Chem. Mater. **1991**, *3*, 557–559

Table VI. Atomic Parameters Used in the Calculations

atom	orbital	H_{ii}, eV	ζ_1	ζ_2	$c_1{}^a$	$c_2{}^a$
H	1s	−13.60	1.30			
B	2s	−15.20	1.30			
	2p	−8.50	1.30			
Ta	6s	−10.10	2.28			
	6p	−6.86	2.241			
	5d	−12.10	4.762	1.938	0.6815	0.5774

[a] Contraction coefficients used in the double-ζ expansion.

pounds are so far unknown (see Table I), although attempts to obtain them were not abandoned until recently.[1-3,6,10] The same situation exists for the borides MB_2 with the AlB_2 crystal structure for d^5–d^{10} metals.[14]

Our calculations of the net charge in the hypothetical symmetrized Ta_3B_4 structure indicate that the largest negative net charge (−1.21) is located on the lateral Ta_2 atoms (see **15**), the Ta_1 atoms bearing smaller negative charge (−0.765). Thus the lateral site should be preferred for a more electronegative substituent than Ta, from the point of view of the topological charge stabilization rule.[48,50] In the case of ternary borides $MoCo_2B_4$,[62] $MoRu_2B_4$,[51] $MoMn_2B_4$,[63] $MoFe_2B_4$,[64] WMn_2B_4,[65] and other TMB with the Ta_3B_4 structure, these should be more stable with the more electronegative metal atom occupying the 4(g) site, in comparison with compound W_2FB_2,[65] Mo_2FeB_4,[10] and W_2MnB_4,[10] in which the stoichiometry does not permit the more electronegative atom to occupy the 4(g) site. These considerations do not take into account a variation in the valence electron count.

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Appendix

All the calculations are of the extended Hückel type, with a tight-binding approach.[26] The atomic parameters for H, B, and Ta atoms are listed in Table VI. The *k* point set used for the calculation of average properties consists of 18k points and was chosen according to the method of Ramirez and Böhm.[66]

Registry No. Ta_3B_4, 12045-92-0.

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(63) Ishi, T.; Shimado, M.; Koizumi, M. *Inorg. Chem.* **1982**, *21*, 1670.

(64) Kuz'ma, Yu. B.; Nuch, O. V.; Skolodra, R. V. *Izv. AN* USSR, *Inorg. Mater.* **1966**, *2*, 1975.

(65) (a) Haschke, H.; Nowotny, H.; Benesovsky, F. *Monatsh. Chem.* **1966**, *B97*, 1459. (b) Kuz'ma, Yu. B.; Chepiga, M. V. *Izv.* AN USSR, *Inorg. Mater.* **1969**, *5*, 49.

(66) Ramirez, R.; Böhm, M. C. *Int. J. Quant. Chem.* **1986**, *30*, 391.

Temperature Behavior of an ESR Copper(II) Ion Pairs Spectrum Formed by Two Nonequivalent Cu^{2+} Ions

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Copper–thorium oxides (Cu/Th > 0.25) prepared by coprecipitation of hydroxides and calcination at 1073 K contain Cu^{2+} ion pairs. Since the two ions are nonequivalent, the ESR parameters of the dimer spectrum change with the recording temperature. No correlation exists between the ESR spectra of the dimer and the single ion as its precursor.

Introduction

In previous work[1-4] it has been shown that the Cu^{2+} ions, occupying different sites in the CuThO catalysts, exhibit different behaviors and reactivities toward hydrogen and/or oxygen treatment.

For a low copper content (Cu/Th < 0.01), the Cu^{2+} ions, occupying substitutional (S) sites both on the surface (S_s or A_1 signal) and in the bulk (S_b or A_2 signal) of the CuThO solids were not susceptible to hydrogen reduction even at high temperature (873 K). On the other hand, for atomic ratios Cu/Th > 0.25, the Cu^{2+} ions, occupying sites on the catalysts surface (M_1, M_2, and D signals), were easily reduced by hydrogen. In the case of the copper(II) ion pairs (D signal) only one of the Cu^{2+} ions was susceptible to the redox treatment, whereas the other one, corresponding to the Cu^{2+} ion in the substitutional surface (S_s) site, remained stable toward the reagents.

The results mentioned above have been obtained from the ESR spectra recorded only at room temperature (293 K). Therefore, it is interesting to study the behavior of Cu^{2+} ions in the CuTh oxides at low temperature (77 K) and, in particular, the copper(II) ion pairs.

Experimental Part

The different solids were prepared at room temperature by coprecipitation of hydroxides by ammonium hydroxide from copper and thorium nitrates up to pH = 6.0. The CuTh oxides were obtained by calcination of the coprecipitated hydroxides at 1073 K for 5 h in a flow of dried air. Samples with different Cu/Th atomic ratios were prepared.

ESR spectra were obtained with a Bruker ER 200D spectrometer operating at X band (9.3 GHz) and using 100-kHz modulation. The spectra were recorded at 77 and 293 K. The *g* values were measured relative to "strong pitch": $g = 2.0028$.

Results and Discussions

Figure 1 shows the ESR spectra recorded at 77 K for CuTh oxides in the oxidized state with different atomic

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(1) Bechara, R.; Wrobel, G.; Aissi, C. F.; Guelton, M.; Bonnelle, J. P.; Abou Kais, A. *Chem. Mater.* **1990**, *2*, 518.

(2) Bechara, R.; D'Huysser, A.; Aissi, C. F.; Guelton, M.; Bonnelle, J. P.; Abou Kais, A. *Chem. Mater.* **1990**, *2*, 522.

(3) Bechara, R.; Abou Kais, A.; Guelton, M.; D'Huysser, A.; Grimblot, J.; Bonnelle, J. P. *Spectrosc. Lett.* **1990**, *23*(10), 1237.

(4) Abou Kais, A.; Bechara, R.; Ghoussoub, D.; Aissi, C. F.; Guelton, M.; Bonnelle, J. P. *J. Chem. Soc., Faraday Trans.* **1991**, *87*(4), 631.

Table I. ESR Parameters of Cu^{2+} Ions in CuTh Oxides at Different Atomic Ratios Cu/Th

CuTh oxides	$g_\parallel$	$g_\perp$	$A_\parallel$, G		$A_\perp$, G
A signal					
A_1	2.2760	2.0445	144.0 153.8	$^{63}Cu^{2+}$ $^{65}Cu^{2+}$	15.66
A_2	2.2470	2.0970	155.0 165.0	$^{63}Cu^{2+}$ $^{65}Cu^{2+}$	18.36
M_1 signal	2.2174	2.0568	82.8		13.5
M2 signal	2.2920	2.0296	80.1		13.0
$\Delta m_s = 1$	2.1928 (293 K)	2.0464 (293 K)	80.5 (293 K)		24.0 (293 K)
D signal	2.2037 (77 K)	2.0419 (77 K)	83.2 (77 K)		22.0 (77 K)
$\Delta m_s = 2$	g(293 K) = 3.9830		g(77 K) = 3.9705		

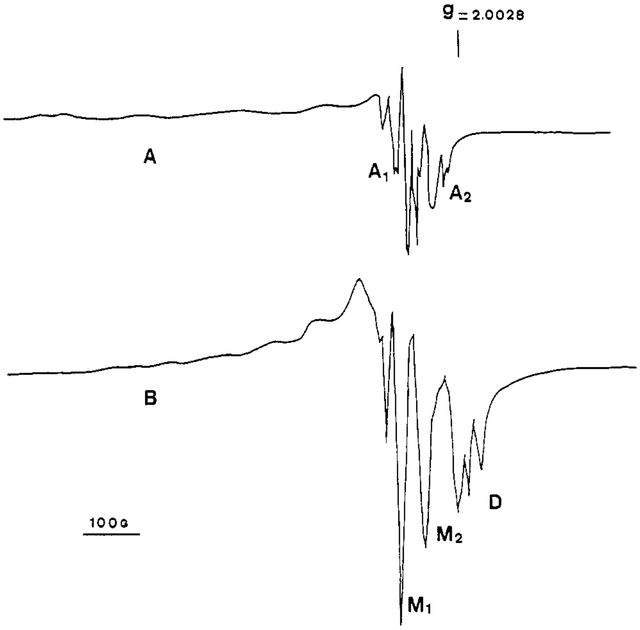

Figure 1. ESR spectra recorded at 77 K of CuTh oxides: A (Cu/Th < 0.01); B (Cu/Th > 0.25).

ratios. For a low copper content (Cu/Th < 0.01), the ESR parameters of the A spectrum (A_1 and A_2 signals) are similar to those obtained at room temperature (Table I). These constant ESR parameters can be explained by the strong stability of Cu^{2+} ions in their substitutional sites either in the bulk (S_b) or on the surface (S_s) of the solids.

On the other hand, for a higher copper content (Cu/Th > 0.25), a significant change of ESR parameters of copper(II) ion pairs spectrum has been observed when the temperature of recording spectra changes from 293 to 77 K (Figure 2, Table I).

As mentioned previously,[2] the copper(II) ion pairs are generally identified by the form of the signal obtained at $\Delta m_s = 1$ (allowed transitions) and the presence of a weak signal at half-normal field intensity which is produced by forbidden transitions at $\Delta m_s = 2$.

If we suppose that the hyperfine interactions will not be included and the Cu^{2+} ions have axial symmetry and that both ions in the pair have the same spin Hamiltonian parameters and principal axis, the spin hamiltonian for the pairs can be written

$$H = g_\parallel \beta H_z S_z + g_\perp \beta (H_x S_x + H_y S_y) + D\{S_z^2 - \tfrac{1}{3}S(S+1)\} + JS_1S_2 \quad \text{(I)}$$

where S_1 and S_2 are spins of electrons 1 and 2, S is the total spin of the two electrons, D is the zero-field splitting tensor, and J is the isotropic exchange interaction constant.

The intensities ratio of the forbidden to the allowed signal is given[5] by the following equation:

$$I_{\mathrm{rel}} = \frac{I(\Delta m_s = 2)}{I(\Delta m_s = 1)} = \frac{C}{r^6}\left(\frac{9.1}{\nu}\right)^2 \quad \text{(II)}$$

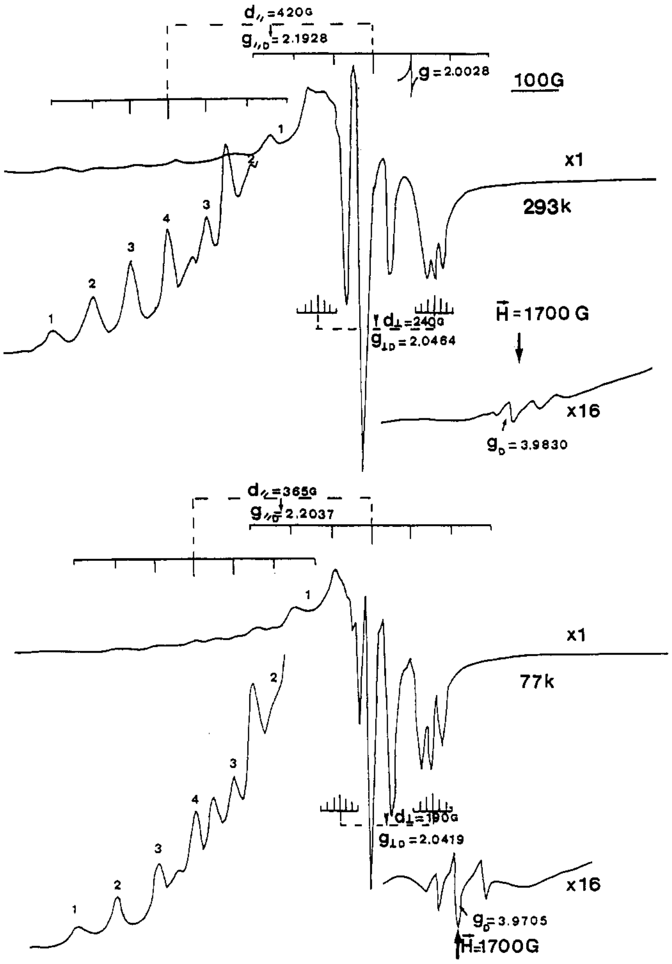

Figure 2. ESR spectra recorded at 293 and 77 K for Cu/Th > 0.25.

C is a constant [$C = (21 \pm 2) \times 10^{-6}$], r (nm) is the interion distance, and ν (GHz) is the microwave frequency. The I_{rel} value was obtained by double integration of the signals observed at $\Delta m_S = 2$ and $\Delta m_S = 1$, respectively, and r can be derived from the eq II.

On the other hand, spectra shown in Figure 2 give a direct experimental evaluation of $d_\perp$ and $d_\parallel$ parameters, which are defined by

$$d_\perp = D/g_\perp\beta \qquad d_\parallel = 2D/g_\parallel\beta \qquad \beta = \text{Bohr magneton} \quad \text{(III)}$$

If we assume that D is due only to dipolar interaction with no contribution from anisotropic exchange, the value of D obtained from eq III can be used in the following equation to also calculate r:[6]

$$D = -\frac{(2g_\parallel^2 + g_\perp^2)\beta^2}{2r^3} \quad \text{(IV)}$$

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[5] Eaton, S. S.; More, K. M.; Sawant, B. M.; Eaton, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 6560.

Since the relative variation of $d_\perp$ and $d_\parallel$ with the temperature is significant (Figure 2), the r values calculated from the dipolar interaction are more accurate than those from I_{rel} (eq II). Then, the difference between the r values derived from spectra recorded at 293 and 77 K must be also significant. r is equal to 0.51 nm at 293 K and changes to 0.55 nm when the spectra are recorded at 77 K. The r values are independent of the Cu/Th atomic ratio (Cu/Th > 0.25).

It has been shown[3] that the copper (II) ion pairs are formed from one Cu^{2+} ion occupying a substitutional bulk (S_b) site and another one present on the solid surface (S_s), which is easily reducible by hydrogen. Since the first species is very stable toward temperature and reactant agent, it seems that the variation of the distance r in the copper(II) ion pairs versus the temperature is due only to the Cu^{2+} ion which is accessible to the reduction. It is then evident to suppose that the copper(II) ion pairs in CuTh oxides are formed from two nonequivalent Cu^{2+} ions.

It has been found[7] that if both ions were equivalent in the dimer and if the pair axis was the same as one of the principal axis of one single ion, the precursor of the dimeric species, the spectra corresponding to those monomer ions should have the same **g** tensor as the **g** tensor of the dimer and the splitting constant tensor of the dimeric spectrum should be half that of the single ion. In addition, the variation of the copper(II) ion pairs signal intensity versus the temperature can be studied. Indeed, the population P of the triplet state will be governed by the Boltzmann distribution and the Curie law following the equation[8]

$$P = \frac{3}{T} \exp\left[\frac{-J}{kT}\right] \qquad \text{(V)}$$

By comparison of ESR spectra intensities recorded at 77 and 293 K of CuTh oxides, the J value has been calculated from the above equation. This value ($J = 46.5$ cm^{-1}) is larger than A_{iso} (41.4×10^{-4} cm^{-1}) of the copper(II) ion pairs. Consequently,[9] the splitting constant of the single ion signal, if it is present, must be double that corresponding to copper(II) ion pairs. In fact, it is not the case for the ESR parameters of all signals previously characterized in CuTh oxides.[1,2] In particular, the A_1 signal has been attributed to Cu^{2+} ions observed after reduction of the copper(II) ion pairs and found as its precursor. On the contrary, the two Cu^{2+} ions of the pairs evidenced in CeO_2[10] were shown to be equivalent. A correlation between the precursor single ion and the copper(II) ion pairs has been established. The ESR parameters of the copper(II) ion pairs in CeO_2 did not change with the temperature as observed in the case of ThO_2.

In conclusion, it seems that if the two ions in one dimer are nonequivalent, the ESR parameters corresponding to this species change with temperature and no correlation can exist between the ESR spectra of the single ion and this dimer. In this case, eq I cannot describe correctly the system.

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(6) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Ions*; Clarendon: Oxford, 1970; p 508.

(7) Mériaudeau, P.; Clerjaud, B.; Che, M. *J. Phys. Chem.* **1983**, *87*, 3872.

(8) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A.* **1952**, *214*, 451.

(9) Dupeyre, R. M.; Lemaire, A.; Rassat, A. *J. Am. Chem. Soc.* **1965**, *87*, 3771.

(10) Abou Kais, A.; Bennani, A.; Aissi, C. F.; Wrobel, G.; Guelton, M.; Vedrine, J. C., submitted to *J. Phys. Chem.*

Metal Complexes in Inorganic Matrices. 7.[1] Nanometer-Sized, Uniform Metal Particles in a SiO_2 Matrix by Sol–Gel Processing of Metal Complexes

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Composites containing nanometer-sized metal particles with a narrow particle size distribution, homogeneously dispersed in a SiO_2 matrix, are prepared by a three-step procedure: In the first step materials of the composition $L_nM[X(CH_2)_3SiO_{3/2}]_y \cdot xSiO_2$ (**4**) are obtained by sol–gel processing of an alkoxysilane of the type $X(CH_2)_3Si(OEt)_3$ ($X = NH_2$, $NHCH_2CH_2NH_2$, CN), a metal salt ($AgNO_3$, AgOAc, $Cd(NO_3)_2$, $Co(OAc)_2$, $Cu(OAc)_2$, $Ni(OAc)_2$, $Pd(acac)_2$, or $Pt(acac)_2$), and, optionally, $Si(OR)_4$. In the second step the polycondensates **4** are heated in air, and thereby the metal oxide/SiO_2 composites $MO_m \cdot (x + y)SiO_2$ (**5**, MO_m = Ag_2O, CdO, CoO, CuO, NiO, PdO or PtO) are formed. The oxidation temperature is optimized by TGA. Reduction of the metal oxide particles of **5** by hydrogen in the third step produces nanocomposites $M \cdot (x + y)SiO_2$ (**6**, M = Ag, Co, Cu, Ni, Pd, or Pt). The metal particles in **6** are homogeneously distributed in the SiO_2 matrix. Depending on the metal and for some metals also on the metal loading, the metal particle sizes are in the range 2–60 nm, as determined by scanning transition electron microscopy. The smallest particles (2–4 nm) are obtained for Cu, Pd, and Pt. The particle size distribution is very narrow and of a Gaussian type. While the size of the metal particles and their size distribution in the Pd/SiO_2 composites is hardly affected by its metal content, the mean size of the metal particles in Ni/SiO_2 increases with increasing metal loading (from 5.9 nm for 2.7 wt % Ni to 57 nm for 44 wt % Ni). At low and high Ni content the particle size distribution is monomodal and, in between, a bimodal distribution is found.

Introduction

The sol–gel route, originally directed toward the synthesis of purely inorganic materials from metal alkoxides, is increasingly extended to prepare organically modified materials by using organically substituted alkoxides, such as alkoxysilanes $RSi(OR')_3$. Materials with both interesting physical and chemical properties are obtained if the organic substituent R bears a functional or polymerizable group. The functional group may also be a metal complex

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