Conf-820869--1 Draft

CONF-820869--1 DRAFT

DE82 020892

Draft

NOTE: ~~This is a draft of a paper being submitted for publication. Contents of this paper should not be quoted nor referred to without permission of the authors.~~

MASTER

MULTILAYER RELAXATION IN METALLIC SURFACES AS DEMONSTRATED BY LEED ANALYSIS

H. L. Davis and J. R. Noonan

SOLID STATE DIVISION
OAK RIDGE NATIONAL LABORATORY
Operated by
UNION CARBIDE CORPORATION
Under
Contract No. W-7405-eng-26
With the
U. S. DEPARTMENT OF ENERGY
OAK RIDGE, TENNESSEE

July, 1982

MULTILAYER RELAXATION IN METALLIC SURFACES AS DEMONSTRATED BY LEED ANALYSIS*

H. L. Davis and J. R. Noonan

Solid State Division, Oak Ridge National Laboratory

Oak Ridge, Tennessee 37830 USA

ABSTRACT

Theoretical motivations are reviewed for investigation of multilayer relaxation in relatively simple metallic surfaces. Results from LEED analyses are presented which serve to demonstrate that multilayer relaxation measurably exists in Cu(100) and Cu(110) surfaces. The results from two independent LEED analyses for Cu(110) are shown to be in much better agreement with each other than the LEED results are with multilayer relaxation results obtained by high energy ion scattering. Multilayer relaxation results for other metallic surfaces also are reviewed briefly, and all available results are discussed in relationship to those obtained by a theoretical, model-type, inquiry of Landman, Hill and Mostoller.

*Research sponsored by the Division of Materials Science, U.S. Department of Energy, under contract W-7405-eng-26 with Union Carbide Corporation.

1. Introduction

Both the atomic coordination and the conduction-electron distribution are different in the surface region than in the bulk of a metallic crystal. These differences influence the surface's crystallography and can cause it to vary from that of the hypothetical truncated bulk crystal. A simple example of a variation, and one pertinent to this work, is a relaxation of atomic layers normal to the surface so that surface-region interlayer spacings differ from bulk values. Early theoretical attempts to calculate any such relaxation were based only on the change of atomic coordination, since they employed pair potentials constructed to mimic bulk properties. These produced the almost universal prediction that the spacing between the first and second atomic layers, d_{12}, should be larger than the bulk value. But this prediction turned out to be in contradiction with the results of many LEED analyses, which have indicated that d_{12} is usually less than the bulk value.

The above dilemma was resolved by more recent theoretical work of Finnis and Heine (FH) [1], who formulated a model for layer relaxation involving an heuristic redistribution of the surface's truncated bulk electronic density. They then showed that this redistribution, by producing electrostatic forces, could result in a d_{12} less than the bulk value. FH's relative success then motivated subsequent theoretical work. In particular, Landman, Hill and Mostoller (LHM) [2] have considered three distinct models for the surface-region electronic

charge density, and then, very importantly, allowed for the participation of several layers in the relaxation process. Although LHM's work must be considered as being a model-type inquiry, their work very definitely illustrated the acute importance of multilayer relaxation. Such an illustration then implies the necessity to consider the possibility of multilayer relaxation when one performs surface crystallography.

LHM's results motivated us to investigate, using modern LEED analysis, whether multilayer relaxation could be demonstrated in some relatively simple metallic surfaces. We first investigated Cu(100) and found clear evidence for multilayer relaxation [3]. The Cu(100) results will be reviewed briefly below in Section 2. The success of the Cu(100) investigation led us to reanalyze existing [4] data for Cu(110), and some new results for Cu(110) are presented in Section 3. Results of an independent Cu(110) analysis by Adams et al. have also become available [5], and their results will be compared with ours in Section 3. Other available LEED results, which provide evidence for metallic surface multilayer relaxation, will be summarized briefly in Section 4. The common trends present in all the available results are then discussed in relationship to LHM's work in Section 5.

2. Cu(100) multilayer relaxation

In the analysis [3] of Cu(100) the data base, for the sample maintained at room temperature, consisted of four inequivalent I-V profiles.

These profiles were obtained from raw data by application of equivalent beam averaging (EBA) [6,7]. These four profiles were then compared with the results of dynamical LEED calculations for 63 different pairs of values of the first, d_{12}, and second, d_{23}, interlayer spacings. Three distinct R-factors were employed, which were R_{ZJ} as defined by Zanazzi and Jona [8], and R_2 and R_5 as defined by Van Hove et al. [9]. In Fig. 1 are topographs of the 4-beam values of these R-factors, which resulted from comparing the experimental profiles with the totality of calculational results. The plots of Fig. 1 display the R values as functions of the relative changes (denoted by Δ) of both d_{12} and d_{23} from the bulk value. The consistency in the values of Δd_{ij} producing the minimal R's is very good for the results of a LEED analysis, especially since 1% of d_{ij} = 0.018 A. Such consistency provides strong evidence that multilayer relaxation measurably exists for Cu(100).

Figure 2 contains plots of experimental (bottom curves) and calculated I-V profiles. The "A" profiles were calculated for the case which produced the minimum 4-beam R_{ZJ} when only Δd_{12} was allowed to deviate from zero. The "B" curves were calculated for the Δd_{12} and Δd_{23} values which lead to the minimum R_{ZJ} of Fig. 1(a). The "A" and "B" profiles have associated with them single-beam R_{ZJ}'s, obtained by comparison with the respective experimental profile. It is noted that, for all four beams, a relaxation of Δd_{23} from zero produces a reduction in R_{ZJ}. This consistency in reduction of R_{ZJ} supports the

contention that multilayer relaxation is a valid characterization of Cu(100)'s crystallography.

A detailed analysis of the room temperature data for Cu(100), including the above, has indicated that $\Delta d_{12} = -1.10 \pm 0.40\%$, $\Delta d_{23} = +1.70 \pm 0.60\%$ and $+1\% \leq \Delta d_{34} \leq +2\%$ [3]. Note these contain what most would believe to be an unusual physical result — d_{23} is expanded from the bulk value more than d_{12} is contracted. In order to test this result an independent analysis of Cu(100) was initiated, in which data would be obtained using different apparatus, a different sample, and the sample maintained at a temperature of 100 K. Preliminary results from such an analysis indicate that $\Delta d_{12} = -1.00 \pm 0.40\%$ and $\Delta d_{23} = +2.00 \pm 0.80\%$ [10]. Thus, it is felt that when the analysis of the 100 K data is completed, a confirmation will be given to the results obtained in the analysis of the room temperature data.

3. Cu(110) multilayer relaxation

Even though an attempt was made to search for possible multilayer relaxation in a previous analysis of Cu(110) [4], a creditable interpretation of the results obtained then only indicated that $\Delta d_{12} = -10.0 \pm 2.5\%$ and $\Delta d_{23} = 0 \pm 2.5\%$. However, the relative success of our Cu(100) investigation provided the motivation to perform a reanalysis of the existing data for Cu(110) (the sample was maintained at room temperature). The same six, as-measured, inequivalent, I-V profiles analyzed previously serve as the data base for the new

investigation. But to avoid the discrepancies noted before [4] in the 60 eV region, these profiles have only been reanalyzed in the 80 to 220 eV energy range.

The first step in the reanalysis was to perform tests in an attempt to obtain more optimal nonstructural parameters than used in the original analysis. As a result of these test, the dynamical calculations for the reanalysis were performed using eight phase shifts obtained from the same potential used in the Cu(100) work. The imaginary component of the optical potential was taken to be 4 eV, and a surface-region Debye temperature of 340 K was used. These parameters lead to a six-beam R_{zj} value of 0.070 for Δd_{12} = - 10% and Δd_{23} = 0%, while the parameters used originally produced a value of 0.123 for the same values of Δd_{12} and Δd_{23}.

New sets of calculations were performed with 49 different pairs of (Δd_{12}, Δd_{23}) values. In these Δd_{12} was varied from -12% to -6%, and Δd_{23} from -2% to +4%, with both being incremented in steps of 1%. These calculations were then compared with the six experimental I-V profiles, and plots similar to Fig. 1 were obtained. These plots had R-factor minima at (Δd_{12}, Δd_{23}) values of (-10.0,+1.90), (-7.90,+2.40), and (-9.50,+2.60), respectively, for R_{ZJ}, R_2, and R_5. The different R-factor algorithms produced minima of, respectively, 0.067, 0.039, and 0.188. As for Cu(100), the Cu(110) analysis has produced reasonable consistency among the optimal (Δd_{12}, Δd_{23}) values selected by the three algorithms.

After the above results were obtained, we became aware of an independent LEED analysis of Cu(110) performed by Adams et al. [5]. The

final results of these authors were $\Delta d_{12} = -8.5 \pm 0.6\%$ and $\Delta d_{23} = +2.3 \pm 0.8\%$. Since Adams et al. used only R_2 to compare experimental and calculated I-V profiles, the agreement with our new analysis is quite striking (8.3 - 7.9 = 0.6% of d_{12} = 0.008 Å). In fact, such agreement might be considered amazing since the two analyses were based on different data, used a different number of I-V profiles, the profiles were analyzed over different energy ranges, and their calculations employed somewhat different nonstructural parameters.

Despite the above agreement, our results for the Δd_{12} values producing the minima of the three R's have a wider range than the range of the estimated error of Adams et al. for Δd_{12}. This is just a reflection of the fact that their estimated error is a statistical consequence and not a true reflection of possible errors in their analysis (or, of course, our analysis). At the present stage of development of LEED analysis, there exists no a priori reason to prefer use of, say, R_2 over R_{ZJ}. To illustrate further this point, Fig. 3 contains plots of experimental and calculated I-V profiles. The profiles denoted "1" were calculated for the Δd_{ij} producing the minimal six-beam R_2, while those denoted "2" were calculated for the Δd_{ij} producing the minimal six-beam R_{ZJ}. An inspection of Fig. 3 verifies the difficulty encountered when attempting to determine, simultaneously for all six subplots, whether the "1" profiles or the "2" profiles have better agreement with the experimental profiles. Thus, realistic error limits for Δd_{12} must at least be wide enough to

contain the two values serving as the bases for the calculations of Fig. 3. In an attempt which might eventually narrow such error limits, we have initiated another Cu(110) analysis where the data base of experimental I-V profiles will be obtained by EBA [6,7]. Since EBA provides a means to enhance normal incidence LEED data, it is possible that the Δd_{ij} producing minimal values of the three R's will then be in closer agreement.

The possibility of multilayer relaxation in Cu(110) has also been investigated by Stensgaard et al. [11] using High Energy Ion Scattering (HEIS). The final results of these authors indicate that $\Delta d_{12} = -5.3 \pm 1.6\%$ and $\Delta d_{23} = +3.3 \pm 1.6\%$. It is worthy of note that all the Δd_{ij} values from both independent LEED analyses are in better agreement with each other than either of the LEED results are with the HEIS results. Thus, we consider it very important that further investigations be performed to attempt to bring LEED and HEIS results in better agreement. Of course, such work would be important for any surface, not just Cu(110). Be that as it may, the presently available LEED and HEIS results provide, pertinent to the subject of this paper, conclusive evidence that multilayer relaxation is a valid reflection of Cu(110)'s crystallography.

4. Other results for multilayer relaxation

Besides the results described above for Cu(100) and Cu(110), four other LEED analyses have been performed which indicate the existence

of multilayer relaxation in metallic surfaces. The results of these will be summarized briefly here. Although the results must be considered tentative since only two experimental I-V profiles were available as a data base, a LEED analysis of Re(10$\bar{1}$0) has indicated that Δd_{12} = - 17% and + 1% < d_{23} < 2% [12]. Work in progress for Ag(110) is more extensive with a data base of seven experimental profiles obtained by EBA, and preliminary indications are Δd_{12} = - 5.7% and Δd_{23} = + 2.2% [13]. Jensen et al. [14] have used the R_2-factor to compare 5 experimental profiles for V(100) with calculational results, and their analysis indicates that Δd_{12} = - 7% and Δd_{23} = + 1%. Finally, a very detailed LEED analysis has recently been preformed for Al(110) by Nielsen et al. [15]. These authors report that Δd_{12} = - 8.4 ± 0.8%, Δd_{23} = + 4.9 ± 1.0%, and Δd_{34} = - 1.6 ± 1.1%.

5. Discussion

A common trend is seen immediately in the available multilayer relaxation results for metallic surfaces. For all six surfaces Δd_{12} is negative while Δd_{23} is always positive; thus, it is of interest to speculate whether this trend will continue as more multilayer relaxation results become available. Obtaining more results will also be of theoretical interest, since the present trend is consistent with the tendency observed by LHM [2], in their results of model calculations, for the layer relaxations to alternate in sign. However, no useful purpose is served by a quantitative comparison of the LEED results

with those calculated by LHM. Their work was based on simple models for the electronic charge distribution, and the electron density was frozen in their calculations rather than being allowed to respond self-consistently to the relaxation. So LHM's results should not be expected to provide quantitatively accurate predictions of multilayer relaxation. But it is reasonable to expect that theoretical investigations will soon be able to provide more reliable predictions. In this regard, due to its simpler electronic structure, theoretical work for Al(110) would probably be the easiest to perform of the six surfaces investigated to date by LEED. So it would also be useful to have HEIS verification of Nielsen et al.'s results for Al(110). Such work might, hopefully, lead to LEED and HEIS results being in better agreement than the results are, at present, for Cu(110).

References

[1] M. W. Finnis and V. Heine, J. Phys. F 4 (1974) L37.

[2] U. Landman, R. N. Hill and M. Mostoller, Phys. Rev. B 21 (1980) 448.

[3] H. L. Davis and J. R. Noonan, J. Vacuum Sci. Technol. 20 (1982) 842.

[4] H. L. Davis, J. R. Noonan and L. H. Jenkirs, Surface Sci. 83 (1979) 559.

[5] D. L. Adams, H. B. Nielsen and J. N. Andersen, preprint and to be published.

[6] H. L. Davis and J. R. Noonan, Physica Scripta, submitted.

[7] H. L. Davis and J. R. Noonan, Surface Sci. 115 (1982) L75.

[8] E. Zanazzi and F. Jona, Surface Sci. 62 (1977) 61.

[9] M. A. Van Hove, S. Y. Tong and M. H. Elconin, Surface Sci. 64 (1977) 85.

[10] J. R. Noonan and H. L. Davis, Bull. Am. Phys. Soc. 27 (1982) 237.

[11] I. Stensgaard, R. Feidenhans'l and J. E. Sorensen, preprint and to be published.

[12] H. L. Davis and D. M. Zehner, J. Vacuum Sci. Technol. 17 (1980) 190.

[13] J. R. Noonan and H. L. Davis, Bull. Am. Phys. Soc. 26 (1981) 224.

[14] V. Jensen, J. N. Andersen, H. B. Nielsen and D. L. Adams, Surface Sci. 116 (1982) 66.

[15] H. B. Nielsen, J. N. Andersen, L. Petersen and D. L. Adams, preprint and to be published.

FIGURE CAPTIONS

Fig. 1. Topographs of four-beam R-factors for Cu(100).

Fig. 2. Calculated and experimental I-V profiles for Cu(100).

Fig. 3. Calculated and experimental I-V profiles for Cu(110). The profiles "1" lead to the minimal six-beam R_2, while the profiles "2" lead to a minimal six-beam R_{ZJ}. The numbers to the right of each subplot are single-beam R's.

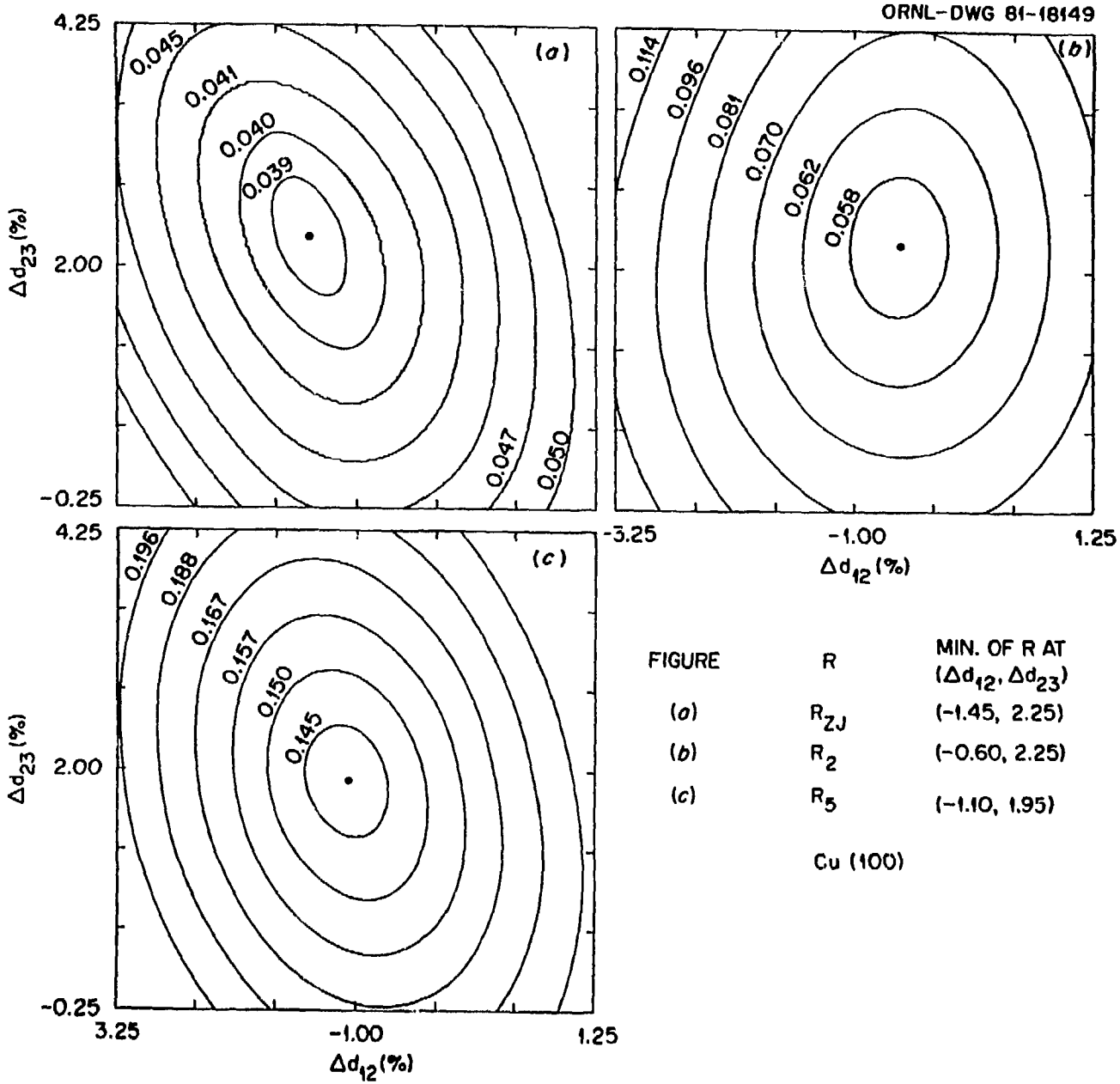
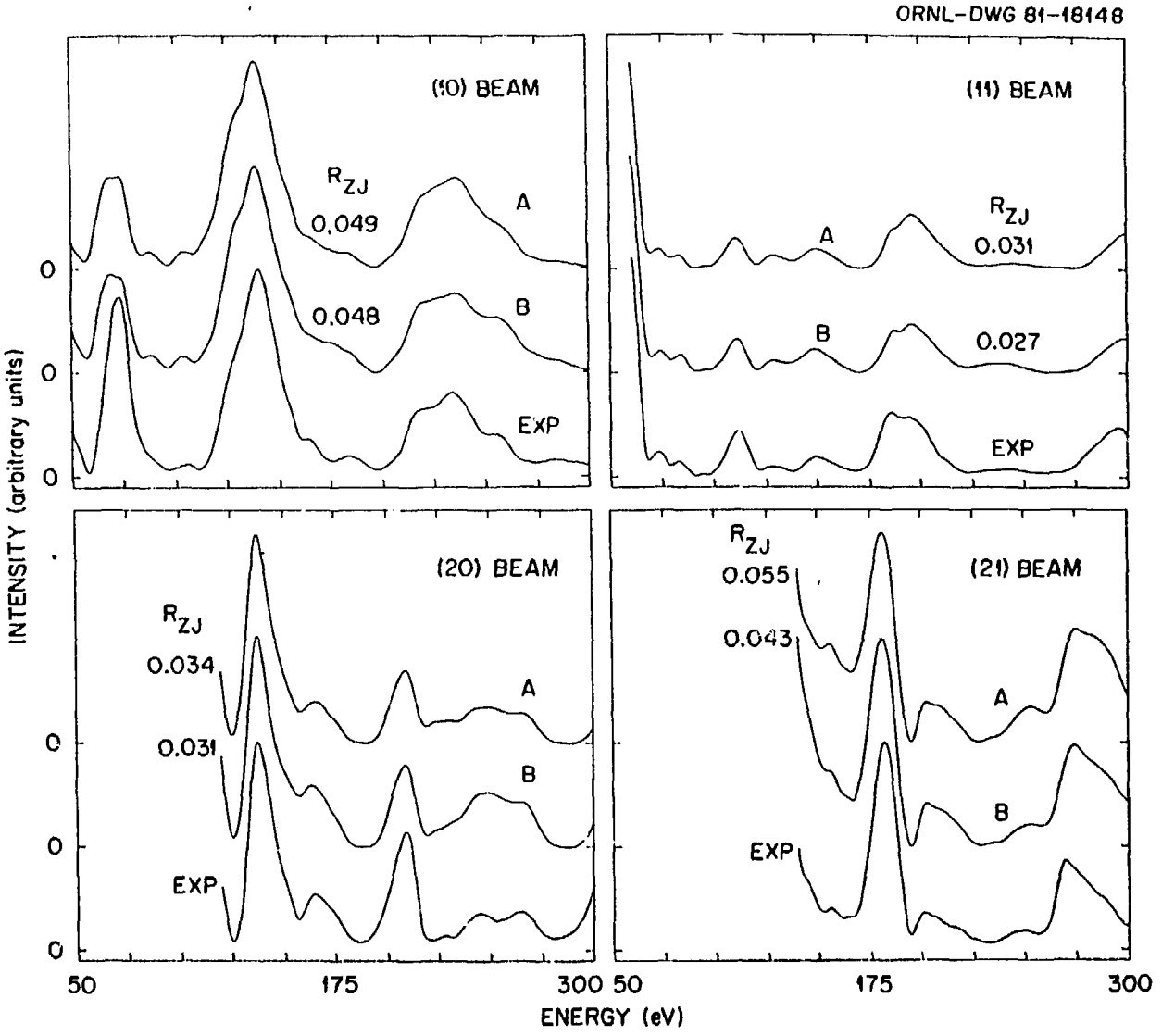

ORNL-DWG 81-18149
(a)
(b)
(c)
0.045
0.041
0.040
0.039
0.047
0.050
0.114
0.096
0.081
0.070
0.062
0.058
0.196
0.188
0.167
0.157
0.150
0.145
4.25
2.00
-0.25
-3.25
-1.00
1.25
3.25
Δd23 (%)
Δd12 (%)
FIGURE
R
MIN. OF R AT (Δd12, Δd23)
(a) RZJ (-1.45, 2.25)
(b) R2 (-0.60, 2.25)
(c) R5 (-1.10, 1.95)
Cu (100)

Fig. 1



Cu (100)

CURVES "A" CALCULATED FOR $\Delta d_{12} = -0.90\%$ AND $\Delta d_{23} = 0.00\%$

CURVES "B" CALCULATED FOR $\Delta d_{12} = -1.45\%$ AND $\Delta d_{23} = 2.25\%$

Fig. 2

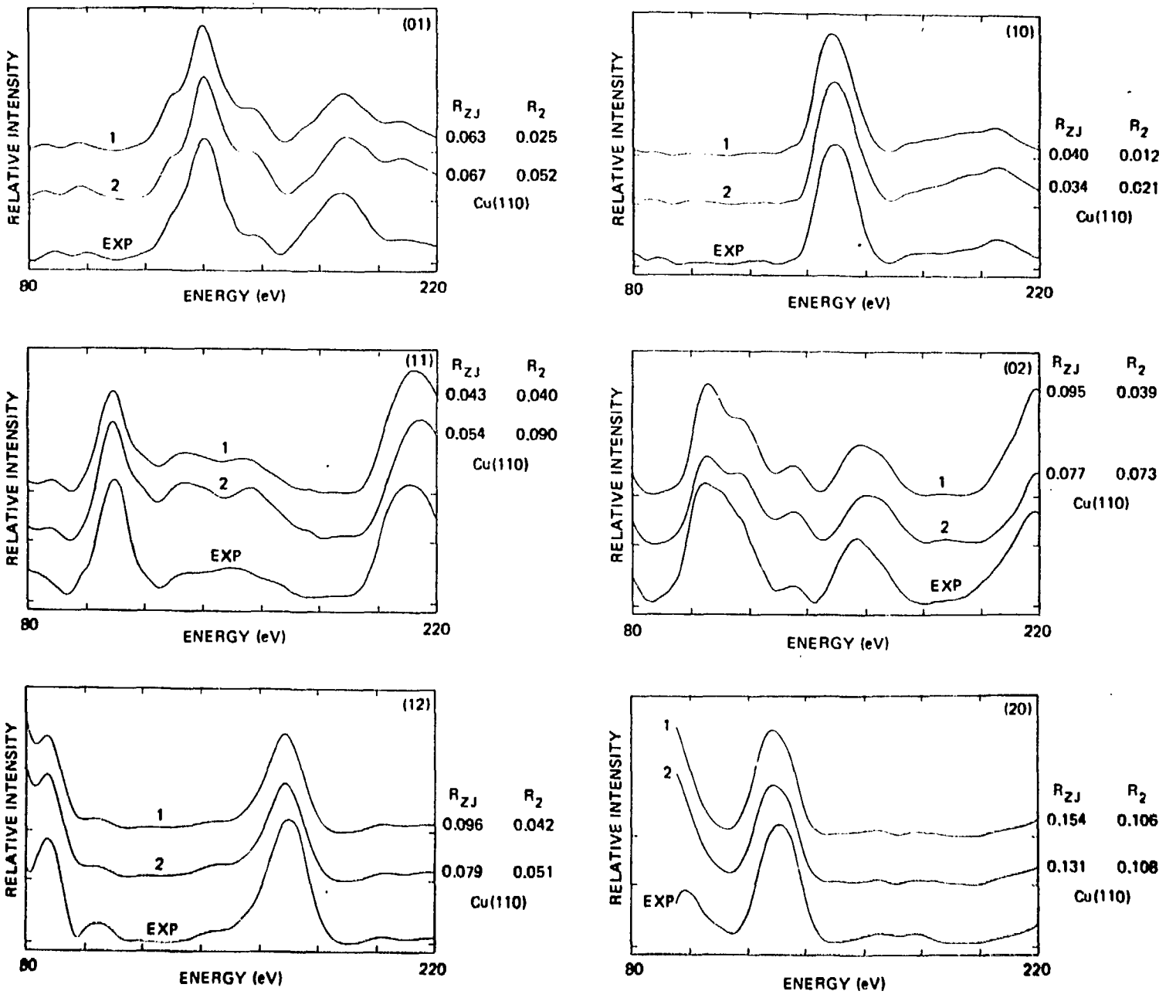

(01)
RELATIVE INTENSITY
1
2
EXP
80
ENERGY (eV)
220
R_{ZJ} R_2
0.063 0.025
0.067 0.052
Cu(110)
(10)
RELATIVE INTENSITY
1
2
EXP
80
ENERGY (eV)
220
R_{ZJ} R_2
0.040 0.012
0.034 0.021
Cu(110)
(11)
RELATIVE INTENSITY
1
2
EXP
80
ENERGY (eV)
220
R_{ZJ} R_2
0.043 0.040
0.054 0.090
Cu(110)
(02)
RELATIVE INTENSITY
1
2
EXP
80
ENERGY (eV)
220
R_{ZJ} R_2
0.095 0.039
0.077 0.073
Cu(110)
(12)
RELATIVE INTENSITY
1
2
EXP
80
ENERGY (eV)
220
R_{ZJ} R_2
0.096 0.042
0.079 0.051
Cu(110)
(20)
RELATIVE INTENSITY
1
2
EXP
80
ENERGY (eV)
220
R_{ZJ} R_2
0.154 0.106
0.131 0.108
Cu(110)

Fig. 3