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Surface Structure and Analysis With Scanning Tunneling Microscopy and Electron Tunneling Spectroscopy

PROGRESS REPORT

May 1, 1987 - April 30, 1992

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Progress Report

May 1, 1986 - April 30, 1992

Summary of Research

I. Charge-Density Waves in Layer Structures

This grant has been primarily engaged in the development and application of the scanning tunneling microscope (STM) with special emphasis on operation at low temperatures. In the last year we have also been applying atomic force microscopy to a number of surface problems.

The low temperature STMs have been applied with great success to the study of charge-density-waves (CDWs) in transition metal dichalcogenides and trichalcogenides. The STM is able to resolve both the atomic modulation and the longer range charge modulation induced by the CDW. Our research group was the first to report the observation of CDWs with the STM. (Phys. Rev. Lett. 55, 394 (1985)). Following that experiment we extended the operating temperature from 77 to 4.2 K and have imaged the CDW structure in at least ten different layer structure dichalcogenides. These have a wide range of CDW structures and transition temperatures and the STM imaging has confirmed the systematic response expected for the various types of CDWs. However, the STM amplitude measured for the strong CDW phases such as 1T-TaSe₂ and 1T-TaS₂ has been anomalously large and the source of this enhanced amplitude is still under study. A complete review of all the layer structure work is published in Advances in Physics, 37 599-644 (1988). Copy attached. The materials studied are listed in Table I from the Advances in Physics volume.

II. Charge-Density Waves in Linear Chain Compounds

In the linear chain transition metal trichalcogenides the CDW structures are rather complex. In NbSe₃ two CDW transitions exist with onset temperatures of 144 and 59 K. We have successfully imaged both the chain structure and the CDW modulation due to both CDWs. At 77 K the high temperature CDW has been imaged and at 4.2 K both CDWs have been separately resolved. The STM scans at 4.2 K show that all three pairs of chains participate in the CDW formation contrary to the

previous analysis from other investigations. The high resolution STM results showing complete resolution of the CDW structure at 4.2 K has been published in Phys. Rev. Lett. 66, 1318 (1991).

STM scanning on TaS₃ has shown phase correlated CDW modulation on two of the three surface chains. The result has confirmed the theoretical conjecture by Wang et al¹ that the initial incommensurate CDW on one chain induces a CDW on the second chain. This work was published as a Rapid Communication in Phys. Rev. B 40, 8042 (1989).

III. Spectroscopy With the STM

We have used the STM for successful measurements of energy gaps in a wide range of layer compounds and in a high temperature superconductor. This work represents the first major systematic measurement of CDW energy gaps in the layer compounds and has been published in Phys. Rev. B 42, 8890 (1990).

Very successful energy gap data has been obtained on NbSe₃ and NbSe₃ doped with impurities such as Fe, Co, and Ni. We have shown that impurities modify the CDW energy gaps by large amounts. For example Fe concentrations in the range 0.01 to 0.10% reduce both CDW gaps by ~ 25-30%. These observations are being correlated with STM scanning measurements of CDW amplitudes. These results require major theoretical analysis of the impurity effects on CDW structure and further systematic measurement of these large gap shifts continue. The initial results are being presented at the "First International Symposium on Atomically Controlled Surfaces and Interfaces" and will be published in Applied Surface Science.

IV. STM Studies of Oxides

We have started a series of studies on the various stages of oxide formation on metal surfaces. FeO_x has proven to be an excellent oxide for study by STM. The effective tunnel barrier remains extremely low (0.008-0.012 meV) and the STM can operate over a very large range of oxide film thickness. The STM images for thick oxide films reflect the internal oriented structure of the oxide film. Such images can be combined with AFM scans which show only the surface structure. These

results have been described in the current progress report (May 1, 1991 to April 30, 1992). (DOE-ER45072-45).

V. Development of Atomic Force Microscopy (AFM).

We have purchased a Nanoscope II AFM under a DOE University Instrumentation Grant. The AFM has been applied to some of the first measurements of CDW structure in layer compounds. The AFM resolves the CDW structure, but the amplitude response is much less than observed with the STM while the atomic structure is better resolved. The first results on CDW structure observed with the AFM has been published as a Rapid Communication in Phys. Rev. B 9255 (1990).

The AFM is being applied to oxide films such as FeO_x , AlO_x and CuO_x as well as other insulating materials such as AgBr, AgCl, KCl and other ionic crystals. These applications have just been started.

VI. Publications

The publications as listed in the last six progress reports are listed below.

TABLE I.

3. STM of 1T Phase Layer Structure Crystals	8
3.1 1T-TaSe ₂ and 1T-TaS ₂	8
3.11 1T-TaSe ₂	9
3.12 1T-TaS ₂	11
3.13 CDW Domain Structure and the Commensurate to Incommensurate Transition in 1T-TaS ₂	13
3.2 1T-TiSe ₂ and 1T-TiS ₂	16
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3.22 1T-TiS ₂	19
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4. STM of 2H Phase Layer Structure Crystals	22
4.1 2H-NbSe ₂	23
4.2 2H-TaSe ₂	25
4.3 2H-TaS ₂	26
5. STM of 4Hb Phase Compounds	28
5.1 4Hb-TaS ₂	28
5.2 4Hb-TaSe ₂	30
6. STM of NbSe ₃	32
6.1 STM Scans of NbSe ₃ at 77K	32
6.11 Atomic Structure of the NbSe ₃ Surface	33
6.12 CDW Modulation in NbSe ₃ at 77K	34
7. Electronic Structure and STM Response of Group V Layer Structure Dichalcogenides	35
7.1 Profiles and Electronic Structure of 1T Phase Crystals	36
7.11 1T-TaS ₂	37
7.12 1T-TaSe ₂	39
7.13 1T-VSe ₂	40

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7.21 Nodal Structure Generated by CDW Formation	41
7.22 Corrugation Enhancement Due to the Tip-Surface Interaction Potential	42
7.23 Atom Scattering Measurement of Surface Corrugation	43
7.3 Profiles and Electronic Structure of the 4Hb Phase Crystals	44
7.31 4Hb-TaS ₂	44
7.32 4Hb-TaSe ₂	46
7.4 Profiles and Electronic Structure of 2H Phase Crystals	47
7.41 2H-TaSe ₂	48
7.42 2H-TaS ₂	51
7.43 2H-NbSe ₂	52
8. Electronic Structure and STM Response of Group IV Layer	
Structure Dichalcogenides	53
8.1 1T-TiSe ₂	54
8.2 1T-TiS ₂	56

II. Publications - 1987-88

1. "Applications of Scanning Tunneling Microscopy to the Study of Charge Density Waves", R. V. Coleman, B. Drake, B. Giambattista, A. Johnson, P. K. Hansma, W. W. McNairy and G. Slough, *Physica Scripta* 36, Dec. (1987) (DOE - ER45072-26).
2. "Detection of Atomic Structure on NbSe₂ and NbSe₃ at 77 and 4.2K Using Scanning Tunneling Microscopy", R. V. Coleman, B. Giambattista, A. Johnson, W. W. McNairy, G. Slough, P. K. Hansma and B. Drake, *Journ. Vac. Science and Technology*, March 1988. (DOE-ER45072-27).
3. "Charge Density Waves Observed at 4.2K by Scanning Tunneling Microscopy", B. Giambattista, A. Johnson, R. V. Coleman, B. Drake and P. K. Hansma, *Phys. Rev. B Rapid Communications* (accepted) (DOE-ER45072-28).
4. "Scanning Tunneling Microscopy of 1T-TiSe₂ and 1T-TiS₂ at 77 and 4.2K", C. G. Slough, B. Giambattista, A. Johnson, W. W. McNairy, C. Wang and R. V. Coleman, *Phys. Rev. B. Rapid Communications*, (submitted) (DOE - ER45072-29).

Reprint of Publication Previously Reported

1. Reprint of DOE-ER45072-23 Reported in 1987
"Images of Charge-Density Waves Obtained With Scanning Tunneling Microscopy," R. V. Coleman, W. W. McNairy, C. G. Slough, P. K. Hansma and B. Drake, *Surface Science* 181, 112 (1987).

II. Publications - 1988-89

A. Publications Prepared During Current Grant Period

1. "Scanning Tunneling Microscopy of Charge-Density-Waves in transition Metal Chalcogenides", R.V. Coleman, B. Giambattista, P.K. Hansma, A. Johnson, W.W. McNairy and C.G. Slough, to be published in "Advances in Physics" 1989. (DOE-ER45072-30).
2. "Correlation of Scanning Tunneling Microscope Image Profiles and Charge-Density-Wave Amplitudes", B. Giambattista, A. Johnson, W.W. McNairy, C.G. Slough and R.V. Coleman, Phys. Rev. B 38, 3545 (1988)(DOE-ER45072-31).
3. "Scanning Tunneling Microscopy of Charge-Density-Waves in NbSe₃", C.G. Slough, B. Giambattista, A. Johnson, W.W. McNairy and R.V. Coleman, submitted to Physical Review Letters. (DOW-ER45072-32).
4. "Scanning Tunneling Microscopy of Atoms and Charge-Density-Waves in 1T-TaS₂, 1T-TaSe₂ and 1T-VSe₂", B. Giambattista, C.G. Slough, W.W. McNairy and R.V. Coleman, submitted to Physical Review B (DOE-ER45072-33).

B. Reprints of Publications Previously Reported

1. Reprint of (DOE-ER45072-26)
"Applications of Scanning Tunneling Microscopy to the Study of Charge-Density-Waves", R.V. Coleman, B. Drake, B. Giambattista, A. Johnson, P.K. Hansma, W.W. McNairy and C.G. Slough, Physica Scripta 38, 235-243, 1988.
2. Reprint of (DOE-ER45072-29)
"Scanning Tunneling Microscopy of 1T-TiSe₂ and 1T-TiS₂ at 77 and 4.2 K", C.G. Slough, B. Giambattista, A. Johnson, W.W. McNairy, C. Wang and R.V. Coleman, Phys. Rev. B 37, 6571 (1988).
3. Reprint of (DOE-ER45072-28)
"Charge-Density-Waves Observed at 4.2 K by Scanning Tunneling Microscopy", B. Giambattista, A. Johnson, R.V. Coleman, B. Drake and P.K. Hansma, Phys. Rev. B 27, 2741 (1988).

Publications - 1989-90

I. Preprints and Reprints of Publications Prepared During Current Grant Period

1. "Scanning Tunneling Microscopy of Orthorhombic TaS_3 ," C.G. Slough and R.V. Coleman, Phys. Rev. B 40, 8042 (1989) (DOE-ER45072-36).
2. "Scanning Tunneling Microscopy of the Linear Chain Compounds NbSe_3 , TaS_3 and TaSe_3 ," Journ. Vacuum Science and Technology, to be published (DOE-ER45072-37).
3. "Energy Gaps Measured by Scanning Tunneling Microscopy," Chen Wang, B. Giambattista, C.G. Slough and R.V. Coleman, submitted to Phys. Rev. B (DOE-ER45072-38).

II. Reprints of Articles Previously Published

1. "Scanning Tunneling Microscopy of Charge-Density Waves in Transition Metal Chalcogenides," R.V. Coleman, B. Giambattista, P.K. Hansma, A. Johnson, W.W. McNairy and C.G. Slough, Advances in Physics 37, 559-644 (1988). (DOE-ER45072-30).
2. "Scanning Tunneling Microscopy of Charge-Density Waves in NbSe_3 ," C.G. Slough, B. Giambattista, A. Johnson, W.W. McNairy, and R.V. Coleman, Phys. Rev. B 39, 5496 (1989). (DOE-ER45072-32).

III. Ph.D. Degrees Awarded

Brian Giambattista, "Scanning Tunneling Microscopy of Atoms and Charge-Density Waves in Transition Metal Chalcogenides at 4.2 K."

Ph.D. Awarded June 1989

IV. Papers Presented at Conferences

1. Gordon Conference on the Phenomenology of High Temperature Superconductors, Invited June 1989
"Tunneling Measurements of Energy Gaps in High Temperature Superconductors"
2. STM '89 Oarai, Japan July 1989
"Scanning Tunneling Microscopy of the Linear Chain Compounds NbSe_3 , TaS_3 and TaSe_3 ."
3. American Physical Society
Anaheim, CA March 1990
"STM Measurements of Energy Gaps in CDW Compounds and Superconductors" (See Abstract Attached).
4. American Physical Society
Anaheim, CA March 1990
"STM Observations of Commensurate and Incommensurate CDWs in 1T Phase Layer Structure Dichalcogenides" (See Abstract Attached).

II. Publications - 1990-91

A. Publications Prepared During Current Grant Period

1. "Atomic Force Microscopy and Scanning Tunneling Microscopy of Charge-Density Waves in IT-TaSe₂ and IT-TaS₂", Phys. Rev. B, 9255 (1990). (DOE-ER45072-40).
2. "Spectroscopy of Dichalcogenides and Trichalcogenides Using Scanning Tunneling Microscopy", Journ. Vac. Science and Technology, to be published (DOE-ER45072-41).
3. "Long Range Modulation of the Charge-Density Wave Structure in IT-TaS₂ Studied by Scanning Tunneling Microscopy", Journ. Vac. Science and Technology, to be published (DOE-ER45072-42).
4. "Atomic Force Microscopy of Charge-Density Waves and Atoms on IT-TaSe₂, IT-TaS₂, IT-TiSe₂ and 2H-NbSe₂", to be published Journ. Vac. Science and Technology, (DOE-ER45072-43).
5. "Charge-Density Wave Structure in NbSe₃ Determined by Scanning Tunneling Microscopy", Submitted to Phys. Rev. Lett. (DOE-ER45072-44).

B. Reprints of previously prepared Articles Published During Current Year.

1. "Energy Gaps Measured by Scanning Tunneling Microscopy", Phys. Rev. B, 8890 (1990). (DOE-ER45072-38).
2. "Scanning Tunneling Microscopy of the Linear Chain Compounds NbSe₃, TaS₃, and TaSe₃", Journ. Vac. Science and Technology, 8, 490 (1990). (DOE-ER4507-37).

III. Ph.D. Degrees Awarded

C. Gray Slough, "Scanning Tunneling Microscopy of Charge-Density Waves at 77K."

Ph.D. Awarded August 1990.

IV. Papers Presented at Conferences

1. STM '90/NANOI, Baltimore, MA, July 1990.
"Spectroscopy of Dichalcogenides and Trichalcogenides Using Scanning Tunneling Microscopy".
2. STM '90/NANOI, Baltimore, MA, July 1990.
"Long Range Modulation of the Charge-Density Wave Structure in IT-TaS₂ Studied by Scanning Tunneling Microscopy."
3. STM '90/NANOI, Baltimore, MA, July 1990.
"Atomic Force Microscopy of Charge-Density Waves and Atoms on IT-TaSe₂, IT-TaS₂, IT-TiSe₂, and 2H-NbSe₂".

I. Publications - 1991-92

A. Reprints of Articles Published During Current Grant Year

1. "Atomic Force Microscopy and Scanning Tunneling Microscopy of Charge-Density Waves in IT-TaSe₂", Phys. Rev. B, 9255 (1990). (DOE-ER45072-40).
2. "Spectroscopy of Dichalcogenides and Trichalcogenides Using Scanning Tunneling Microscopy", Journ. Vac. Science and Technology, 2, 1048 (1991).
3. "Long Range Modulation of the Charge-Density Wave Structure in IT-TaS₂ Studied by Scanning Tunneling Microscopy", Journ. Vac. Science and Technology, 2, 490 (1991), (DOE-ER45072-42).
4. "Atomic Force Microscopy of Charge-Density Waves and Atoms on IT-TaSe₂, IT-TaS₂, IT-TiSe₂ and 2H-NbSe₂", Journ. Vac. Science and Technology, 2, 1032 (1991), (DOE-ER45072-43).
5. "Charge-Density Wave Structure in NbSe₃ Determined by Scanning Tunneling Microscopy", Phys. Rev. Lett. 66, 1318 (1991), (DOE-ER45072-44).

B. Publications Prepared During Current Grant Period

1. "Amplitude Modulation of Charge-Density-Wave Domains in IT-TaS₂ at 300 K", R.V. Coleman, W.W. McNairy, and C.G. Slough, Phys. Rev. B, to be published, (DOE-ER45072-46).
2. "STM and AFM of Layer Structure Crystals", R.V. Coleman, Zhenxi Dai, W.W. McNairy, C.G. Slough, and Chen Wang" to be published as a chapter in a book on layer compounds (Published by Kluwer) (DOE-ER45072-47).
3. "Charge-Density-Waves by STM", R.V. Coleman, Zhenxi Dai, W.W. McNairy, C.G. Slough and Chen Wang to be published as a chapter in a book on STM, (published by Academic Press). (DOE-ER45072-48).

II. Papers Presented at Conference

1. "Surface Structure of Charge-Density-Wave Materials Using Scanning Tunneling Microscopy", R.V. Coleman, Zhenxi Dai, W.W. McNairy, C.G. Slough and Chen Wang, to be presented at "First International Symposium on Atomically Controlled Surfaces and Interfaces", University of Tokyo, Tokyo Japan, Nov. 19-22, 1991. (Abstract attached).

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