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Crystal Structures of V_3S_4 and V_5S_8

ISAO KAWADA, MITSUKO NAKANO-ONODA, MOTOHIKO ISHII, MASANOBU SAEKI

National Institute for Researches in Inorganic Materials, Kurakake, Sakura-mura, Niihari-gun, Ibaraki 300-31, Japan

AND

MITSUOKI NAKAHIRA

Okayama College of Science, Laboratory for Solid State Chemistry 1–1, Ridai-cho, Okayama 700, Japan

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Crystal structures of the ordered phases of V_3S_4 and V_5S_8 were refined with single crystal data. Both are monoclinic. Chemical compositions, space groups and lattice constants are as follows: $VS_{1.47}$, $I2/m$ (No. 12), $a = 5.831(1)$, $b = 3.267(1)$, $c = 11.317(2)$ Å, $\beta = 91.78(1)°$ and $VS_{1.64}$, $F2/m$ (No. 12), $a = 11.396(11)$, $b = 6.645(7)$, $c = 11.293(4)$ Å, $\beta = 91.45(6)°$. In both structures, short metal–metal bonds were found between the layers as well as within them. In comparison with the structure of Fe_7S_8, the stability of NiAs-type structure was discussed based on the detailed metal–sulfur distances.

Introduction

In the system VS–V_5S_8, various ordered structures have been described, i.e., orthorhombic, hexagonal, monoclinic *I* and monoclinic *II* with increasing sulfur content. Each structure is based on the NiAs-type, in which the ordering of metal vacancies mainly affects the lattice distortions.

V_3S_4 and V_5S_8 have relatively wide ranges of homogeneity. Their structures with ideal atomic parameters were given for V_3S_4 by Chevreton and Sapet (*1*) and for V_5S_8 by Brunie and Chevreton (*2*), respectively, by the X-ray powder method. De Vries (*3*) has refined these atomic parameters, also using powder data.

Recently in our laboratory single crystals were synthesized by the chemical transport method under well-controlled sulfur partial pressures. To elucidate the bonding characteristics of the system, the present work was undertaken with the data obtained from these single crystals.

Experimental

The samples were synthesized by the chemical transport method in an evacuated silica tube from 900°C to 750°C. The chemical compositions of the crystals used for structure determination were $VS_{1.47}$ of the V_3S_4 phase and $VS_{1.64}$ within the V_5S_8 phase, respectively. Details of the chemical analysis have been described in our previous paper (*4*). (Note: According to our P_{S_2}-composition diagram, $VS_{1.47}$ belongs, instead, to the phase adjacent to the V_3S_4 phase, but the powder pattern of the quenched specimen is the same as that of the latter. In comparison with the structure of V_3S_4 by de Vries ($VS_{1.25}$–$VS_{1.49}$) (*3*),

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therefore, $VS_{1.47}$ is tentatively regarded as of the V_3S_4 phase in the present report.)

Crystal Data

$VS_{1.47}$ (V_3S_4-phase):

Monoclinic, space group $I2/m$ (No. 12); $a = 5.831(1)$, $b = 3.267(1)$, $c = 11.317(2)$ Å, $\beta = 91.78(1)°$, $V = 215.49(4)$ Å^3, $Z = 2$ (according to the formula V_3S_4); $D_m = 4.10$ g cm^{-3}; $D_x = 4.11$ g cm^{-3}. Shape and size: platy and elongated, 0.3 × 0.1 × 0.03 mm^3.

$VS_{1.64}$ (V_5S_8-phase):

Monoclinic, space group $F2/m$ (No. 12); $a = 11.396(11)$, $b = 6.645(7)$, $c = 11.293(4)$ Å, $\beta = 91{,}45(6)°$; $V = 854.90(13)$ Å^3; $Z = 4$ (according to the formula V_5S_8); $D_m = 3.90$ g cm^{-3}; $D_x = 3.92$ g cm^{-3}. Shape and size: platy with approximately hexagonal edges, 0.7 × 0.45 × 0.03 mm^3.

The space group was indicated in terms of the unreduced lattice for a comparison with the basic NiAs structure. In the reduced lattice, $VS_{1.47}$ has the space group $A2/m$ (No. 12) with lattice constants $a' = 5.831(1)$, $b' = 3.267(1)$, $c' = 12.891(1)$ Å, and $\beta' = 118.66(1)°$ and $VS_{1.64}$ has $C2/m$ (No. 12) with $a' = 11.396(11)$, $b' = 6.645(7)$, $c' = 8.123(5)$ Å, and $\beta' = 135.98(6)°$, respectively.

The relations between both presentations of lattices are as follows.

$VS_{1.47}$: $\mathbf{a} = \mathbf{a}'$; $\mathbf{b} = \mathbf{b}'$; $\mathbf{c} = \mathbf{a}' + \mathbf{c}'$.

$VS_{1.64}$: $\mathbf{a} = \mathbf{a}'$; $\mathbf{b} = \mathbf{b}'$; $\mathbf{c} = \mathbf{a}' + 2\mathbf{c}'$.

The unit cell dimensions were calculated by the least-squares method from the data of powder diffractometer measurements using Cu$K\alpha_1$ radiation ($\lambda = 1.5405$ Å). Preliminary examinations of these single crystals were made by a precession camera and then the intensity data were collected on a Rigaku four-circle diffractometer using Mo$K\alpha_1$ radiation ($\lambda = 0.70926$ Å).

Refinement of the Structures

$VS_{1.47}$ (V_3S_4-Phase)

The distribution of the diffraction intensities showed a remarkable feature on the precession photographs; on the $l = 4n + 1$ layer the intensities in the region of $h > 0$ are distinctly stronger than those of $h < 0$. On the contrary, on the $l = 4n + 3$ layer, those of $h < 0$ are stronger than those of $h > 0$. The intensity distribution on $l = 2n$ does not exhibit any particular character. These features were used in the following refinements.

Independent reflections (1567, of which 536 were below the limit of observation) were measured on a four-circle goniometer. De Vries' parameters were used to begin the refinement. Since a trial using all terms was

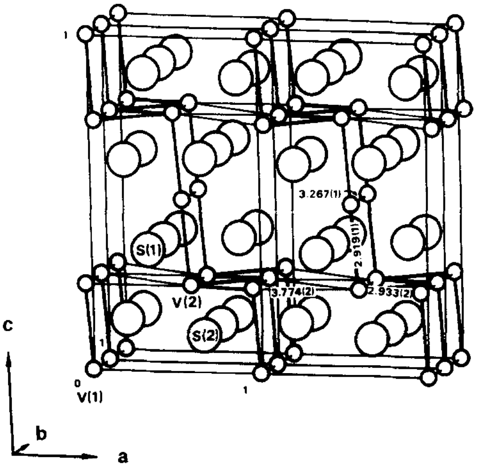

FIG. 1. Crystal structure of $VS_{1.47}$. V–V distances are indicated in Å. Four unit cells are depicted.

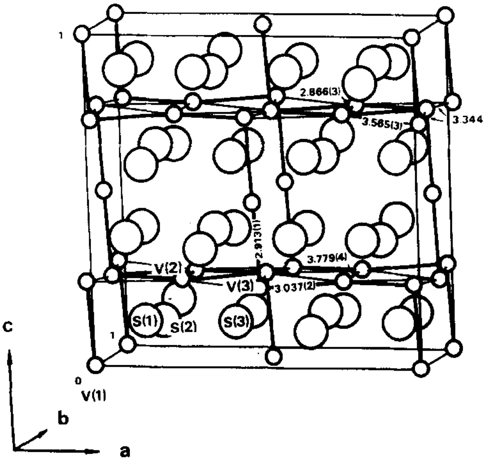

FIG. 2. Crystal structure of $VS_{1.64}$. V–V distances are indicated in Å.

TABLE I

ATOMIC COORDINATES[a]

	Position	Weight	x	y	z
$VS_{1.47}$					
V(1)	2(a)	0.724	0.0	0.0	0.0
V(2)	4(i)	1.0	0.54113(18)	0.5	0.24362(10)
S(1)	4(i)	1.0	0.33862(24)	0.0	0.36289(13)
S(2)	4(i)	1.0	0.66359(25)	0.0	0.11246(13)
$VS_{1.64}$					
V(1)	4(a)	1.0	0.0	0.0	0.0
V(2)	8(g)	1.0	0.25	0.28437(10)	0.25
V(3)	8(i)	1.0	0.51498(7)	0.0	0.24286(7)
S(1)	8(i)	1.0	0.16263(9)	0.0	0.14069(10)
S(2)	8(i)	1.0	0.16674(9)	0.5	0.11098(10)
S(3)	16(j)	1.0	0.41329(6)	0.25100(10)	0.12347(7)

[a] Wyckoff notations are based on the standard orientation of the space group $I2/m$ and $F2/m$.

unsuccessful, the refinement was restarted only with the terms of $l = 4n + 1$ and $\sin^2\theta < 0.3$ ($\theta < 33.21°$). After three cycles of the least squares, R reached 0.067. For further refinement, the angular range was made wider. The same procedure was also applied to the data of $l = 4n + 3$. In both cases, the least squares converged. The refinement was further conducted with all the terms of $l = 2n + 1$.

Finally, three cycles of least squares using ORFLS program (5) with all terms including those of $l = 2n$ were performed to reach the R-value of 0.052 (weighted R was 0.064) for

TABLE II

ANISOTROPIC TEMPERATURE FACTORS[a]

	$\beta \times 10^5$					
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
$VS_{1.47}$						
V(1)	302(35)	812(112)	96(10)	0	14(15)	0
V(2)	356(19)	1340(65)	115(5)	0	7(8)	0
S(1)	309(28)	807(87)	149(8)	0	2(12)	0
S(2)	360(28)	925(88)	139(8)	0	9(12)	0
$VS_{1.64}$						
V(1)	68(4)	331(12)	87(4)	0	−5(3)	0
V(2)	93(3)	346(9)	106(3)	0	−11(2)	0
V(3)	115(4)	682(12)	101(3)	0	−10(3)	0
S(1)	68(5)	331(13)	131(5)	0	−24(4)	0
S(2)	89(5)	382(14)	114(5)	0	−13(4)	0
S(3)	79(3)	311(9)	136(4)	−3(4)	9(3)	7(4)

[a] The factors are expressed as $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

the observed intensities. No. absorption correction was applied (average $\mu r = 1.20$).

$VS_{1.64}$ (V_5S_8-*Phase*)

Independent reflections (2486, of which 124 were below the limit of observation) were measured. De Vries' parameters were used as the starting parameters for the refinement. At first the refinements were performed with the intensity data not corrected for the absorption effects. After four cycles of the refinements with anisotropic temperature factors the R-value was 0.114 for all observed intensities. Then, because of the platy shape of the specimen, the intensities were corrected for absorption effect using the program written by Kato (*6*) with modified versions of Burnham's subroutines. After five cycles of further refinement with these data, the final R-value reached 0.057 (weighted R was 0.070) for the observed intensities.

The atomic scattering factors for V and S were taken from "International Tables for X-ray Crystallography" (*7*), Vol. 3, pp. 202–206.

The comparison between the observed and calculated structure factors is given in a separate table for both $VS_{1.47}$ and $VS_{1.64}$.[1]

Description of the Structures

The structures are of the NiAs-type with ordered vacancies in the vanadium sites. The metal-full layer and the metal-deficient one are stacked alternately between the approximately hexagonal close-packed sulfur layers. The vanadium atoms are surrounded by six sulfur atoms in octahedral arrangement and the metal–metal interactions are also essential to the structures.

The structures are illustrated in Figs. 1 and 2. To compare the same regions of the atomic arrangement in $VS_{1.47}$ and $VS_{1.64}$, four unit cells of $VS_{1.47}$ are depicted in Fig. 1. It is to be noted that the occupied vanadium site (V(1)) in the metal-deficient layer of $VS_{1.47}$ is only about 72% occupied. This is consistent with the chemical composition of the specimen used. On the other hand, since the composition

TABLE III

INTERATOMIC DISTANCES (Å) IN $VS_{1.47}$

V–S			
	V(1)[a]		V(2)[b]
$S(1^{i})$	2.423(1)	S(1)	2.446(1)
$S(1^{ii})$	2.423(1)	$S(1^{vii})$	2.446(1)
$S(1^{iii})$	2.423(1)	$S(1^{viii})$	2.488(2)
$S(1^{iv})$	2.423(1)	S(2)	2.334(1)
$S(2^{v})$	2.371(2)	$S(2^{vii})$	2.334(1)
$S(2^{vi})$	2.371(2)	$S(2^{ix})$	2.333(2)
Average	2.406	Average	2.397
S–S in the coordination polyhedra			
	Around V(1)		Around V(2)
Min.	3.267(1)	Min.	3.178(3)
Max.	3.579(3)	Max.	3.630(3)
Average	3.401	Average	3.373
S–S in regard to sulfur packing			
	S(1)		S(2)
Min.	3.178(3)	Min.	3.133(3)
Max.	3.579(3)	Max.	3.630(3)
Aver. (over 12)	3.353	Aver. (over 12)	3.391
Position code			
i:	$-\frac{1}{2}+x$,	$\frac{1}{2}+y$,	$-\frac{1}{2}+z$
ii:	$-\frac{1}{2}+x$,	$-\frac{1}{2}+y$,	$-\frac{1}{2}+z$
iii:	$\frac{1}{2}-x$,	$\frac{1}{2}-y$,	$\frac{1}{2}-z$
iv:	$\frac{1}{2}-x$,	$-\frac{1}{2}-y$,	$\frac{1}{2}-z$
v:	$-1+x$,	y,	z
vi:	$1-x$,	y,	$-z$
vii:	x,	$1-y$,	z
viii:	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$
ix:	$\frac{3}{2}-x$,	$\frac{1}{2}-y$,	$\frac{1}{2}-z$

[a] In metal-deficient layer.

[b] In metal-full layer.

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[1] See NAPS document No. 02587 for 20 pages of supplementary material. Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10017. Remit in advance for each NAPS accession number $1.50 for microfiche or $5.00 for photocopies up to 30 pages, 15¢ for each additional page. Make checks payable to Microfiche Publications. Outside the United States and Canada, postage is $2.00 for a photocopy and $0.50 for a microfiche.

TABLE IV

INTERATOMIC DISTANCES (Å) IN $VS_{1.64}$

V–S					
	V(1)^a		V(2)^b		V(3)^b
S(1)	2.410(2)	S(1)	2.454(2)	S(1^{vi})	2.442(3)
S(1^{i})	2.410(2)	S(1^{vi})	2.454(2)	S(2^{vii})	2.311(2)
S(3^{ii})	2.393(2)	S(2)	2.312(2)	S(3)	2.421(2)
S(3^{iii})	2.393(2)	S(2^{vi})	2.312(2)	S(3^{viii})	2.421(2)
S(3^{iv})	2.393(2)	S(3)	2.385(2)	S(3^{ix})	2.371(2)
S(3^{v})	2.393(2)	S(3^{vi})	2.385(2)	S(3^{x})	2.371(2)
Average	2.399	Average	2.384	Average	2.390

S–S in the coordination polyhedra					
	Around V(1)		Around V(2)		Around V(3)
Min.	3.290(3)	Min.	3.132(3)	Min.	3.277(2)
Max.	3.501(2)	Max.	3.628(3)	Max.	3.564(2)
Average	3.392	Average	3.357	Average	3.371

S–S in regard to sulfur packing					
	S(1)		S(2)		S(3)
Min.	3.132(3)	Min.	3.241(2)	Min.	3.241(2)
Max.	3.501(2)	Max.	3.628(3)	Max.	3.564(2)
Aver. (over 12)	3.339	Aver. (12)	3.384	Aver. (12)	3.361

Position code				Position code			
i:	$-x$,	$-y$,	$-z$	vi:	$\frac{1}{2}-x$,	y,	$\frac{1}{2}-z$
ii:	$\frac{1}{2}-x$,	$\frac{1}{2}-y$,	$-z$	vii:	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	z
iii:	$\frac{1}{2}-x$,	$-\frac{1}{2}+y$,	$-z$	viii:	x,	$-y$,	z
iv:	$-\frac{1}{2}+x$,	$-\frac{1}{2}+y$,	z	ix:	$1-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$
v:	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	z	x:	$1-x$,	$\frac{1}{2}-y$,	$\frac{1}{2}-z$

[a] In metal-deficient layer.

[b] In metal-full layer.

of the specimen does not deviate much from that of the stoichiometric one, the V(1) site of $VS_{1.64}$ is almost fully occupied. The vanadium sites within the metal-full layer are fully occupied in both cases.

Metal–metal bond distances are shown in Figs. 1 and 2. As can be seen in the figures, even the full layers are distorted from the ideal positions of the NiAs-type structure.

In $VS_{1.47}$, the metal–metal bonds make zigzag chains with 2.933 and 2.919 Å distances. The distances between these chains are 3.267 and 3.774 Å. Within the full layer of $VS_{1.64}$, metal clusters are formed with bond lengths 2.866 and 3.037 Å, and these clusters are combined with an interlayer bonding of 2.913 Å. The distances between clusters of the same layer are 3.344, 3.565, and 3.779 Å.

Atomic coordinates and thermal parameters of these structures are given in Tables I and II, and interatomic distances of V–S and S–S in Tables III and IV. The apparent high value of β_{22} of V(2) in $VS_{1.47}$ suggests that this atom actually deviates very slightly from the mirror

TABLE V

Bond Angles around V Atoms (<S–V–S) in $VS_{1.47}$[a]

Around V(1) atom

	$S(1^{ii})$	$S(1^{iii})$	$S(1^{iv})$	$S(2^{v})$	$S(2^{vi})$
$S(1^{i})$	84.78(5)	95.22(5)	180.00	91.86(5)	88.14(5)
$S(1^{ii})$		180.00	95.22(5)	91.86(5)	88.14(5)
$S(1^{iii})$			84.78(5)	88.14(5)	91.86(5)
$S(1^{iv})$				88.14(5)	91.86(5)
$S(2^{v})$					180.00

Around V(2) atom

	$S(1^{vii})$	$S(1^{viii})$	S(2)	$S(2^{vii})$	$S(2^{ix})$
S(1)	83.79(6)	80.20(5)	92.64(4)	168.75(7)	88.47(5)
$S(1^{vii})$		80.20(5)	168.75(7)	92.64(4)	88.47(5)
$(S1^{viii})$			88.69(5)	88.69(5)	164.71(7)
S(2)				88.84(7)	102.14(5)
$S(2^{vii})$					102.14(5)

[a] For position code, see Table III.

TABLE VI

Bond Angles around V Atoms (<S–V–S) in $VS_{1.64}$[a]

Around V(1) atom

	$S(1^{i})$	$S(3^{ii})$	$S(3^{iii})$	$S(3^{iv})$	$S(3^{v})$
S(1)	180.00	93.56(5)	93.56(5)	86.44(5)	86.44(5)
$S(1^{i})$		86.44(5)	86.44(5)	93.56(5)	93.56(5)
$S(3^{ii})$			87.47(8)	180.00	92.53(8)
$S(3^{iii})$				92.53(8)	180.00
$S(3^{iv})$					87.47(8)

Around V(2) atom

	$S(1^{vi})$	S(2)	$S(2^{vi})$	S(3)	$S(3^{vi})$
S(1)	79.31(8)	88.93(7)	166.71(3)	86.55(5)	85.24(5)
$S(1^{vi})$		166.71(3)	88.93(7)	85.24(5)	86.55(5)
S(2)			103.39(8)	87.93(5)	98.71(6)
$S(2^{vi})$				98.71(6)	87.93(5)
S(3)					169.33(5)

Around V(3) atom

	$S(2^{vii})$	S(3)	$S(3^{viii})$	$S(3^{ix})$	$S(3^{x})$
$S(1^{vi})$	172.46(6)	84.74(5)	84.74(5)	86.23(5)	86.23(5)
$S(2^{vii})$		89.80(5)	89.80(5)	99.13(5)	99.13(5)
S(3)			87.07(8)	170.95(4)	91.50(7)
$S(3^{viii})$				91.50(7)	170.95(4)
$S(3^{ix})$					88.50(8)

[a] For position code, see Table IV.

plane. Bond angles around vanadium atoms are listed in Tables V and VI. These are calculated by the program ORFFE (*8*).

Discussion

It has been well established that the stability of the NiAs-type structure for the first series transition-metal chalcogenides arises from the metal–metal bonding involved in the structure (*9*). In all of these compounds the metal–metal distances are only 10%–15% larger than twice the atomic radius of the respective metal. This is also the case in the present analyses. The average value of metallic V–V bond distances is about 2.92 Å for both $VS_{1.47}$ and $VS_{1.64}$, about 8% larger than twice the atomic radius of vanadium (*10*). The same is true of Fe_7S_8, where the NiAs-type structure extends only to a range of small excess of sulfur as compared with that of the V–S system. The average Fe–Fe distance is 2.92 Å (*11*), about 5% larger than twice the atomic radius.

As can be read from Tables III and IV, the average V–S distances in the present analyses lie between 2.38 and 2.41 Å. In an ionoc model, the V–S distance should be larger than that of Fe–S. On the contrary, the result indicates that this is not the case. The V–S distances are much smaller than that of Fe–S (2.449 Å (*11*)). (Note: In the "International Tables for X-ray Crystallography" (*7*), Vol. 3, p. 269, Fe–S distances are shown as 2.27 and 2.25 Å but these are of pyrite structure where a σ-bond is involved through the hybrid $d_{e_g}^2sp^3$.) This may suggest that, contrary to Fe–S, the π-bond ($d_{t_{2g}}(V)$–$p_\pi(S)$) interaction between the vanadium and sulfur atoms cannot be neglected and the stability of the NiAs-type structure is maintained, in addition to the V–V bonds, through these bonds. However, with increasing atomic number, as in the Fe, Co, and Ni analogs, the radial extension of the electron wavefunction contracts and the possibility of π-bond formation will decrease. Consequently, the stability of NiAs-type structures of these compounds is maintained only through the weak metal–metal bond and the increased metal vacancies destroy the linkage and destabilize the structure.

It may be worthwhile to state here that in our approximate estimate of the overlap integrals for the σ- and π-bonds in this octahedral coordination using the above-mentioned atomic distances, the same trend as the above is clearly suggested. Details of the molecular orbital calculations and the optical properties will be reported in the near future.

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References

1. M. Chevreton and A. Sapet, *C. R. Acad. Sci. Paris* **261**, 928 (1965).
2. S. Brunie and M. Chevreton, *C. R. Acad. Sci. Paris* **258**, 5847 (1964).
3. A. B. de Vries, Dissertation, University of Groningen (1972).
4. M. Saeki, M. Nakano, and M. Nakahira, *J. Cryst. Growth* **24/25**, 154 (1974).
5. W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1962).
6. K. Kato, private communication.
7. "International Tables for X-ray Crystallography" (K. Lonsdale, Ed.), 2nd ed., Vol. 3, Tables 3.3.1, 4.1.1., Kynoch Press, Birmingham (1968).
8. W. R. Busing, K. O. Martin, and H. A. Levy, ORFFE. Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1964).
9. F. Jellinek, *in* "Proceedings of the Fifth Materials Research Symposium" (R. S. Roth and S. J. Schneider, Eds.), p. 625, N.B.S. Special Publication 364, Solid State Chemistry (1972).
10. J. C. Slater, "Quantum Theory of Molecules and Solids," Vol. 2, p. 103, McGraw-Hill, New York (1965).
11. M. Tokonami, K. Nishiguchi, and N. Morimoto, *Amer. Mineral.* **57**, 1066 (1972).