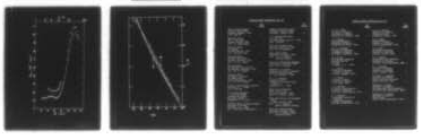
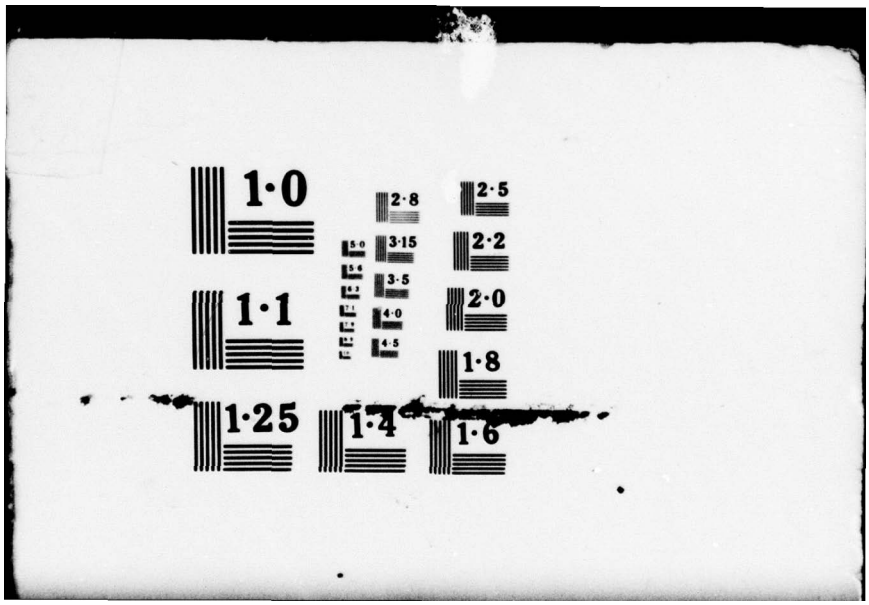
AD-A065 191 VERMONT UNIV BURLINGTON DEPT OF CHEMISTRY F/G 7/3
THE EFFECT OF INTERCLUSTER INTERACTIONS ON THE THERMAL AND MAGN--ETC(U)
JAN 79 J T WROBLESKI, C T DZIOBKOWSKI N00014-75-C-0756
UNCLASSIFIED TR-13 NL

| OF |
ADA
065191



END
DATE FILMED
4-79
DDC


1·0
1·1
1·25
1·4
1·6
1·8
2·0
2·2
2·5
2·8
3·15
3·5
4·0
4·5

OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0756

Task No. NR 356-593

TECHNICAL REPORT NO. 13

The Effect of Intercluster Interactions on the Thermal and Magnetic Properties of $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl\cdot 6H_2O$

by

James T. Wrobleski, Chester T. Dziobkowski, and David B. Brown

Submitted for publication

Physical Review Letters

University of Vermont

Department of Chemistry

Burlington, Vermont 05405

January 17, 1979

DISCLAIMER NOTICE

THIS DOCUMENT IS BEST QUALITY PRACTICABLE. THE COPY FURNISHED TO DDC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: 13 (14) TR-13
2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle): (6) The Effect of Intercluster Interactions on the Thermal and Magnetic Properties of $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl \cdot 6H_2O$
5. TYPE OF REPORT & PERIOD COVERED: (9) Technical Report
6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s): (10) James T. Wrobleski, Chester T. Dziobkowski, and David B. Brown
8. CONTRACT OR GRANT NUMBER(s): (15) N00014-75-C-0756

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Department of Chemistry
University of Vermont
Burlington, Vermont 05405
408 892
10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: (11) 17 Jan 79

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research
Department of the Navy
Arlington, Virginia 22217
12. REPORT DATE: January 17, 1979
13. NUMBER OF PAGES: 10

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): (12) 15 p.
15. SECURITY CLASS. (of this report): Unclassified
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release and sale; its distribution is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Submitted for publication in Physical Review Letters

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Heat capacity, magnetism, acetate complexes, trimers, intercluster exchange

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Inclusion in the hamiltonian of a perturbing term which describes the pairwise spin exchange between $[Cr_3O(CH_3COO)_6(H_2O)_3]^+$ equilateral triangular clusters in $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl \cdot 6H_2O$ splits the unperturbed ground state into two nondegenerate Kramers doublets. The effect of this splitting is to introduce a Schottky type anomaly in the theoretical heat capacity curve. →over

1473

408 892

Excellent agreement between experimental and theoretical heat capacities is found when two crystallographically inequivalent pairs of equilateral trimer sites with different intercluster exchange parameters are assumed. Low-temperature magnetic susceptibility data for this complex are well reproduced by using the parameters which are obtained from the heat capacity data.

The Effect of Intercluster Interactions on the Thermal and Magnetic Properties of $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl\cdot 6H_2O$

James T. Wrobleski, Chester T. Dziobkowski, and David B. Brown
Department of Chemistry, University of Vermont, Burlington, Vermont 05405

Inclusion in the hamiltonian of a perturbing term which describes the pairwise spin exchange between $[Cr_3O(CH_3COO)_6(H_2O)_3]^+$ equilateral triangular clusters in $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl\cdot 6H_2O$ splits the unperturbed ground state into two nondegenerate Kramers doublets. The effect of this splitting is to introduce a Schottky type anomaly in the theoretical heat capacity curve. Excellent agreement between experimental and theoretical heat capacities is found when two crystallographically inequivalent pairs of equilateral trimer sites with different intercluster exchange parameters are assumed. Low-temperature magnetic susceptibility data for this complex are well reproduced by using the parameters which are obtained from the heat capacity data.

Previous theoretical models[1-6] proposed to account for the low-temperature thermal and magnetic susceptibility behavior of $[Cr_3O(CH_3COO)_6(H_2O)_3]C\ell \cdot 6H_2O$ are based on physically unsubstantiated assumptions. These assumptions derive from a necessity to lift the degeneracy of the two Kramers doublets which comprise the ground spin level. Although the $\underline{C_{2v}}$ (isosceles triangle) model of Kambe which is given by

$$\underline{H} = \underline{J}_0(\underline{S}_1 \cdot \underline{S}_2 + \underline{S}_1 \cdot \underline{S}_3) + \underline{J}_1(\underline{S}_2 \cdot \underline{S}_3), \qquad (1)$$

where $\underline{S}_1$, $\underline{S}_2$, and $\underline{S}_3$ are spin operators, describes the low-temperature heat capacity data for this compound, direct evidence for a structurally-distorted Cr_3O cluster is not available. Furthermore, this model cannot simultaneously describe the magnetic susceptibility and heat capacity data for this compound. Alternatively Mishima and Uryu[6] have recently calculated the magnetic heat capacity for this material based on the Dzyaloshinskii-Moriya exchange interaction given by

$$\underline{H} = \frac{\underline{iD}}{2} \sum_{\underline{ij}} (\underline{S}_{\underline{i}}^{+} \underline{S}_{\underline{j}}^{-} - \underline{S}_{\underline{i}}^{-} \underline{S}_{\underline{j}}^{+}). \qquad (2)$$

This "antisymmetric" exchange hamiltonian splits the ground state as required but fails to describe the magnetic heat capacity data of the chromium acetate complex. In actuality the Dzyaloshinskii-Moriya exchange interaction also requires a structurally-distorted Cr_3O cluster in order that $|\underline{D}| \neq 0$. Finally, Uryu and Friedberg[4] have calculated the magnetic susceptibility and heat capacity functions derived from an axial crystal field model given by

$$\underline{H} = \underline{H}_0 + \sum_{\underline{i}=1}^{3} \underline{D}_i[(S_i \underline{i})^2 - 1/3\ \underline{S}_i(\underline{S}_i+1)], \qquad (3)$$

where $\underline{H}_o = \underline{J}_o(\underline{S}_1\cdot\underline{S}_2+\underline{S}_2\cdot\underline{S}_3+\underline{S}_3\cdot\underline{S}_1)$. In the same paper[4] they also investigated the effect of inclusion in the hamiltonian of higher spin coupling terms given by

$$\underline{H} = \underline{H}_o+\underline{J}'[(\underline{S}_1\cdot\underline{S}_2)(\underline{S}_2\cdot\underline{S}_3)+(\underline{S}_2\cdot\underline{S}_3)(\underline{S}_3\cdot\underline{S}_1)+(\underline{S}_3\cdot\underline{S}_1)(\underline{S}_1\cdot\underline{S}_2)]. \qquad (4)$$

Whereas Eq. (3) is not a satisfactory description of the thermal and magnetic data for the chromium acetate complex, Eq. (4) is Hermitian only if an additional term of the type

$$\underline{J}'[(\underline{S}_3\cdot\underline{S}_2)(\underline{S}_2\cdot\underline{S}_1)+(\underline{S}_1\cdot\underline{S}_3)(\underline{S}_3\cdot\underline{S}_2)+(\underline{S}_2\cdot\underline{S}_1)(\underline{S}_1\cdot\underline{S}_3)] \qquad (5)$$

is added to Eq. (4).[7] The effect of this additional term is to restore the degeneracy of the two Kramers ground state doublets.[5]

In view of the apparent failure of the above models to describe the properties of the chromium acetate trimer and because of our initial success in modeling the low-temperature magnetic susceptibility data for similar Fe(III) trimers[8] with an intercluster spin exchange model, we felt it would be appropriate to consider the possible influence of such a model on the properties of the chromium compound. We took as our hamiltonian

$$\underline{H} = \underline{J}_0(\underline{S}_1\cdot\underline{S}_2+\underline{S}_2\cdot\underline{S}_3+\underline{S}_3\cdot\underline{S}_1)+\underline{j}(\underline{S}_A\cdot\underline{S}_B), \qquad (6)$$

where $\underline{S}_A$ and $\underline{S}_B$ are spin operators which couple cluster A with cluster B. Basis spin levels $\underline{S}_{iA}$ and $\underline{S}_{iB}$ were assumed to be the unperturbed spin vectors of the individual trimeric Cr_3O clusters. This analysis results in a 128-fold degenerate six-spin problem.

The effect of the hamiltonian given by Eq. (6) is to split the ground state into two Kramers doublets separated by 2j. The first unperturbed excited state is split into four spin levels with 12j total separation. Although only the lowest few of the 30 spin levels which result from Eq. (6) contribute to the low temperature limiting form of the appropriate partition function, we found it no less convenient to include all levels in the ensuing calculations.

Heat capacities for $[Cr_3O(CH_3COO)_6(H_2O)_3]C\ell \cdot 6H_2O$ obtained by Sorai et al.[5] and by Wucher and Wasscher[2] were independently fit to the heat capacity expression for Eq. (6). Because there is substantial disagreement between the two data sets we have chosen the more complete set of Sorai et al. to serve as a more critical test of our model than the limited set of Wucher and Wasscher. Lattice heat corrections were applied to the experimental $\underline{C}_{\underline{V}}$ as

$$\underline{C}_{\underline{V}}^{D} = 523.9718 \underline{x}_0^{-3} \int_0^{\underline{x}_0} [\underline{x}^4 \underline{e}^{\underline{x}} / (\underline{e}^{\underline{x}} - 1)^2] d\underline{x} \qquad (7)$$

for the Debye heat capacity, where $\underline{x}_o = 120/T$,[2] and

$$\underline{C}_{\underline{V}}^{E} = 54 \underline{R}\ \underline{y}_0^2\ [\underline{e}^{\underline{y}_o} / \underline{e}^{\underline{y}_o} - 1)^2] \qquad (8)$$

for the Einstein heat capacity, where $\underline{y}_o = 270/\underline{T}$ and $\underline{R}$ is the gas constant. The magnetic heat capacity, $\underline{C}_{\underline{m}}$, was obtained as

$$\underline{C}_{\underline{m}}(\text{obsd}) = \underline{C}_{\underline{p}}(\text{obsd}) - \underline{C}_{\underline{V}}^{D} - \underline{C}_{\underline{V}}^{E} . \qquad (9)$$

The experimental values of $\underline{C}_{\underline{m}}$ were fit to Eq. (6) by using the Simplex optimization algorithm.[9] Figure 1 compares the data

of Sorai et al.[5] (open circles) and Wucher and Wasser[2] (full circles) with best fit curves calculated by Eq. (6). In order to adequately describe the low-temperature heat capacity data of Sorai et al. it was necessary to consider the presence of two different equilateral Cr_3O trimer sites having distinct values of $\underline{j}$. A distribution function of the type

$$\underline{C_m}\ (\text{calcd}) = \underline{zC_m}(\underline{J_o},\underline{j_1})+(1-\underline{z})\underline{C_m}(\underline{J_o},\underline{j_2}) \qquad (10)$$

was employed. Parameters $\underline{J}o = -35\underline{k}$, $j_1 = +0.9\underline{k}$, $\underline{j_2} = +3.6\underline{k}$, and $\underline{Z}=0.80$, where $\underline{k}$ is Boltzman's constant, were obtained for the 1-6K data of Sorai et al. The $\underline{C_m}$ curve calculated with these values is shown in Fig. 1. Data of Wucher and Wasscher were well described with $\underline{J_o}=-44\underline{k}$, $j_1=+1.5\underline{k}$, $\underline{j_2}=0.0\underline{k}$, and $\underline{Z}=1.0$.

In order to test the validity of these parameters, the magnetic susceptibility data of Schriempf and Friedberg[3] were modeled with parameters obtained from fitting the heat capacity data of Sorai et al. Results of this calculation are shown in Fig. 2. The experimental susceptibilities are reproducible to $\pm$3%, an accuracy within the quoted experimental uncertainty.[3]

The mechanism for intercluster spin exchange is undoubtedly associated with the hydrogen bonding between trimer centers. The hydrogen bonding network in crystals of $[Cr_3O(CH_3COO)_6(H_2O)_3]$ $C\ell\cdot 6H_2O$ involves carboxyl oxygens, lattice water molecules and chloride ions.[10] Because of the observed[10] room-temperature disorder of the lattice water and halide sites we would anticipate several possible types of intertrimer spin-exchange pathways in this material. It is however, not possible to make an <u>a priori</u>

statement about the number and magnitude of these pathways based on current data. A finite value of z however indicates that two or more intercluster exchange pathways are available at low temperatures in this material.

We believe that the intercluster model proposed above provides a physically realistic basis for understanding the properties of numerous similar cluster compounds. We propose that such a model be applied as a perturbation to the normal Heisenberg spin exchange model in those cases in which models such as Eqs. (1) - (4) are not substantiated by direct physical measurements.

References

1. J. Wucher and H.M. Gijsman, Physica, 20, 361 (1954).

2. J. Wucher and J.D. Wasscher, Physica, 20, 721 (1954).

3. J.T. Schriempf and S.A. Friedberg, J. Chem. Phys., 40, 296, (1964).

4. N. Uryû and S.A. Friedberg, Phys. Rev. A, 140, 1803 (1965).

5. M. Sorai, M. Tachiki, H. Suga, and S. Seki, J. Phys. Soc. Jpn. 30, 750 (1971).

6. M. Mishima and N. Uryû, Phys. Lett. A, 67,64 (1978).

7. Quoted from reference 5 as a personal communication from Dr. P. Kislius.

8. C.T. Dziobkowski, J.T. Wrobleski, and D.B. Brown, Inorg. Chem., in preparation. A preliminary account of the Fe(III) work has appeared: C.T. Dziobkowski, J.T. Wrobleski, and D.B. Brown, Abstracts of Papers, 8th Northeast Regional ACS Meeting, #INOR 17, 1978.

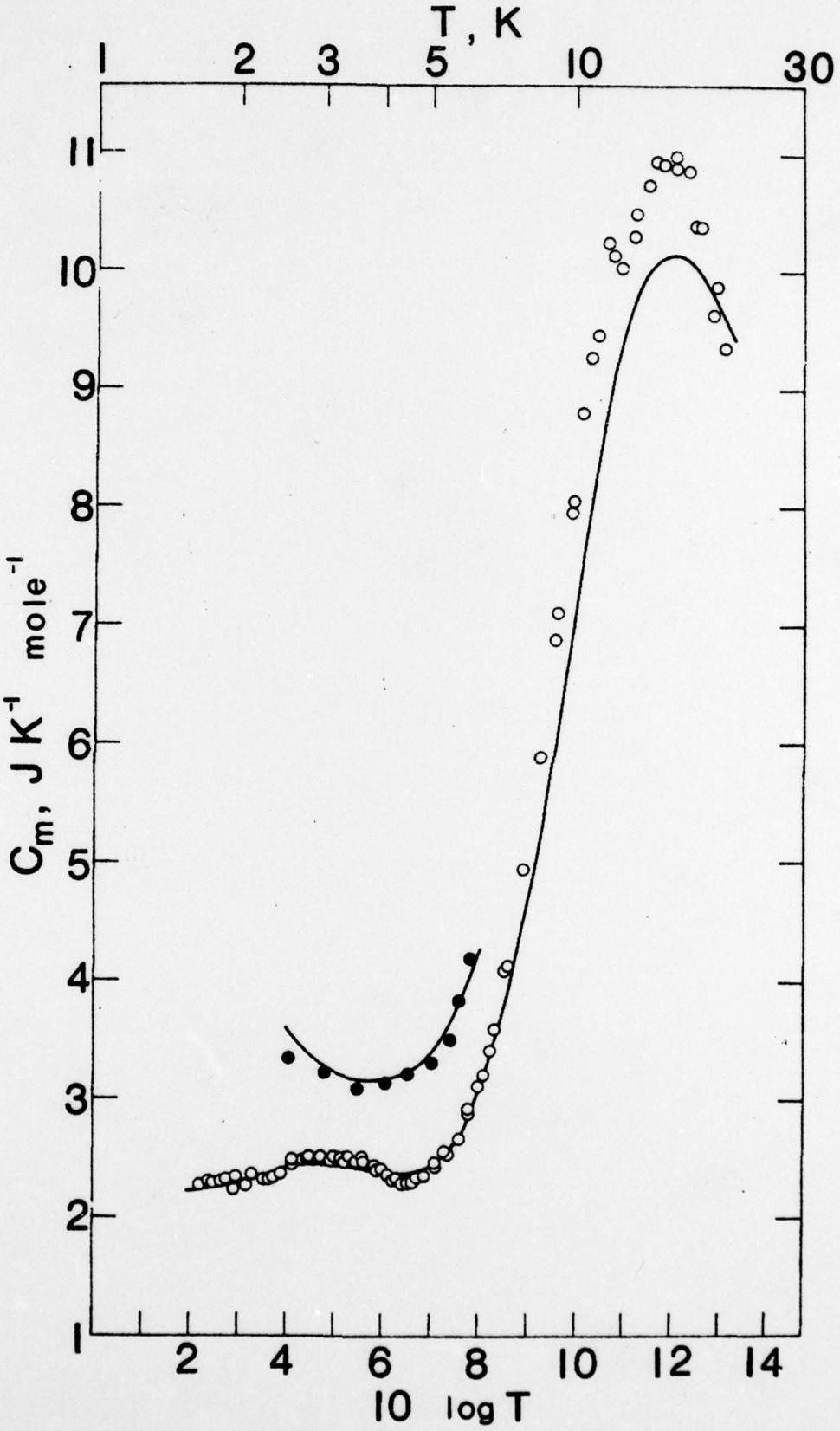
9. S.N. Deming and S.L. Morgan, Anal. Chem., 45, 278A (1973) and references therein.

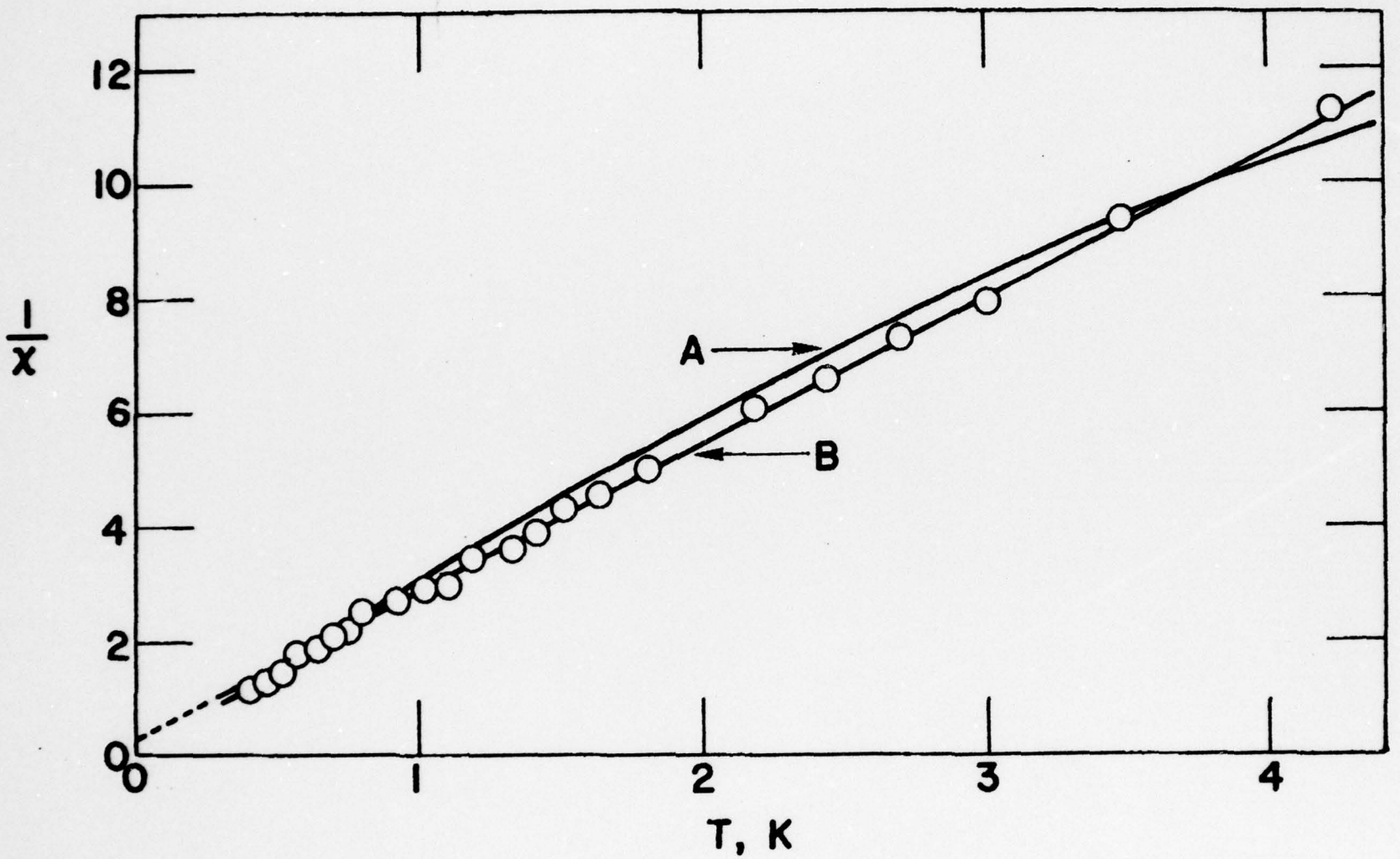
10. S.C. Chang and G.A. Jeffrey, Acta Cryst. B, 26, 673 (1970).

Figure Captions

Fig. 1. Magnetic heat capacity of $[Cr_3O(CH_3COO)_6(H_2O)]Cl \cdot 6H_2O$ versus 10 log T. Data of Sorai et al.[5] (O) fit to curve A with parameters given in the text. Data of Wucher and Wasshcer[2] (●) fit to curve B with parameters given in the text.

Fig. 2. Reciprocal magnetic susceptibility versus T.[3] The smooth curve A represents the intercluster fit with parameters given in the text. Curve B represents the Curie-Weiss law fit with C = 0.393 and Θ = -0.13K.


T, K
1
2
3
5
10
30
11
10
9
8
7
6
5
4
3
2
1
C_m, J K^{-1} $mole^{-1}$
2
4
6
8
10
12
14
10 log T


12
10
8
6
4
2
0
0
1
2
3
4
1/χ
T, K
A
B

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217 Attn: Code 472	2
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. George Sandoz	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1
ONR Area Office One Hallidie Plaza, Suite 601 San Francisco, California 94102 Attn: Dr. P. A. Miller	1
ONR Branch Office Building 114, Section D 666 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1
Director, Naval Research Laboratory Washington, D. C. 20390 Attn: Code 6100	1
The Assistant Secretary of the Navy (R,E&S) Department of the Navy Room 4E736, Pentagon Washington, D. C. 20350	1
Commander, Naval Air Systems Command Department of the Navy Washington, D. C. 20360 Attn: Code 310C (H. Rosenwasser)	1
Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
U. S. Army Research Office P. O. Box 1211 Research Triangle Park, N.C. 27709 Attn: CRD-AA-IP	1
Naval Ocean Systems Center San Diego, California 92152 Attn: Mr. Joe McCartney	1
Naval Weapons Center China Lake, California 93555 Attn: Dr. A. B. Amster Chemistry Division	1
Naval Civil Engineering Laboratory Port Hueneme, California 93401 Attn: Dr. R. W. Drisko	1
Professor K. E. Woehler Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D. C. 20380	1
Office of Naval Research 800 N. Quincy Street Arlington, Virginia 22217 Attn: Dr. Richard S. Miller	1
Naval Ship Research and Development Center Annapolis, Maryland 21401 Attn: Dr. G. Bosmajian Applied Chemistry Division	1
Naval Ocean Systems Center San Diego, California 91232 Attn: Dr. S. Yamamoto, Marine Sciences Division	1

TECHNICAL REPORT DISTRIBUTION LIST, 053

	No. Copies
Dr. R. N. Grimes University of Virginia Department of Chemistry Charlottsville, Virginia 22901	1
Dr. M. Tsutsui Texas A&M University Department of Chemistry College Station, Texas 77843	1
Dr. M. F. Hawthorne University of California Department of Chemistry Los Angeles, California 90024	1
Dr. W. B. Fox Naval Research Laboratory Chemistry Division Code 6130 Washington, D. C. 20375	1
Dr. J. Adcock University of Tennessee Department of Chemistry Knoxville, Tennessee 37916	1
Dr. A. Cowley University of Texas Department of Chemistry Austin, Texas 78712	1
Dr. W. Hatfield University of North Carolina Department of Chemistry Chapel Hill, North Carolina 27514	1
Dr. D. Seyferth Massachusetts Institute of Technology Department of Chemistry Cambridge, Massachusetts 02139	1
Dr. M. H. Chisholm Department of Chemistry Indiana University Bloomington, Indiana 47401	1
Dr. B. Foxman Brandeis University Department of Chemistry Waltham, Massachusetts 02154	1
Dr. T. Marks Northwestern University Department of Chemistry Evanston, Illinois 60201	1
Dr. G. Geoffrey Pennsylvania State University Department of Chemistry University Park, Pennsylvania 16802	1
Dr. J. Zuckerman University of Oklahoma Department of Chemistry Norman, Oklahoma 73019	1
Professor O. T. Beachley Department of Chemistry State University of New York Buffalo, New York 14214	1
Professor P. S. Skell Department of Chemistry The Pennsylvania State University University Park, Pennsylvania 16802	1
Professor K. M. Nicholas Department of Chemistry Boston College Chestnut Hill, Massachusetts 02167	1