

Structural Transformations and Deviations from the Pure Anion Vacancy Model in Lime Zirconia *

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Small but not negligible deviations from the pure anion vacancy model have been observed in samples of lime zirconia with a lime content ranging from 10 to 14 mole percent lime. Such deviations have been discussed in terms of the subsolid equilibria occurring within this composition range.

In order to discuss the results of dielectric constant measurements, which have been carried out¹ on samples of pure zirconia and of lime zirconia as a function of the lime content, the pycnometric density of samples coming from the same batches used for the dielectric measurements was determined.

As a standard procedure a 25 ml pycnometer filled with pure benzene (sodium dried and distilled) or carbon tetrachloride and 2 g samples was used. Measurements were carried out, after a preliminary careful outgassing of the samples and of the pycnometer, at $25^\circ\text{C} \pm 0.05$.

Density measurements on 30–40 g samples were carried out, as well, by the gas pycnometric method, in order to verify the possible influence of the smallest open porosities and of some closed porosities on the measurements made by the liquid pycnometric method.

A Beckmann mod. 930 air compensation pycnometer (which gives a nominal accuracy of 0.05 cm^3 over the 50 cm^3 volume of the sample holder) and helium as pycnometric gas were used, measurements being made after the purging of the samples under vacuum.

Finely powdered samples were prepared by ball milling zirconia and lime zirconia, sintered at 1600°C and furnace cooled to room temperature.

X-ray diffraction spectra of the powdered samples were also recorded, showing the pattern of the cubic solid solution when the CaO concentration ranges between 10 and 20 mole-%². On the same samples X-ray fluorescence and chemical analyses were used for Ca determination.

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¹ M. SANESI, S. PIZZINI, V. WAGNER, and G. CREMANTE, work in progress.

² See R. C. GARVIE, J. Amer. Ceram. Soc. **51**, 553 [1968].

³ A. M. DINESS and R. ROY, Solid State Commun. **3**, 123 [1965].

⁴ F. HUND, Z. Phys. Chem. **199**, 123 [1952].

⁵ R. E. CARTER and W. L. ROTH, in Electromotive Force Measurements in High-Temperature Systems, C. B. ALCOCK

Results are given in Fig. 1, where some literature data^{3–9} are also reported together with the theoretical plots corresponding to the "pure anion vacancy" model calculated from their own X-ray diffraction data by DINESS and ROY³ for the 1600°C isotherm and by HUND⁴ for the 1460°C isotherm.

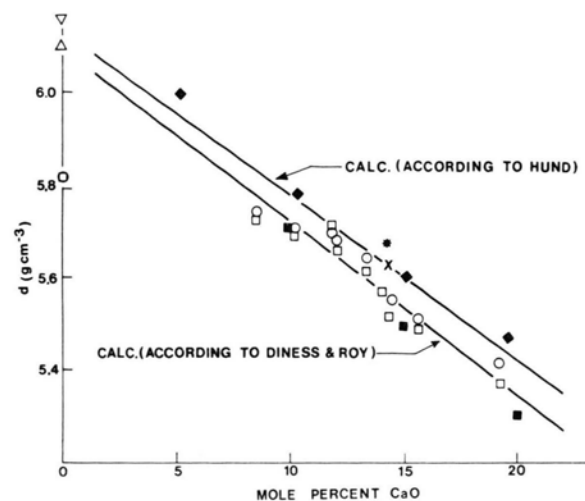


Fig. 1. Plot of the pycnometric densities of stabilized zirconia as a function of the lime content. Solid lines are calculated according to the X-ray data of DINESS and ROY³ and HUND⁴. $\circ$ present work, liquid pycnometry, $\square$ present work, helium pycnometry, $\blacklozenge$ HUND (Ref. 4), $\blacktriangle$ DINESS and ROY (Ref. 3, samples quenched from 1600°C), $\bullet$ KINGERY and PAPPIS (Ref. 6), $*$ CARTER and ROTH (Ref. 5, samples cooled from 1600°C), $\times$ HOFFMANN and FISCHER (Ref. 9), ∇ RUFF and EBERT (Ref. 7, tetragonal ZrO_2), $\triangle$ PASCAL (Ref. 8, tetragonal ZrO_2). The value by McCULLOUGH and TRUEBLOOD (Ref. 10, monoclinic ZrO_2), not shown in diagram, is coinciding with those found in the present work.

For pure zirconia the average density value (for samples coming from different sources, after annealing at 1600°C) is 5.825 g cm^{-3} which well agrees with the value 5.82 for baddeleyite (monoclinic zirconia)¹⁰. For tetragonal zirconia the reported values are 6.10^7 and 6.16^8 .

Edit., The Institute of Mining and Metall., London 1968, p. 125.

⁶ W. D. KINGERY and I. PAPPIS, J. Amer. Ceram. Soc. **42**, 393 [1959].

⁷ O. RUFF and F. EBERT, Z. Anorg. Allg. Chem. **180**, 19 [1929].

⁸ P. PASCAL, Nouveau Traité de Chimie Minérale, Vol. 9, Masson & Cie., Paris 1963, p. 463.

⁹ A. HOFFMANN and W. FISCHER, Z. Phys. Chem. N. F. **17**, 30 [1958].

¹⁰ J. D. McCULLOUGH and K. N. TRUEBLOOD, Acta Cryst. **12**, 507 [1959].

¹¹ From Fig. 1 it can be seen that a satisfactory agreement was generally found within the values determined by the liquid- and by the gas-pycnometric methods.

From Fig. 1 it appears that our present results¹¹ fit fairly well the plot of the calculated results by Diness and Roy and only deviate in the composition range 10 to 14% mole. The corresponding excess densities, plotted in Fig. 2, reach a maximum at about 14 mole percent lime. Single results by CARTER and ROTH⁵ and by HOFFMANN and FISCHER⁹ are also reported in Fig. 2 to support the conclusion that the observed trend is truly representative of a property of the system. Incidentally we remark that the sample used by Carter and Roth was a single crystal specimen.

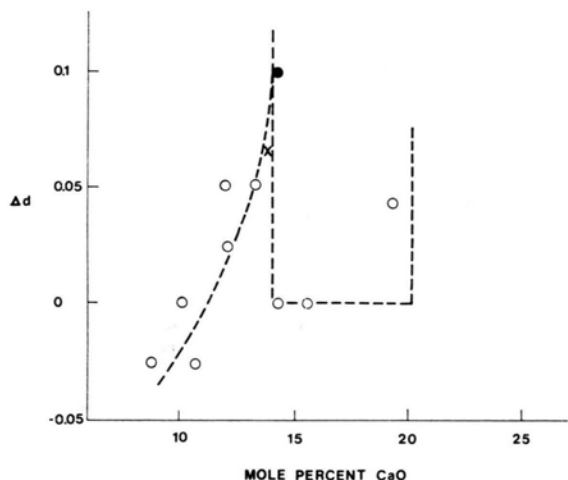


Fig. 2. Plot of the experimental excess density values of lime stabilized zirconia as a function of the lime content.
○ present work, ● Ref. 5, × Ref. 9.

It might be pointed out also that the main difference between our samples and those of Diness and Roy is

in the quenching procedure. These authors claim for a quenching rate of $1000^{\circ}\text{C sec}^{-1}$, whereas our samples are furnace cooled (and those of Carter and Roth were quenched at a rate of $200^{\circ}\text{C sec}^{-1}$). The former only can be considered therefore as truly representative of the 1600°C isotherm, while our samples (and presumably also those of Carter and Roth) reflect the metastable equilibrium conditions within the broad range of temperatures where ordering processes⁵ and subsolidus equilibria are sufficiently fast¹².

According to the phase diagrams reported by GARVIE² (who also critically reviewed the earlier results in literature), corresponding to the isotherm of 1600°C the lower limit of stability of the cubic solid solution is about 10% lime. At lower temperatures a tetragonal solid solution is reported to be stable in equilibrium with the cubic phase, the lower limit of stability of the cubic phase at 1000°C being about 14% lime. If this would be the case, then the precipitation of the tetragonal phase could account fairly well for the excess density values as well as for the maximum at about 14% lime.

There is, however, the contradictory evidence of the results by DINESS¹², COCCO¹³ and BARBARIOL¹⁴, who reported, on the basis of long term annealing experiments, a value for the lower limit of stability of the cubic phase ranging between 10 and 12% lime at temperatures as low as 1000°C . The latter results, however, do not exclude that another mechanism might be operative, such as superlattice formation².

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¹² A. M. DINESS, Thesis, Penn. State University, Dept. Mat. Sci. 1967.

¹³ A. COCCO, Chim. Ind. (Milan) **41**, 882 [1959].

¹⁴ I. BARBARIOL, Ann. Chim. (Rome) **55**, 321 [1965].

Calculation of the Proton Chemical Shifts in Strongly Hydrogen Bonded Systems

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The all-electrons semiempirical SCF methods render the study of changes in the electron configuration with hydrogen bonding relatively easy. We wish to show that such methods can give valuable information about the magnetic properties of hydrogen bonded systems.

Proton shielding constants (σ) were calculated for

HF, HF_2^- and H_2F_3^- using the well known expression by POPLÉ¹

$$\sigma = (e^2/3 m c^2) \sum_A^{\infty} P_{\mu\mu}(r^{-1})_{\mu\mu} - 2 N^{-1} \langle r^{-3} \rangle_A \chi_p^A - \frac{1}{3} N^{-1} \sum_{B \neq (A)} \chi_{ay}^B R_B^{-5} (R_B^2 \delta_{ay} - 3 R_{By} R_{Ba}).$$

All matrix elements were calculated with Slater orbitals and with Slater ζ values. The parametrization of the INDO method² was that proposed by SICHEL and WHITEHEAD³ and the basic set consists only of 1s, 2s and 2p atomic orbitals.

Calculated values (Table 1) are separated into diamagnetic (σ_d) and paramagnetic (σ_p) parts. Though

¹ J. A. POPLÉ, J. Chem. Phys. **37**, 53 [1962].

² J. A. POPLÉ, D. L. BEVERIDE, and P. A. DOBOSH, J. Chem. Phys. **47**, 2026 [1967].

³ J. M. SICHEL and M. A. WHITEHEAD, Theoret. Chim. Acta **11**, 220 [1968].

	σ_d	σ_p	σ	
HF	12.24	-4.84	7.40	Table 1. Calculated proton shielding con- stants (ppm).
HF ₂ ⁻	12.02	-2.61	9.41	
H ₂ F ₃ ⁻	12.07	-2.60	9.47	

only the calculated value of HF can be compared with the measured one we believe that the results characterize the hydrogen bonding in the treated systems. The calculated $\sigma(\text{HF})$ is much smaller than the experimental one⁴ (27.9 ppm) but this is not too surprising because of the use of various approximations inherent in the calculation. Thus only changes of σ using $\sigma(\text{HF})$ as a standard are meaningful. The diamagnetic part changes only slightly and almost all of the change in σ comes from the paramagnetic part. SCHNEIDER et al.⁴

⁴ W. G. SCHNEIDER, H. J. BERNSTEIN, and J. A. POPLE, J. Chem. Phys. **28**, 601 [1958].

⁵ L. W. REEVES and W. G. SCHNEIDER, Can. J. Chem. **35**, 251 [1957].

were first to try to explained the change in σ with the occurrence of the hydrogen bond.

We can not separate σ in a manner as they did but it is nevertheless interesting that changes in σ_p show the trend predicted by them.

σ_p can change to a positive value in the linear hydrogen bond systems and such systems were this explanation seems to be the correct one have been in fact observed⁵. Paramagnetic parts in HF₂⁻ and H₂F₃⁻ are almost equal. This can be described qualitatively as was done by SCHNEIDER et al.: the anisotropy of the paramagnetic term is removed as a consequence of the non-linearity of H₂F₃⁻ system. We believe that semi-empirical all valence electrons SCF wave functions can describe changes of σ with hydrogen bonding in larger systems and so obtained results are more reliable than results based on models used⁶ so far.

⁶ J. W. EMSLEY, J. FEENEY, and L. H. SUTCLIFFE, High Resolution Nuclear Magnetic Resonance Spectroscopy, Pergamon Press, London 1967, Vol. 1, p. 537.

Abschätzung der Frequenzen des IR-Spektrums des Schwefeldifluorids

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Estimation of the IR-Frequencies of Sulphurdifluoride

The theoretical IR-frequencies of sulphurdifluoride are computed from force constants, which are evaluated by means of molecules with S-F-bonds:

$$\nu_1 = 795 \pm 10 \text{ cm}^{-1}, \quad \nu_2 = 430 \pm 5 \text{ cm}^{-1}, \quad \nu_3 = 830 \pm 10 \text{ cm}^{-1}.$$

Bisher sind verschiedene Verfahren zur Darstellung und zum Nachweis von Schwefeldifluorid beschrieben worden. GLEMSE, HEUSSNER und HAAS¹ berichteten, Schwefeldifluorid durch Zersetzung von Dischwefeldifluorid hergestellt zu haben und außerdem ebenso wie PADMA und SATYANARAYANA² direkt bei der Silberfluorid-Schwefel-Reaktion. Der Nachweis, der in beiden Fällen durch Elementaranalyse erfolgt ist, ist inzwischen mehrfach angezweifelt worden^{3,4}, zumal sich auch die von PADMA und SATYANARAYANA angegebenen chemischen Reaktionen nicht reproduzieren ließen.

Außerdem wurden von SEEL, HEINRICH, GOMBLER und BUDENZ⁵ und von WANCZEK⁶ massenspektro-

pische Nachweise der Existenz dieser instabilen Verbindung geführt. Aber das IR-Spektrum des Schwefeldifluorids ist noch unbekannt. Wohl haben SEEL, BUDENZ und WANCZEK⁴ vermutet, daß die im IR-Spektrum des bei der Silberfluorid-Schwefel-Reaktion entstehenden Gasgemisches aus hauptsächlich Schwefeltetrafluorid, Dischwefeldifluorid und 1,2-Difluordisulfan-1,1-difluorid zeitweise auftretende Bande bei 830 cm⁻¹ dem Schwefeldifluorid zuzuordnen sei, das mit seinem Dimeren, dem 1,2-Difluordisulfan-1,1-difluorid im Gleichgewicht stehen kann. Daher sind die zu erwartenden IR-Frequenzen des Schwefeldifluorids mit Hilfe der FG-Matrix-Methode nach WILSON, DECIUS und CROSS⁷ abgeschätzt worden.

Die Molekülstruktur des Schwefeldifluorids ist aus mikrowellenspektroskopischen Messungen von JOHNSON und POWELL⁸ bekannt. Die Daten sind in Tab. 1 aufgeführt. Die zur Berechnung des MVFF (modified valence force field) benötigten Kraftkonstanten f_r (S-F-Bindung), f_a (Winkel-Deformation) und f_{ra} sind graphisch abgeschätzt worden, f_{rr} wurde Null gesetzt. Als Beispiel ist in Abb. 1 die Abschätzung von f_r dargestellt. Die dazu benötigten Daten einiger Moleküle mit S-F-Bindung sind ebenso wie der erhaltene Bereich für die Kraftkonstanten des Schwefeldifluorids in Tab. 1 angegeben.

Sonderdruckanforderungen an Dr. K.-P. WANCZEK, Institut für Physikalische Chemie der Universität Frankfurt, D-6000 Frankfurt, Robert-Mayer-Str. 11.

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³ F. SEEL, Chimia **22**, 79 [1968].

⁴ F. SEEL, R. BUDENZ u. K. P. WANCZEK, Chem. Ber., im Druck.

⁵ F. SEEL, E. HEINRICH, W. GOMBLER u. R. BUDENZ, Chimia **23**, 73 [1969].

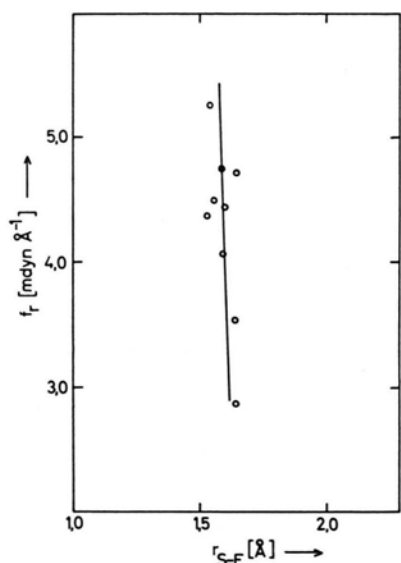
⁶ K. P. WANCZEK, Dissertation, Saarbrücken 1970.

⁷ E. B. WILSON JR., J. C. DECIUS u. P. C. CROSS, Molecular Vibrations, McGraw-Hill Book Company, London 1955.

⁸ D. R. JOHNSON u. F. X. POWELL, Science **164**, 950 [1969].

	r_{S-F} [Å]	δ_{FSF}	f_r	f_a	f_{ra}	$\nu_{SF,s}$	$\nu_{SF,as}$	δ_{SF_2}
SF ₄	(a) 1,646 ¹⁷ (e) 1,545	186° 56' 17 101° 33'	4,7237 ¹⁶ 5,1346					
SOF ₂	1,585 ¹⁹	92° 49' 19	4,0388 ¹⁴	0,7364 ¹⁶	0,1565 ¹⁶	895 ²²	728	558
SSF ₂	1,598 ¹⁸	92,5° 18	4,45 ¹⁵	0,4816 ¹⁴	0,2622 ¹⁴	808 ²³	748	530
FSSF				0,697 ¹⁵	0,22 ¹⁵	760 ¹⁵	692	411
SF ₆	1,58 ⁹	90°	4,89 ¹¹			713 ⁶	677	—
SO ₂ F ₂	1,53 ¹²	96,1° 12	4,38 ¹³			769 ²¹	640	522
NSF	1,65 ¹⁰		2,88 ¹⁰	0,460 ¹³	0,2814 ¹³	848 ²⁴	885	384
NSF ₃	1,55 ²⁰	109°	5,6 ²⁰					
S ₂ F ₄						820 ⁴	678	530
SF ₂	1,589 ⁸	98° 16' 8	4,6–4,8	0,6–0,7	0,13–0,16			

Tab. 1. Strukturparameter einiger Moleküle mit S-F-Bindungen, die zur Abschätzung der Kraftkonstanten des Schwefeldifluorids benutzt worden sind. Es sind die S-F-Abstände r_{S-F} und die FSF-Winkel δ_{FSF} angegeben. (a) bedeutet axial, (e) äquatorial. Ferner sind die symmetrische Valenzschwingung $\nu_{SF,s}$ und die antisymmetrische Valenzschwingung $\nu_{SF,as}$ der S-F-Bindung und die Deformationsschwingung der SF₂-Gruppe aufgeführt. Alle Kraftkonstanten sind in m dyn Å⁻¹, die Frequenzen in cm⁻¹ und die Abstände in Å.



← Abb. 1. Abhängigkeit der Kraftkonstanten f_r von der Bindungslänge r_{S-F} bei Verbindungen mit S-F-Bindungen.

Man erhält als Bereich für die Schwingungsfrequenzen des Schwefeldifluorids:

$$\nu_1 = 795 \pm 10 \text{ cm}^{-1},$$

$$\nu_2 = 430 \pm 5 \text{ cm}^{-1},$$

$$\nu_3 = 830 \pm 10 \text{ cm}^{-1}.$$

Die Auffindung der IR-Banden des Schwefeldifluorids wird durch die bei der Darstellung entstehenden Nebenprodukte sehr erschwert, wie man an den in Tab. 1 angegebenen in Frage kommenden IR-Frequenzen sehen kann. Jedoch bestätigt diese Abschätzung der Schwingungsfrequenzen die Vermutung von SEEL, BUDENZ und WANCZEK⁴, die die verschiedentlich im IR-Spektrum des Reaktionsgemisches der Silberfluorid-Schwefel-Reaktion auftretende Bande bei 830 cm⁻¹ dem Schwefeldifluorid zuordnen.

⁹ D. M. JOST, C. C. STEFFENS u. S. T. GROSS, J. Chem. Phys. **2**, 311 [1934].

¹⁰ W. SAWODNY, A. FADINI u. K. BALLEIN, Spectrochim. Acta **21**, 995 [1965].

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¹⁶ M. G. KRISHNA PILLAI, K. RAMASWAMY u. R. PICHAI, Can. J. Chem. **43**, 463 [1965].

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²³ J. K. O'LOANE u. M. K. WILSON, J. Chem. Phys. **23**, 1313 [1955].

²⁴ D. R. LIDE, D. E. MANN u. J. J. COMEFORD, Spectrochim. Acta **21**, 497 [1965].