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SOLID STATE PHYSICS

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$ .X]PLQ $ .DOLQNR $ $QVSRNV - 7LPRVKHQ

,QVWLWXWH RI 6ROLG 6WDWH 3K\VLFV 8QLY
.HQJDUDJD 6WU 5LJD /9 /$79,$
H PDLO D NX]PLQ#F¿ OX OY

; UD\ GLuUDFWLRQ DQG [UD\ DEVRUSWLRQ VSHFW
ZHUH XVHG WR VWXG\ WKH DWRPLF VWUXFWXUH LQ F
7H[WXUHG QDQRFU\VWDOOLQH ¿OPV DUH REWDLQHG X
VXEVWUDWHV KHDWHG DERYH DQG GLVRUGHUHG ¿OPV KDYLQ
GLVRUGHUHG VWUXFWXUH DOUHDG\ LQ WKH VHFRQG F
SRVLWHG LQ WKH DEVHQFH RI KHDWLQJ

Keywords FRSSHU QLWULGH WKLQ ¿OP [UD\ GLüUDF
spectroscopy.

,1752'8&7,21

&RSSHU QLWULGH &X1 KDV D FXELF DQWL5H2 VWUXFWXUH)LJ
ODWWLFH SDUDPHWHU D DQG LV FRPSRVHG RI &X1 RFWDKHGUD MRLQ
FRUQHUV > @ > @ 3UDFWLFDO LQWHUHVW LQ WKH I
UHFHQW \HDUV PRWLYDWHG E\ LWV SRVVLEOH DSSOL
IRU ZULWH RQFH UHDG PDQ\ :250 RSWLFDO VWRUDJ
WLRQ RI ORZ UHVLVWDQFH PDJQHWLF WXQQHO MXQF
DFFHVV PHPRULHV > @ DV SURPLVLQJ FDWKRGLF HO
LQ RSWLFDO OLWKRJUDSK\ IRU IDEULFDWLRQ RI PLFU
FHQWO\ DV DQ DEVRUEHU IRU SKRWRYROWDLF DQG S

Fig. 1. &U\VWDO VWUXFWXUH RI FXELF DQWL5H2 VWUXFWXUH RI &X1 Fm m
ODU RFWDKHGUD /DUJH EDOOV DUH FRSSHU DWRPV VPD

7KH DWRPLF VWUXFWXUH RI &X DQLVRWURSLF WK
DWRPV ZKRVH WKHUPDO HOOLSVRLGV DUH ÀDWWHQH
&X±1 DWRPLF FKDLQV > @ DQG DFFHSWV WKH SUHVH
FRSSHU LQWHUVWLWLDO GRSDQWV WKDW PD\ UHVXO
XS WR r c > @ > @

&KHPLFDO ERQGLQJ DQG HOHFWURQLF SURSHUWLHV
LWV DWRPLF VWUXFWXUH 7KH &X±1 ERQGV DORQJ F
WLDOO\ FRYDOHQW GXH WR DQ DGPL[WXUH RI &X V
ZKLFK GR QRW OHDG WR D FRYDOHQW HQHUJ\ JDS
± H9 > @ VHPLFRQGXFWRU +RZHYHU VPDOO
WZHHQ FRSSHU DWRPV VWLPXODWHG E\ WKH IRUPDW
IXUWKHU EDQG JDS QDUURZLQJ RU HYHQ EDQG RYHU
GLVWDQFH RI DERXW c LV VOLJKWO\ ODUJHU WKDQ
LQ PHWDOOLF FRSSHU 7KH PHWDOOLF FKDUDFWHU RI &X DQ
FRSSHU GRSLQJ > @ > @ RU E\ DSSO\LQJ KLJK SUH
tion on the local atomic structure and disorder in CuW KLQ ¿OPV LV LPSRUWD
XQGHUVWDQGLQJ DQG WXQLQJ RI WKHLU SURSHUWLH

,Q WKLV VWXG\ ZH KDYH SHUIRUPHG FRPSOHPH
DEVRUSWLRQ VSHFWURVFRS\ LQYHVWLJDWLRQV RI V
SURGXFHG E\ GF PDJQHWURQ VSXWWHULQJ DV D IXQ

(;3(5,0(17$/ $1' '$7$ 1/<6,6

3RO\FU\VWDOOLQH &X ¿OPV ZHUH SUHSDUHG E\ GF PD
PHWDO FRSSHU WDUJHW LQ SXUH QLWURJHQ DQG SRO\L
DYHUDJH GHSRVLWLRQ UDWH RI QP VHF XVLQJ PR
V\VWHP 891 7KH GHSRVLWLRQ SDUDPHWHUV DQG W
7DEOH 7KH ¿OP WKLFNQHVV ZDV PHDVXUHG E\ SUR
FU\VWDOOLQH &XULW\ OIDHVDU ZDV XVHG IRU FR

; UD\ SRZGHU GLIIUDFWLRQ ;5' SDWWHUQV)LJ
SHUDWXUH XVLQJ %UDJJ %UHQWDQR SRZGHU GLIIU
;¶3HUW 3UR 03' HTXLSSHG ZLWK FRSSHU DQRGH [U
radiation, O QP

; UD\ DEVRUSWLRQ PHDVXUHPHQWV ZHUH SHUIRU
LQ WUDQVPLVVLRQ PRGH DW WKH +$6</$% '(6< & EH
URRP WHPSHUDWXUH 7KH VWRUDJH ULQJ 3(75$,,, RS
P$ 7KH KLJKHU RUGHU KDUPRQLFV ZHUH UHGXFHG E
PDWRU 6L FU\VWDO WR URFNLQJ FXUYH PD[LPXP
VWDELOL]DWLRQ IHHGEDFN FRQWURO 7KH [UD\ EHD
FKDPEHUV ¿OOHG ZLWK DUJRQ DQG NU\SWRQ JDVHV

; UD\ DEVRUSWLRQ VSHFWUD ZHUH DQDO\VHG XVL
7KH H[WHQGHG ; UD\ DEVRUSWLRQ ¿QH VWUXFWXUH (;$)6 $ k) was isolated f
D FRQYHQWLRQDO SURFHGXUH > @ 7KH FRQWULEXWLRQ
RQG &X±&X FRRUGLQDWLRQ VKHOOV ZDV LVRODWHG
WKH UDQJH RI ± c DQG DQDO\VHG ZLWKLQ WKH

PDWLRQ WR GHWHUPLQH VWUXFWXUDO SDUDPHWHUV
VFDWWHULQJ)()) FRGH > @ > @ ZDV XVHG WR JH
DQG SKDVH VKLIW IXQFWLRQV IRU &X±1 DQG &X±&X D
data of Cu1 > @ 7KH FRPSOH[H[FKDQJH FRUUHODWLRQ +
XVHG WR DFFRXQW IRU LQHODVWLF HuHFWV 7KH FU
W\SH DQG WKH YDOXHV RI WKH 0 DQG L ZHUH

Table 1

Thin Film Preparation Conditions, Thickness and Lattice Parameter of Cu_3N Samples

6DPSOH	'HSRVLWLRQ WLPH (sec)	6XEVWUDWH WHPSHUDWXUH (qC)	)LOP WKLFNHVV (nm)	F/DWWLFH SDUDPHWHU c
%XON &X				
7)				
7)				
7)				

Fig. 2. ; UD\ GLuUDFWLRQ VSHFWUD RI ¿OPV IRUPHG RQ EDUH VKRZ SRV
SHDNV IRU 1 ESXON &X-&3'6 1R

5(68/76 $1' ',6&866,21

7KH WKLQ ¿OP 7) GHSRVLWHG DW URRP WHPSHUD
SKRXV)LJ DQG LWV ;5' SDWWHUQ RULJLQDWHG I
RWKHU ¿OPV GHSRVLWHG DW KLJKHU WHPSHUDWXUH
DUH QDQRFU\VWDOOLQH DQG VWURQJO\ WH[WXUHG Z
GLuUDFWLRQ SDWWHUQV DUH LQGH[HG WR WKH
WKDW VLPLODU SUHIHUHQWLDO RULHQWDWLRQ RI &X
> @ > @ > @ IRU ¿OPV SURGXFHG E\ UHDFWLYH U
WHULQJ 7KH ODWWLFH SDUDPHWHUV 7) DQG 7)
WKH SRVLWLRQ RI WKH DQG SHDN7DEOH OLJK
WKDW LQGLFDWHV VRPH VXEVWUDWH\ RI W

Fig. 3.)RXULHU WUDQVIRUPV WKLQ OLQHV ± LPDJLQDU\ SDUWV DQ
. HGJH (;$)6 for(k)Cu 1   6ROLG OLQH ± WKH VLJQDO LQFOXGLQJ DOO
EXWLRQV XS WR WKH WK RUGHU GDVKHG OLQH ± WKH VLJQDO L
WLRQV 1RWH WKDW WKH SRVLWLRQV RI WKH SHDNV GLuHU IURP
SUHVHQW LQ (;$)6

Table 2

Interatomic Distances (R, r0.01 Å) and Mean-Squared Relative Displacements (V², r0.0007 Å²) for Nearest Cu–N and Cu–Cu Atom Pairs Obtained from the Analysis of the Cu K-edge EXAFS Spectra

6DPSOH	&X±1		&X±&X	
	R c	V ǫ	R c	V ǫ
%XON &X				
7)				
7)				
7)				

Since Cu1 KDV DQWL SHURYVNLWH W\SH VWUXFWXU
FKDLQV RQH FDQ H[SHFW VLJQL¿FDQW FRQWULEXW
IHFWV > @ LQWR (;$)6 7KHUHIRUH ZH KDYH SHUIRU
FDOFXODWLRQV E\ WKH)()) FRGH > @ WR HVWLPDWH WKH
UDQJH ZKHUH VXFK FRQWULEXWLRQV DUH LPSRUWDQ
FDOFXODWLRQV OHDGLQJ WR RYHUHVWLPDWHG SHD
SRUWHG LQ)LJ   DQG VXJJHVW WKDW WKH ¿UVW W
(;$)6 ZKLFK FRUUHVSRQG WR WKH ¿UVW &X±1 DWRP
SDLU FRRUGLQDWLRQ VKHOOV RI FRSSHU DUH IUHH
DQDO\VHG ZLWKLQ WKH VLQJOH VFDWWHULQJ 66 DS
FRPSRQHQW DQDO\VLV SURFHGXUH > @ > @ 7KH D
LQFOXVLRQ RI WKH 06 HuHFWV WKURXJK VRPH VSK
GHVFULEHG LQ > @ DQG ZLOO QRW EH GLVFXVVHG

7KH VKDSH RI WKH &X . HGJH (;$)6 IRU WKH ¿OPV
KHDWHG VXEVWUDWHV 1VH[FRPSRVLWLRQ DW WKH IDQWXEVWUD
)LJ $ FRPSDULVRQ RI WKHLU)RXULHU WUDQVIRUP
WXUH RI WKH ¿OPV DSSHDULQJ DV SURJUHVVLYH UHG
GXH WR D FRQWULEXWLRQ RI XQGHU FRRUGLQDWHG
IDFH 7KH KLJK IUHTXHQF\ FRQWULEXWLRQV IURP W

PDWLFDOO\ UHGXFHG LQ (;$)6 RI WKH ¿OP 7) GHSRV
UHÀHFWV GLVDSSHDUDQFH RI WKH ORQJ UDQJH RUG
GDWD)LJ

Fig. 4. ([SHULPHQWDO &XF(k)HDQG (W)6LU)RXULHU WUDQVIRU
ERWK LPDJLQDU\ SDUWV DQG PRGXOL DUH VKRZQ
Cu 1 DQG WKLQ ¿OPV

7KH YDOXHV RI VWUXFWXUDO SDUDPHWHUV LQ
VTXDUHG UHODWLYH GLVSODFHPHQW RI 6WKH DQDO\
WZR SHDNV LQ)7V DUH UHSUHVHQWHG LQ TABLE I
FRRUGLQDWLRQ QXPEHUV IRU &X±1 DQG &X±&X ¿OPV U
WKH EXON ZLWKLQ WKH HUURU RI WKH ¿W $OVR WKH
YDOXHV LQ DOO ¿OPV DUH FORRUVHR WHRUWKHLQ EXON
WKH &X±1 065'V LQGLFDWH VWURQJ ERQGLQJ WKURX
ZLWK WKH &X G 1 S EDQGV HVWLPDWHG E\ WKH ¿U
FDOFXODWLRQV LQ > @ 7KH LQWHQVLW\ RI WKH VH
UHGXFHG LQ WKH ¿OPV GXH WR LQFUHDVLQJ GLVRUG
YDOXH LQFUHDVHV QHDUO\ WZLFH LQ WKH. DMRUSKRX

&21&/86,216

7KH DWRPLF VWUXFWXUH RI FRSSHU QLWULGH W
VSXWWHULQJ ZDV VWXGLHG E\ [UD\ GLuUDFWLRQ DQ
&X . HGJH :H IRXQG WKDW WKH QHDUHVW LQWHUDW
QRW FKDQJH VLJQL¿FDQWO\ XSRQ VXEVWUDWH KHDW
LQGLFDWLQJ VWURQJ ERQGLQJ EHWZHHQ FRSSHU DQ
VHFRQG &X±&X DQG RXWHU FRRUGLQDWLRQ VKHOOV
GLVRUGHU ZKLFK FRXOG EH UHGXFHG E\ VXEVWUDW

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3URJUDP ,0,6 7KH (;$)6 PHDVXUHPHQWV KDYH EHHQ
Community's Seventh Framework Programme under grant agreement No. 226716
(Project I-20100098 EC).

5()(5(1&(6

=DFKZLHMD 8 DQG -DFREV + $PPRQRNWKHUPDOV
J. Less Common Metals 161 ± '2, *

3DQLFRQL * 6WRHYD = 'REHUVWHLQ + 6PLWK 5
' + 6WUXFWXUDO SKRWRHPLVVLRQ VWXG\ RI &X1 FUHDWHG E\ DPPRQR
Solid State Sci. 9 ± '2, M VROLGVWDWHVFLHQFHV

$VDQR 0 8PHGD . DQG 7DVDNL $ &X1 ¿OP IRU D QHZ OLJKW
media. Jpn. J. Appl. Phys. 29 ± '2, --$3

0DUX\DPD 7 DQG 0RULVKLWD 7 &RSSHU QLWULG
RQFH RSWLFDO Appl. Phys. Lett. 69 PHGLD '2,

%RUVD ' 0 *UDFKHY 6 3UHVVXUD & DQG %RHUPD '
ties of Cu 1 ¿OPV DQG ¶&X1 DQG)H Appl. Phys. Lett. 80 ± '2,

:X + DQG &KHQ : &RSSHU QLWULGH QDQRFXEH
DSSOLFDWLRQ DV FDWKRGH J. Am. Chem. Soc. 133 DONDOLQH I
'2, MD X

0D\D / 'HSRVLWLRQ RI FU\VWDOOLQH ELQDU\ QLWU
E\ UHDFWLYH J. Vac. Sci. Technol. A 11 ± '2,

%RUVD ' 0 DQG %RHUPD ' 2 *URZWK VWUXFWX
Cu 1 ¿OPV Surf. Sci. 548 ± '2, M VXVF

=DNXWD\HY $ &DVNH\ &K 0)LRUHWWL $ 1 *LQOH\
(DQG /DQ\ 6 'HIHFW WROHUDQW VHPLFRQGXFW
Phys. Chem. Lett. 5 ± '2, M]

&DVNH\ &K 0 5LFKDUGV 5 0 *LQOH\D ' 6 DQG =D
V\QWKHVLV DQG SURSHUWLHV RI FRSSHU QLWULGH D P
Mater. Horiz. 1, ± '2, F PK K

3LHUVRQ -) 6WUXFWXUH DQG SURSHUWLHV RI F
PDJQHWURQ VSXWWHULQJ Vacuum 66 ± '2, 6 ;

0DUX\DPD 7 DQG 0RULVKLWD 7 &RSSHU QLWUL
IUHTXHQF\ UHDFWLYH VSXWWHULQJ J. Appl. Phys. 78 '2,

+DKQ 8 DQG :HEHU : (OHFWURQLF VWUXFWXUH
of Cu N, Cu 1 3G DQG UHODWHG FRPSRXQGV Phys. Rev. B 53 '2,
3K\V5HY%

0RUHQR $UPHQWD 0 * 0DUWtQH] 5XL] $ DQG 7DNHX
HQHUJ\ FDOFXODWLRQV RI FRSSHU QLWULGH 7KH HuHF
LQ WKH HOHFWURQLF SURSHUWLHV Solid State Sci. ± '2, M VROLGVWD
HV

+RX =) (uHFWV RI &X 1 DQG /L LQWHUFDODWL
HOHFWURQLF VWUXFWXUH RI FXELF &X N. Solid State Sci. ± '2, M VRO
LGVWDWHVFLHQFHV

=KDR - * <DQJ / ; DQG <X < 3UHVVXUH LQGXF
evolution of Cu N. Phys. Stat. Sol. (b) ± '2, SVVE

:RV\OXV $ 6FKZDU] 8 $NVHOUXG / 7XFNHU 0 *
.XQWVFKHU & YRQ $SSHQ - 'URQVNRZVNL 5 5DX
SUHVVXUH SKDVH WUDQVLWLRQ H[SHULPHQWDO DQG WKHRUHWLFDO VWXG\ RI &X
Z. Anorg. Allg. Chem. ± '2,]DDF

5LFNHUV . 'UXEH : 6FKXOWH 6FKUHSSLQJ + :HOWH
0 +HXHU - DQG 6FKXO] 5LWWHU + 1HZ ;$)6)DF
DW %HDPOLQH & DW +$6</$% $IP Conf. Proc. 882 ± '2,
.X]PLQ $ ('$ (;$)6 GDWD DQDO\VLV ZDUH SD Physica B 208-209
± '2, *
$NVHQRY 9 / .X]PLQ $ <X 3XUDQV - DQG 7\XW\XQQ
RI 0HWKRGV RI (;$)6 6SHFWURVFRS\ RQ 6\QFKURWURQ 5 Crystal-
logr. Rep. 51 ± '2, 6
.X]PLQ $ DQG &KDER\ - (;$)6 DQG ;$1(6 DQDO\
noscale. IUCrJ 1 ± '2, 6
$QNXGLQRY $ / 5DYHO % 5HKU - - DQG &RQUDGVRQ
VFDWWHULQJ FDOFXODWLRQ DQG LQWHUSUHWDWLRQ R Phys.
Rev. B 58 ± '2, 3K\V5HY%
5HKU - - DQG $OEHUV 5 & 7KHRUHWLFDO DSSUR
ture. Rev. Mod. Phys. ± '2, 5HY0RG3K\V
;LDR - /L < DQG -LDQJ $ 6WUXFWXUH RSWLF
FRSSHU QLWULGH ¿OPV SUHSDUHG E\ UHDFWLYH UDGLR J. Mater.
Sci. Technol. 27 ± '2, 6
<XH * + <DQD 3 ; DQG :DQJ - 6WXG\ RQ WKH
RI FRSSHU QLWULGH ¿OPV J. Cryst. Growth 274 ± '2, M MFU\V
JUR
.X]PLQ $ DQG 3XUDQV - $ QHZ IDVW VSKHULFD
RI PXOWLSOH VFDWWHULQJ FRQWULEXWLRQ LQ WKH ;
SOLFDWLRQ WR 5H2 J. Phys.: Condensed Matter 5 ± '2,

$QVSRNV $ .DOLQNR $ .DOHQGDUHY 5 DQG .X]PLQ
OD[DWLRQ LQ QDQRFU\VWDOOLQH 1L2 VWXGLHG E\ (;$)6
cies. Phys. Rev. B 86 ± '2, 3K\V5HY%

9$5$ 1,75®'$ 3/–12 .–57,»8 6758.7Ë5$6 3œ7®-8

$ .X]PLQV $ .DOLQNR $ $QVSRNV
- 7LPRãHQNR 5 .DOHQGDUHY

.RSVDYLONXPV

âDM— GDUE— P•V]L¼RMDP SOU— QLWUL¼X GLH
IUDNFLMDV XQ UHQWJHQDEVRUEFLMDV VSHNWURVNR
QDQRNULVWl—OLVN—V SO—Q—V NDUWL¼DV WLND LH
L]SXWLQ—ãDQDV SURFHVX X] SDPDWQ•P NDV NDUV•
SO—Q—V N—UWL¼DV DU VWLSUL QHVDN—UWRWX VWU
VDJDWDYRWDV EH] SDPDWQHV NDUV•ãDQDV