

QUARTERLY

TECHNICAL PROGRESS REPORT

Submitted to U. S. Department of Energy

GRANT TITLE: NQR-NMR Studies of Higher Alcohol
Synthesis Cu-Co Catalysts

GRANT NO: DE-FG22 89PC89762 (GSU: 5-5374)

STARTING DATE: 09-15-89

ENDING DATE: 09-14-91 (Under no cost extension till 9-14-1992)

PROJECT DIRECTOR: A. N. Murty
Physics Department

INSTITUTION: Grambling State University
Grambling, Louisiana 71245

*U.S./DOE Patent Clearance is not required prior to the publication of this document.

A. Narasimhan Murty
Project Director

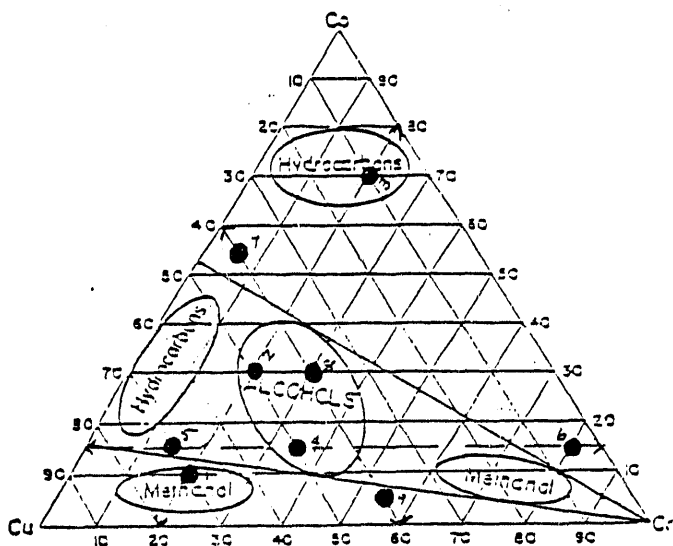
April 15, 1992
Date

MASTER
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MAY 04 1992

QUARTERLY TECHNICAL PROGRESS REPORT
(Period December 15, '91 to March 15, '92

During this period, we focused our attention in analyzing the magnetic nature of the extensively used trimetallic catalyst system [1] Cu-Co-Cr for the production of higher alcohols. The catalytic results of the IFP group [1] are summarized in the selectivity phase diagram Fig. I.



The Cu/Co intermetallic ratio seems to determine the product selectivity. In the cobalt rich field $Cu/Co < 1$, hydrocarbons, in copper rich field $Cu/Co > 3$, methanols and in the intermediate range alcohols are reported to be the major products. However, several investigators, preparing catalysts following IFP

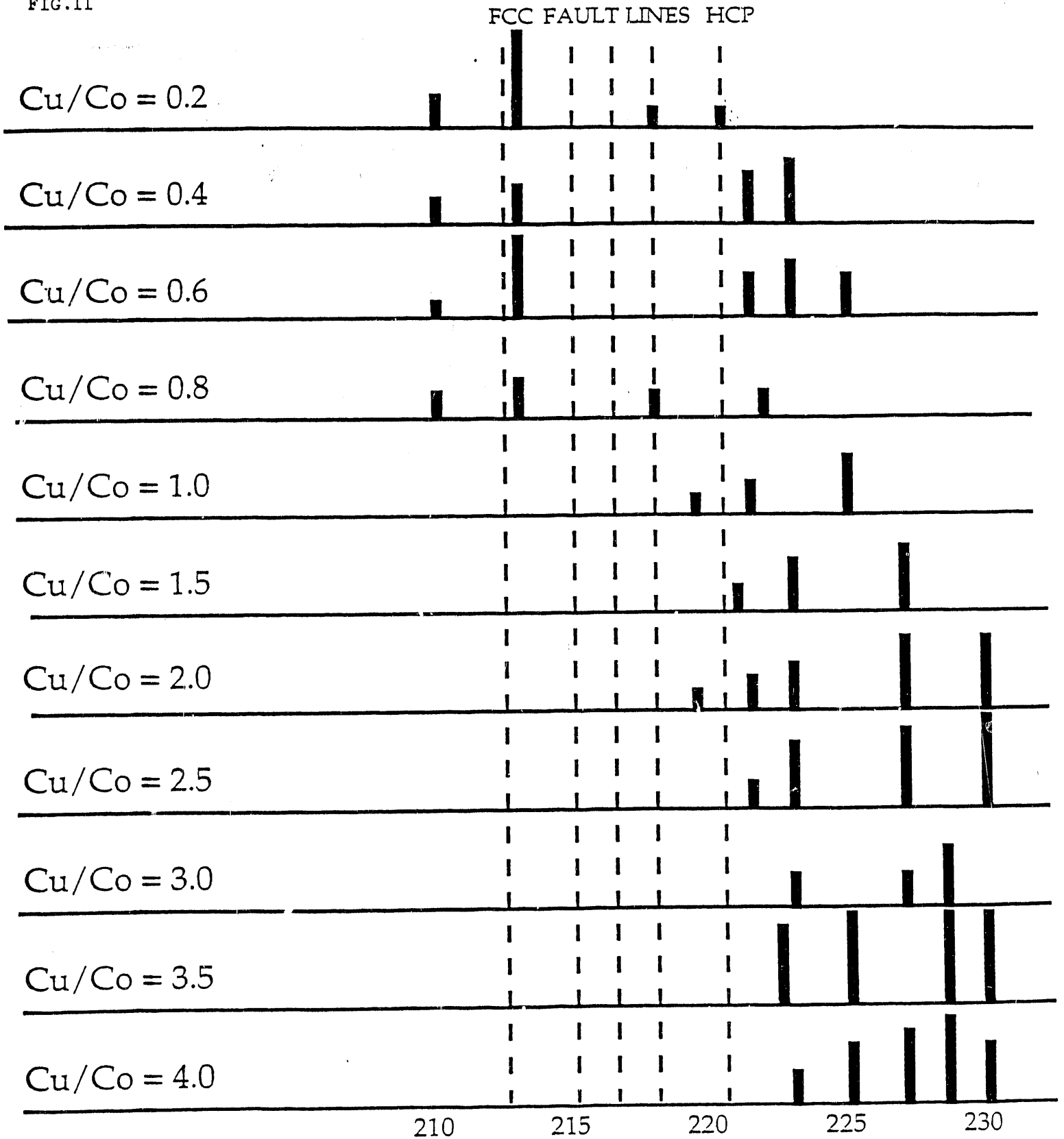
prescription found difficulty in reproducing IFP results [2]. It is generally accepted that not only the intermetallic ratio, but the method of preparation - precipitation pH and temperature, drying, calcination and reduction temperatures and duration, all play significant roles in determining the catalytic behavior of the system.

We believe that there could be some correspondence between the catalytic and magnetic behaviors of the transition metal catalyst systems. Both the morphology and metallic charge distribution of the particles are known to govern the catalytic as well as the magnetic properties of the system. Based on this concept, we have

extensively examined the Cu/Co system varying Cu/Co ratio from 0.2 - 4. [3]. The NMR results summarized in Fig. II clearly reveal that when copper content increases beyond 50%, the Cu/Co metal clusters exhibit strong intermetallic interactions. The hyperfine field at the Co nuclear site is drastically modified compared to the pure Co powder spectrum (broken, vertical lines). The entire spectrum is shifted to higher frequencies. Such a shift could occur if the electron charge density decreases in the vicinity of Co nucleus due to charge transfer from Co to Cu. In our previous studies on Co-TiO₂ catalysts [4], we observed a shift of Co NMR lines to higher frequencies due to SMSI between cobalt and titania. The conclusion that the shift to high frequencies is a result of charge transfer from cobalt to the support is based on the magnetization results which show a corresponding increase in the magnetic moment of cobalt. Unfortunately, in Cu/Co system, no such easily discernible increase is evident [5]. There lies an inherent ambiguity in the magnetization data. The instrument only measures the magnetic moment per gram sample (emu/g). If the measured moment is greater than what is expected of the sample, for example, greater than 161 emu/g for cobalt loaded samples, one can with certainty conclude that the ferromagnetic character of the sample has changed and that Co charge distribution is leaning towards iron which has one less electron and a magnetic moment of 218 emu/g. On the other hand, if the measured value is less than the maximum possible value, one normally attributes the entire loss to the decrease in the percent reduction of the metal oxide. One cannot distinguish between the contributions to the observed magnetic

NMR SPECTRA OF COBALT IN Cu/Co CATALYSTS

FIG. II



moment from the pure ferromagnetic metal particles and that due to metal particles which might suffer a change in their magnetic character. For example, even if the actual reduction is only 50% due to CuCo_2O_4 spinel formations, the instrument may detect 60% or 40% ferromagnetic metal due to + or - charges in the magnetic character of the metal which could occur as a result of intermetallic interactions. This seems to be the case for Cu/Co magnetization results. Table I clearly shows, that the percent ferromagnetic metal present in the system for catalysts with Cu/Co ratio less than 1 averages about 50%, while it is about 80% in catalysts with Cu/Co > 1. That means, as cobalt content decreases, we are finding more ferromagnetic metal in the system--an obvious paradox! We believe that due to the strong possibility of CuCo_2O_4 type spinel formations which tend to be irreducible, the average reduction achievable in these systems may be only 50%, as shown by the catalysts with Cu/Co < 1. Hence, the 80% metal detected in the Cu/Co > 1 systems might be due to Cu-Co clusters where strong intermetallic interaction is present, and Co charge distribution is modified to yield a higher moment and greater hyperfine field at the Co nuclear site. NMR results unambiguously support this view.(FIG.II).

In the higher alcohol synthesis catalysts, in addition to Cu and Co, there is the third element Cr (Fig. I). The role and function of chromium is not apparent in the sequence of dissociation, association and insertion of syngas reactions with the catalyst for the generation of alcohols [2]. This being the primary objective of this study, a series of nine catalysts were

Table I: MAGNETIZATION DATA Cu-Co CATALYSTS

ROOM TEMPERATURE MEASUREMENTS

SAMPLE	CODE	S(s)	% FERROMAGNETIC METAL
1. Cu/Co=0.2	XU11A	109.0	81%
2. Cu/Co=0.4	XU12A	49.72	43%
3. Cu/Co=0.6	XU13A	35.64	35%
4. Cu/Co=0.8	XU14A	43.12	48%
5. Cu/Co=1.5	XU16	51.16	80%
6. Cu/Co=2.0	XU17	48.10	89%
7. Cu/Co=2.5	XU18	37.61	82%
8. Cu/Co=3.0	XU19	32.11	80%
9. Cu/Co=3.5	XU20	27.71	77%
10. Cu/Co=4.0	XU21	24.80	77%

Table 2: MAGNETIZATION DATA Cu/Co/Cr CATALYSTS

Cu/Co RATIO	Cu/Co/Cr COMPOSITION	CODE	SAT. MAG. S(s)	% METAL FERROMAGNETIC
1. 0.2	10/70/20	GSU3(H)	0.24	0.2
2. 0.3	5/15/80	GSU6(H)	1.31	5.0
3. 0.7	40/55/5	GSU7(H)	2.86	3.0
4. 1.3	40/30/30	GSU8(A)	0.58	1.2
5. 1.7	50/30/20	GSU2(A)	14.49	30.0
6. 3.3	50/15/35	GSU4(A)	12.90	53.0
7. 4.6	70/15/15	GSU5(M)	14.41	60.0
8. 7.0	70/10/20	GSU1(M)	1.08	7.0
9. 8.0	40/5/55	GSU9(M)	0.70	9.0

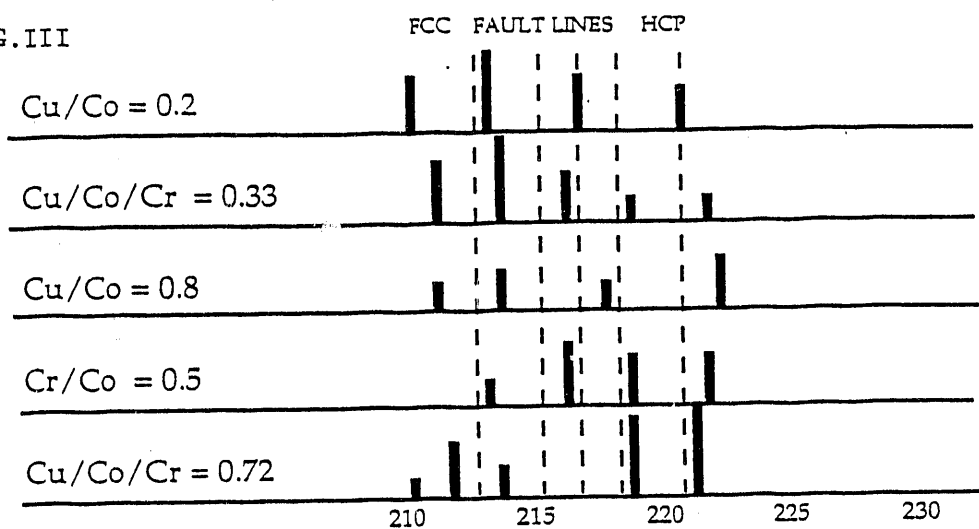
chosen from the selectivity phase diagram (Fig. I) as indicated by ● marks. The selection of the samples is made by keeping the proportion of one element constant while varying the other two so that the selectivity spans the three primary products hydrocarbons, alcohols, and methanols. The results of the magnetization studies on these catalysts are presented in table II. The data is arranged in the order of increasing Cu/Co ratio to discern similarities between Cu/Co and Cu/Co/Cr systems. For $\text{Cu/Co} < 1$, the percent ferromagnetic metal detected is very low indicating that most of the cobalt might be in CuCo_2O_4 or CrCo_2O_4 spinel structures. Then the metal content gradually increases to as high as 50% for catalysts $1.5 < \text{Cu/Co} < 5$ and drops again as Cu/Co increases. Obviously we need a few more measurements to confirm this trend. It seems in the region $1.5 < \text{Cu/Co} < 5$ Cu-Co clusters form with moderate intermetallic interactions between Cu and Co enhancing the Ferromagnetic character of Co. For catalysts with $\text{Co/Co} > 5$, perhaps Cu-Co may form alloy clusters, most of which are not ferromagnetic. Similarly for $\text{Cu/Co} < 1.5$ again, most of the cobalt metal may lie in irreducible spinel structures. These tentative conclusions need to be further verified and confirmed.

Figures III and IV show the NMR spectra for Cu/Co/Cr catalysts with $\text{Cu/Co} < 1$ and $\text{Cu/Co} > 1$. The comparable ratio Cu/Co catalyst spectra without chromium are also presented for comparison.

Fig. III represents the NMR data of the usual hydrocarbon catalysts--cobalt rich systems. As expected, either with or without chromium, the normal cobalt character is preserved in all the catalysts. There seem no significant changes between pure Co,

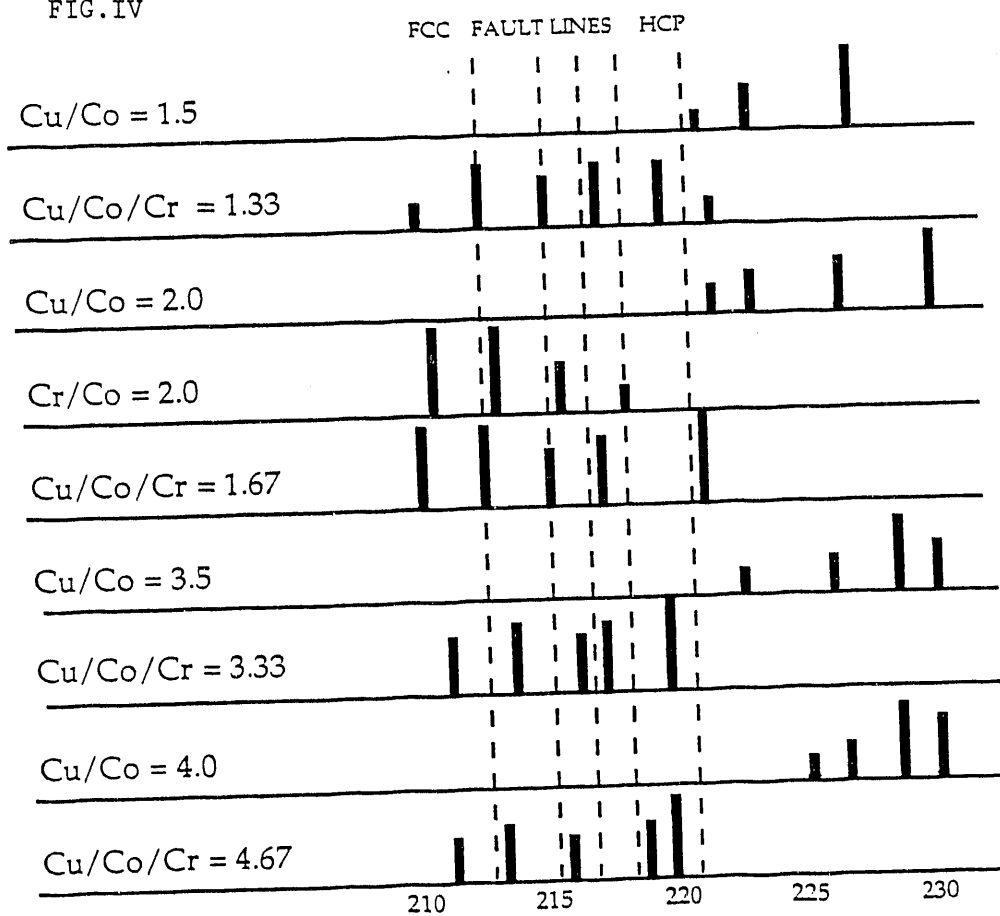
NMR SPECTRA OF COBALT IN Cu/Co/Cr CATALYSTS

FIG. III



NMR SPECTRA OF COBALT IN Cu/Co/Cr CATALYSTS

FIG. IV



Cu/Co and Cu/Co/Cr spectra. On the other hand, Fig. IV, NMR Spectra for catalysts with Cu/Co ratio > 1 , the role of chromium is strikingly evident. In the absence of chromium, NMR spectra appear beyond the normally expected cobalt region 210-221 MHz, indicating the presence of intermetallic interactions in Cu/Co metal clusters. The addition of chromium interestingly seems to eliminate this interaction between Cu and Co, bringing the spectrum back into the normal region. That means Cr in the form of Cr_2O_3 , may be performing the role of a support dispersing Cu/Co atoms. Both the Cu/Co and Cu/Co/Cr catalysts were prepared following the same coprecipitation technique starting with metal nitrates and identical reduction procedures. But the percent metal reduction is in general lower in Cu/Co/Cr catalysts than in Cu/Co catalysts. It is likely that most of the cobalt might be locked in CuCo_2O_4 and CrCo_2O_4 spinels, which might not be easily reducible. A series of catalysts are now being made by Xavier group with titania as support. Comparison of Cu/Co/Cr and Cu/Co/ TiO_2 catalysts may shed more light on the nature of the intermetallic interactions.

Most of these results are presented at the 6th Annual High Tech EXPO meeting (NAFEO) Washington, DC, March 20, 1992, by the participating students. Abstracts of the presented papers are enclosed.

*Abstract
revised.
ds*

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

REFERENCES

1. Courty Ph., D. Durand, E. Freund, and A. Sugier. J. Mol. Catal. 17, 241 (1982)
2. Xiaoding Xu, E.B.M. Doesburg and J.J.F. Scholten. Catalysis Today 2, 125 (1987)
3. Murty A. N., M. A. Akundi, L. Ebanks., and C. Harris "NMR Spectra of Cu-Co bimetallics: Effect of method of preparatoin" 66th annual LA. Acad. Sci. Meeting, BatonRouge, LA. Feb.6-8 (1992)
4. Murty A. N., M. Seamster, A. N. Thorpe, R.T. Obermyer., and V. U. S.Rao J.APPL.Phys. 67, 5847 (1990)
5. Murty A. N. D.O.E. Technical report 12/7/91

**DATE
FILMED**

8/12/92

