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forbidden transitions ought to be observed in the K signal and X- and Q-band spectra.

On the other side, it has been demonstrated[5] that the position of the low-field edge of the half-field signal in a powder spectrum is given by

$$H_{\min}(\Delta m_s = 2) = \frac{1}{2g\beta}\left[(h\nu)^2 - 4\left(\frac{D^2}{3} + E^2\right)\right]^{1/2} \qquad (1)$$

where ν is the spectrometer operating frequency and D and E are the zero-field splitting parameters. For axial symmetry, $E = 0$.

From eq 1, it is then possible to determine the $H_{\min}$ position of the half-field signal when the X-band frequency is replaced by the Q band. The value obtained ($H = 5813$ G) is shifted more than 250 G to a higher field from that directly obtained ($H = 5558$ G) by the usual equation of Zeeman effect ($h\nu = g\beta H$). Despite this shift, the value obtained corresponds to a magnetic field already recorded by Q band. Since no EPR signal has been observed, it is then possible to suppose that the intensity of this signal can be very weak. In fact, the relative intensity $I_{\rm rel}$ between the signal observed at $\Delta m_s = 2$ and that obtained at $\Delta m_s = 1$ is given by[5]

$$I_{\rm relative} = \frac{I(\Delta m_s = 2)}{I(\Delta m_s = 1)} = \frac{A}{r^6}\left(\frac{9.1}{\nu}\right)^2 \qquad (2)$$

A is a constant ($A = (21 \pm 2) \times 10^{-6}$), r is the interion distance, and ν is the microwave frequency. From eq 2, the $I_{\rm rel}$ will be decreased approximately 15 times less when the X band is replaced by the Q band. But, despite this decrease, the sensitivity of the EPR spectrometer remains able to detect such intensity of signal if this latter exists. Then, no trace of the half-field signal has been evidenced even with the highest gain on the spectrometer. The absence of the half-field signal in the Q-band spectrum, where should it exist, allows us to suppose that a shift has occurred.

To our knowledge, generally, no shift of the half-field signal does occur from the low magnetic field to the high field, when the X-band frequency has been replaced by the Q band. In fact, in the case of CuTh oxide,[6,7] a dimer and monomers have been evidenced by EPR. One of signals is similar to $A_2(X)$ obtained in CuCe oxide. Despite that the thoria and the ceria have the same crystallographic structure, the $A_2(Q)$ signal was not obtained in CuTh oxide when the X band was replaced by the Q band.

However, in one particular case, a significant case of one low-field signal had been obtained by Jones et al.[8] in copper acetate monohydrate. Indeed, this latter compound had been widely studied by Bleaney and Bowers.[9] The EPR spectrum of Cu^{2+} ion pairs coupled via an antiferromagnetic exchange interaction to form a singlet ground state and a thermally accessible ($J = -260$ cm^{-1}) triplet state. A signal at low magnetic field had been observed in the X-band EPR spectrum. When the experiment on copper acetate monohydrate was repeated at Q-band frequency by Jones et al., the low-field signal significantly shifted to a higher field with a concomitant splitting of the lines and significant increase of the signal intensity. But, in that case, the low-field signal observed at X-band frequency, in copper acetate, by Bleaney and Bowers is similar to that obtained from the superconducting oxides below T_c.[10] Therefore, the significant shift of this signal observed by Jones et al. at Q-band frequency has been explained by the superconductivity properties. However, this low-field signal is completely different from the half-field signal of the CuCe oxide samples, and then it is not allowed to suppose that the half-field signal, observed at the X-band spectrum, can shift with the microwave frequency.

In conclusion, the origin and the nature of the $A_2(Q)$ signal remain unresolved, and if we suppose that this signal is different than $A_2(X)$ signal, a particular theoretical work should be necessary to explain that. In addition, measurements have to be made at intermediate frequencies (between X and Q bands) and at low temperatures (4.2 K) to follow the behavior of the dimer spectrum and specifically the $A_2(Q)$ signal.

Registry No. Cu^{2+}, 15158-11-9; copper cerium oxide, 12525-67-6.

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

[6] Bechara, R.; Wrobel, G.; Aissi, C. F.; Guelton, M.; Bonnelle, J. P.; Aboukais, A. *Chem. Mater.* **1990**, *2*, 518.

[7] Bechara, R.; D'Huysser, A.; Aissi, C. F.; Guelton, M.; Bonnelle, J. P.; Aboukais, A. *Chem. Mater.* **1990**, *2*, 522.

[8] Jones, R.; Janes, R.; Armstrong, R.; Singh, K. K.; Edwards, P. P.; Keeble, D. J.; Harrison, M. R. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 683.

[9] Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451.

[10] Khachaturyan, K.; Wekber, E. R.; Tejedor, P.; Stacy, A. M.; Portis, A. M. *Phys. Rev.* **1987**, *B36*, 8309.

[CF$_3$Au(C≡NMe)] as a Precursor for CVD of Gold

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Introduction

The high conductivity and stability to corrosion of gold have led to its widespread use in modern electronics and hence to interest in chemical vapor deposition (CVD) of gold.[1-5] Established precursors for CVD of gold include organogold(III) complexes such as [AuMe$_2$(CF$_3$COCHCOCF$_3$)][1] and [AuMe$_3$L],[2-4] where L = PMe$_3$ or PEt$_3$, and organogold(I) complexes such as [AuMeL],[2,4,5] where L = PMe$_3$, PEt$_3$, or MeNC. CVD of gold from these alkylgold(I) complexes can be carried out at low temperature but the compounds have poor thermal and photochemical stability and so are not easily stored.[2] Since trifluoromethylgold(I) complexes are more stable than the corresponding methylgold(I) complexes,[6] their use as precursors for CVD of gold has now been investigated.

The new organogold(I) complex [CF$_3$AuCNMe] was prepared according to

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[1] (a) Kodas, T. T.; Baum, T. H.; Comita, P. *J. Cryst. Growth* **1988**, *87*, 378. (b) Baum, T. H. *J. Electrochem. Soc.* **1987**, *134*, 2616. (c) Larson, C. E.; Baum, T. H.; Jackson, R. L. *J. Electrochem. Soc.* **1987**, *134*, 266. (d) Baum, T. H.; Jones, C. R. *Appl. Phys. Lett.* **1985**, *47*, 538.

[2] Puddephatt, R. J.; Treurnicht, I. *J. Organomet. Chem.* **1987**, *319*, 129.

[3] Aylett, M. R. *Chemtronics* **1986**, *1*, 146.

[4] Messelhauser, J.; Flint, E. B.; Suhr, H. *Appl. Surf. Sci.* **1992**, *54*, 64.

[5] Jubber, M.; Wilson, J. I. B.; Davidson, J. L.; Fernie, P. A.; John, P. *Appl. Phys. Lett.* **1989**, *55*, 1477.

[6] (a) Sanner, R. D.; Satcher, J. H. Jr.; Droeger, M. W. *Organometallics* **1989**, *8*, 1498. (b) Morrison, J. A. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 293.

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$$2[ClAuCNMe] + (CF_3)_2Cd \rightarrow 2[CF_3AuCNMe] + CdCl_2 \quad (1)$$

It was readily purified by sublimation under vacuum and was characterized by its spectroscopic properties.[7] The complex can be stored indefinitely at 5 °C in the dark; it is slowly decomposed if stored in the light but is much more stable both thermally and photochemically than [MeAuCNMe].[2]

CVD was carried out by using a vertical, low-pressure (10^{-2} mmHg base pressure, dynamic vacuum) CVD reactor with the reservoir containing the gold complex warmed to 60–70 °C and the glass or silicon substrate at 260 °C. The volatile products were identified as C_2F_6, MeNC, and MeCN and indicate the stoichiometry of eq 2.[8]

$$2[CF_3AuCNMe] \rightarrow 2Au + C_2F_6 + 2MeNC/MeCN \quad (2)$$

Analysis of the film by XPS, after argon ion sputtering to remove surface impurities, showed that the film contained >99% gold with less than 1% carbon impurity and no detectable impurities of fluorine or nitrogen. These analytical data were confirmed by nuclear reaction analysis, NRA. A gold film on glass was grown to a thickness of several microns to ensure sufficient conductivity for examination by both scanning electron microscopy (SEM) and scanning tunneling microscopy (STM). The SEM shows a rough honeycomb surface with particles of mean diameter 2000 Å, each with its own honeycomb substructure which was further studied by STM. The STM image is shown in Figure 1 and clearly shows the presence of mounds and hills of diameter 25–75 Å, though the depth of the accompanying valleys (Figure 1) could not be determined.

In an attempt to determine the mechanism of CVD, the rate of decomposition of $[CF_3AuCNMe]$ at 250 °C in a closed, evacuated 10-cm path-length gas cell (vapor pressure of precursor at 250 °C ca. 1 Torr) was monitored by FTIR. Under these experimental conditions, the primary product MeNC is unstable and rearranges quantitatively to MeCN. The progress of the reaction could be followed by the decay of the bands due to $[CF_3AuCNMe]$ at 1136 or 995 cm^{-1} [ν(CF), Figure 2]. A typical decay curve is shown as (a) in Figure 3. The half-life of the precursor is approximately 30 min, but the decay does not follow a simple first-order rate law: the curve shows some evidence for a slower induction period followed by a more rapid decay. However, if the cell contained a preformed gold film, there was no evidence for very selective deposition on this film rather than on the glass walls, and so significant catalysis of CVD by gold is not indicated. The addition of low pressures of hydrogen gas had very little effect on the rate of decay of $[CF_3AuCNMe]$ as shown by curve (b) in Figure 3.[8] Both of the above observations are in strong contrast to CVD of platinum from $[PtMe_2(CNMe)_2]$, which is catalyzed by platinum films and is strongly accelerated by hydrogen.[9] The difference is consistent with the much lower catalytic activity of gold,

Figure 1. STM image of a gold film grown by CVD on a glass substrate. The image is obtained using a Pt/Ir tip with a bias of 1.00 V and a tunneling current of 2.0 nA. The image is 400 × 400 Å and the vertical scale is 40 Å from darkest to lightest.

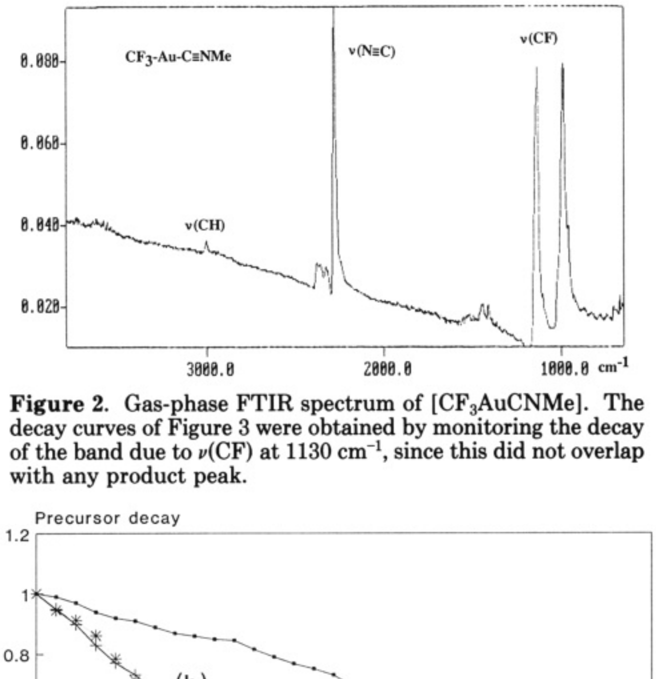

Figure 2. Gas-phase FTIR spectrum of $[CF_3AuCNMe]$. The decay curves of Figure 3 were obtained by monitoring the decay of the band due to ν(CF) at 1130 cm^{-1}, since this did not overlap with any product peak.

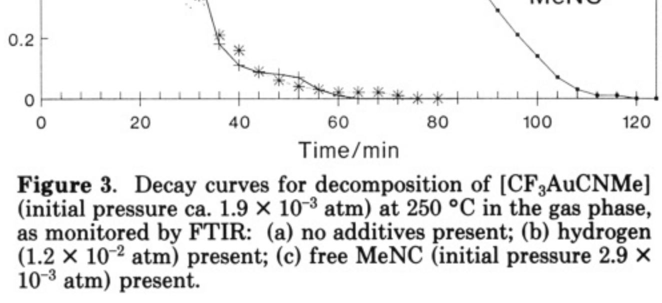

Figure 3. Decay curves for decomposition of $[CF_3AuCNMe]$ (initial pressure ca. 1.9×10^{-3} atm) at 250 °C in the gas phase, as monitored by FTIR: (a) no additives present; (b) hydrogen (1.2×10^{-2} atm) present; (c) free MeNC (initial pressure 2.9×10^{-3} atm) present.

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(7) Solid $[Cd(CF_3)_2 \cdot MeOCH_2CH_2OMe]$ (1.0 mmol) was added to [AuCl(CNMe)] (1.8 mmol) in CH_2Cl_2 (30 mL), and the mixture was stirred in the dark for 3 days. The product $[CF_3AuCNMe]$ was purified by sublimation [90–100 °C/2×10^{-3} mmHg, yield 78%; MP 109–110 °C; IR (KBr disk) 2280, ν(N≡C); 1130, 989, ν(CF), see text for gas-phase IR; ^1H NMR (C_6D_6) $\delta = 1.53$ (1:1:1 t, ^2J(NH) = 2.6, Me); MS *m/e* (rel intensity); 307 (16) [M]; 288 (30) [M – F]; 238 (60) [M – CF_3]; 69 (100) [CF_3].

(8) The volatile products of thermolysis were trapped at −178 °C and subjected to FTIR and GC-MS analysis. MeNC and MeCN have the same molecular mass but were clearly identified by FTIR [ν(C≡N) = 2166, 2282 cm^{-1}, respectively], while C_2F_6 was characterized by both FTIR and GC-MS [ν(CF) = 1250, 1115 cm^{-1}, *m/e* = 119 (M – F)]. Pinchas, S.; Laulicht, I. *Infrared Spectra of Labelled Compounds*; Academic Press: New York, 1971. While hydrogen does not affect the rate of CVD, it does appear to affect the nature of the organic products of CVD, giving a mixture which is not yet fully characterized.

including its inability to chemisorb hydrogen. The decomposition of [CF_3AuCNMe] is strongly retarded by free ligand MeNC as shown by by curve (c) in Figure 3. After about 1 h at 250 °C, the isomerization of free MeNC to MeCN was essentially complete as monitored by the FTIR spectra [disappearance of band at 2166 cm^{-1} due to ν(C≡N) of free MeNC] and it was at this stage that the rate of decay of [CF_3AuCNMe] increased (Figure 3). A similar retardation by free ligand has been observed for the thermolysis of [$PtMe_2(CNMe)_2$] in a closed gas cell[9] and also for the solution phase thermolysis of [MeAuL], where L = PPh_3.[10] The mechanism of decomposition of [RAuL] in the gas cell (R = CF_3, L = MeNC) is therefore likely to be similar to that in solution (R = Me, L = PPh_3),[10] and the proposed mechanism is shown in eqs 3 and 4.

$$[\mathrm{RAuL}] \rightleftharpoons [\mathrm{RAu}] + \mathrm{L} \tag{3}$$

$$[\mathrm{RAu}] + [\mathrm{RAuL}] \rightarrow \mathrm{R{-}R} + 2\mathrm{Au} + \mathrm{L} \tag{4}$$

Present data cannot distinguish between a gas-phase and a surface-mediated, but uncatalyzed, decomposition mechanism. The complex kinetics observed in the gas cell may be due to changes in the concentration of free MeNC as it is formed and then decomposes during the reaction and to a higher activation energy to deposition on glass compared to gold.[11] Clearly the trifluoromethylgold(I) precursor has significant advantages in both ease of handling and in CVD usage compared to the methylgold(I) analog.[2,12]

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[9] (a) Nixon, B.; Norton, P. R.; Ou, E. C.; Puddephatt, R. J.; Roy, S.; Young, P. A. *Chem. Mater.* **1991**, *3*, 222. (b) Dryden, N. H.; Kumar, R.; Ou, E.; Rashidi, M.; Roy, S.; Norton, P. R.; Puddephatt, R. J.; Scott, J. D. *Chem. Mater.* **1991**, *3*, 677.

[10] Tamaki, A.; Kochi, J. K. *J. Organomet. Chem.* **1973**, *61*, 441. A referee notes correctly that our kinetic data are also consistent with the final step 2RAu → R–R + 2Au.

[11] For decomposition of [CF_3AuCNMe] in a closed FTIR cell, the steady-state concentration of MeNC is too low to measure. Hence, when CVD is carried out in the presence of free MeNC, essentially all of the FTIR signal of ν(N≡C) is attributed to free MeNC. Under normal CVD conditions, the MeNC formed during thermolysis is pumped away from the hot zone and it can then be trapped as major product and identified.[8]

[12] The complex [CF_3AuPMe_3][6] can also give CVD of gold but it requires a higher temperature and gives less pure gold films [CVD temp 340 °C; XPS analysis of film: Au, 86; C, 13; F, 1%; volatile products: C_2F_6 and PMe_3 only] than [CF_3AuCNMe].

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c-Axis Oriented Orthorhombic $YBa_2Cu_3O_{7-\delta}$ on Silver from Organic Solvent Solutions of Metal Iodides

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It has been known for some time that highly oriented or single crystals of $YBa_2Cu_3O_{7-\delta}$ (YBCO) formed on substrates such as single-crystal strontium titanate generally show a much higher critical current density (J_c) than bulk samples.[1] Usually these thin films of YBCO are produced by high-energy vapor processes such as sputtering,[2] laser ablation,[3] and molecular beam epitaxy.[4] Hamdi et al.[5] have reported growth of YBCO on $SrTiO_3$ single crystals from solutions of yttrium, barium, and copper neodecanoates. Single-crystal ionic substrates preclude any formation of long lengths of YBCO on flexible substrates. This thin-film study was undertaken to find thin-film processes which might yield YBCO in ribbon or wire configurations. Silver would appear to be a good choice for such a substrate.

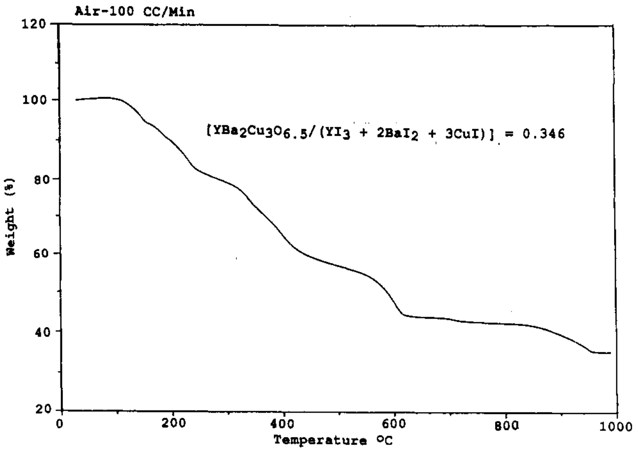

Figure 1. TGA of a metal iodide solid heated at 10 °C/min.

Greuter et al.[6] reported orienting YBCO powder on silver foil by coating a suspension of oxides centrifugally (or by dip coating) to yield microcrystalline *c*-axis oriented textured material. A film of a thickness of the order of 1 μm was achieved after firing at 930 °C. Thus, an investigation of the *c*-axis orientation of YBCO from the solution processing of iodide precursors[7,8] on silver began.

Iodide precursors were expected to offer an advantage over other metalloorganic or solution process routes, as the latter often require temperatures in excess of 850 °C to remove residual carbon in order to produce high-purity YBCO. The metals density of the iodide film is larger than a metalloorganic precursor moiety which should expedite the contraction to an oxide superconductor.[8] Figure 1, the TGA of a 1:2:3 molar mixture of YI_3:BaI_2:CuI, clearly shows that oxidation to YBCO occurs at temperatures well below the melting point of silver (935 °C in oxygen). XRD analysis confirmed the presence of YBCO.[9]

Attempts to produce thin films of the order of 1 μm thickness, necessary for adequate conductivities, were undertaken by both spin and flow coating the precursor onto silver foil substrates. Solution coating via either flow coating or spin coating requires a high concentration of precursors or an increased viscosity to obtain adequate coverage of deposited material with one coating cycle.

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[1] Jin, S.; Sherwood, R. C.; Gyorgy, E. M.; Tiefel, T. H.; van Dover, R. B.; Nakahara, S.; Schneemeyer, L. F.; Fastnacht, R. A.; Davis, M. E. *Appl. Phys. Lett.* **1989**, *54*, 584.

[2] Lathrop, D. K.; Russek, S. E.; Buhrman, R. A. High Temperature Superconductors. *Mater. Res. Soc. Symp.* Proc. **1988**, *99*, 113.

[3] Dam, B.; Baller, T. S.; van Veen, G. N. A.; van Hal, H. A. M.; De Vries, J. W. C.; Stollman, G. M. In ref 2, p 303.

[4] Kwo, J.; Hsieh, T. C.; Hong, M.; Fleming, R. M.; Liou, S. H.; Davidson, B. A. In ref 2, p 339.

[5] Hamdi, A. H.; Mantese, J. V.; Micheli, A. L.; Laugal, R. C. O.; Dungan, D. F.; Zhang, Z. H.; Padmanabhan, K. R. *Appl. Phys. Lett.* **1987**, *51*, 2152.

[6] Greuter, F.; Schuler, C.; Kluge-Weiss, P.; Paul, W. *Highly Oriented YBCO Ceramic Layers Through Reactive Sintering*, Paper WB-4; 2nd International Symposium on Superconductivity, Tsukuba, Ibaraki, Japan, Nov 14–17, 1989.

[7] Baney, R. H.; Bergstrom, D. F.; Justice, B. H. U.S. Patent 4,994,420, Feb 19, 1991.

[8] Baney, R. H.; Bergstrom, D. F.; Justice, B. H. *Chem. Mater.*, following paper in this issue.

[9] Wong-Ng, W.; McMurdie, H.; Paretzkin, B.; Hubbard, C.; Dragoo, A. USNBS, Joint Comm. on Powder Diff. Stds. Grant in Aid Rept., 1987.

0897-4756/92/2804-0981$03.00/0