12); the spectrum of the same beam was monitored at the completion of the third atomic layer (second panel from the bottom in Fig. 12), although a model calculation could not be performed in this case; finally, the spectrum of the same beam from the four-layer-thick Cd film was matched by a calculation for a semi-infinite crystal. The experimental curves in Fig. 12 summarize the observed changes in the intensities of the LEED beams, while the theoretical curves confirm that the model calculations do keep pace with the observed changes more than adequately.

Note added in proof. After submission of this article we found an error that affects the energy scale of all LEED spectra. To correct for this error, each number on the energy scale of each LEED spectrum must be increased by 3 eV (i.e., instead of 0, read 3 eV; instead of 40 eV, read 43 eV, etc.). Accordingly, the values of V_0 and V_0^S quoted in the text should be decreased by 3 eV. The conclusions of the paper are otherwise not affected.

[1]H. D. Shih, F. Jona, D. W. Jepsen, and P. M. Marcus, preceding paper, Phys. Rev. B 15, 5550 (1977).
[2]P. M. Marcus, D. W. Jepsen, and F. Jona, Surf. Sci. 31, 180 (1972).
[3]H. D. Shih, F. Jona, D. W. Jepsen, and P. M. Marcus, Commun. Phys. 1, 25 (1976).
[4]H. D. Shih, F. Jona, D. W. Jepsen, and P. M. Marcus, J. Phys. C 9, 1405 (1976).