Highly Resolved Electron Paramagnetic Resonance Spectrum of Copper(II) Ion Pairs in CuCe Oxide

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A copper–cerium oxide sample prepared with an atomic ratio, Cu : Ce, of 0.01 has been studied by electron paramagnetic resonance (EPR) spectroscopy. A well resolved spectrum of copper(II) ion pairs has been evidenced and the hyperfine structure of the perpendicular components clearly appears. The high resolution can be explained by the presence of two nearly equivalent Cu^{2+} ions separated by an oxygen ion. A correlation in EPR parameters has been found between the signal corresponding to a single Cu^{2+} ion, a precursor of the dimer, and the copper(II) ion pair spectrum.

Systems containing two unpaired electrons have been studied widely by physicists and chemists.^{1–4} When these unpaired electrons are strongly coupled, the magnetic properties of the system resemble those of paramagnetic ions with $S = 1$.

Most of the attention in this field has been given to copper(II) dimers consisting of pairs of similar ions (d^9). Thus there exists in these systems the possibility of an anisotropic exchange interaction or a zero-field splitting, D , and an isotropic exchange interaction, J . In addition, hyperfine nuclear interactions also occur ($I = \frac{3}{2}$).

Generally, of the dimers or binuclear complexes of copper(II) which have been studied^{5–17} by far the majority are antiferromagnetically coupled and J is large. These cases may have their EPR spectra described in terms of the triplet state alone. Perhaps, the best known example is copper(II) acetate.⁵ However, when J is large, we have to consider not only the triplet state well above the singlet state in energy, but also the zero-field splitting, D , within the triplet which can have a large pseudo-dipolar contribution as well as a dipolar contribution and which may, in some cases, be comparable to the microwave frequency, $h\nu$. Furthermore, when J is large, it has been shown that the dimer signal intensity and the linewidths due to the dipolar interactions vary closely with the temperature.

In this paper we present an EPR spectrum of Cu^{2+} ion pairs with a high hyperfine resolution of the perpendicular components and establish a correlation between the single Cu^{2+} ion precursors of the copper(II) ion pairs and these dimers.

Experimental

Solid Preparation

A CuCe oxide sample with an atomic ratio, Cu : Ce, of 0.01 was prepared by calcination of the coprecipitated hydroxides of cerium and copper at 1173 K for 3 h in a flow of a dry air.

EPR Measurements

The EPR spectra were recorded at 77, 293 and 473 K with a Varian (V4502) spectrometer using the 9.3 GHz (X band) and 35 GHz (Q band) microwave frequencies. In X band mode, a dual cavity was used and the g values were measured by comparison with a DPPH sample ($g = 2.0036$). In Q band mode, they were determined by measuring the magnetic field, H , and the microwave frequency.

Theory

It is well known that the EPR spectrum of the pairs is radically different from that of a single ion, since at a certain separation for the pairs, the coupling between the two unpaired electrons becomes significant and the system splits into a triplet state ($S = 1$) and a singlet state ($S = 0$). Only the triplet state is paramagnetic. Taking into account the isotropic exchange interaction, the anisotropic exchange interaction and the dipole–dipole interaction between the electrons, the EPR spectrum can be interpreted by means of a spin Hamiltonian which uses the total spin angular momentum operators:

$$H = H_1 + H_2 + \hat{S}D\hat{S} + J\hat{S}_1\hat{S}_2 \quad (1)$$

$$H_i = \sum_{j=x_i, y_i, z_i} (\beta g_j \hat{S}_{ij} H_j + A_j \hat{S}_{ij} I_{ij}); \quad i = 1, 2 \quad (2)$$

where H_1 and H_2 are the separate spin Hamiltonians of ions 1 and 2 including hyperfine interactions; H_j , A_j and I_{ij} ($j = x_i, y_i, z_i$) are, respectively, the j components of the applied field, the hyperfine interaction and the nuclear spin of ion i with respect to the x_i, y_i, z_i axes; $\hat{S}$ is the total spin operator; $\hat{S}_1$ and $\hat{S}_2$ are spin operators of ions 1 and 2; J is the isotropic exchange interaction constant or the splitting between the singlet and the triplet state (Fig. 1). J will be negative (by convention) if the interaction is antiferromagnetic in nature, which is the case for Cu^{2+} ions, and positive if it is ferromagnetic in nature. D is the anisotropic exchange interaction constant or the splitting between the triplet $M_s = +1$ levels and the triplet $M_s = 0$ level when the magnetic field is equal to zero.

Assuming that the symmetry of the ion pairs is axial, the spin Hamiltonian derived from eqn. (1) and (2) may be written:

$$H = g_{\parallel} \beta H_z \hat{S}_z + g_{\perp} \beta (H_x \hat{S}_x + H_y \hat{S}_y) + A_{\parallel} \hat{S}_z (I_{1z} + I_{2z}) + A_{\perp} [\hat{S}_x (I_{1x} + I_{2x}) + \hat{S}_y (I_{1y} + I_{2y})] + D [\hat{S}_z^2 - \frac{1}{3} \hat{S}(\hat{S} + 1)] + E (\hat{S}_x^2 - \hat{S}_y^2) + J \hat{S}_1 \hat{S}_2 \quad (3)$$

For axial symmetry $E = 0$.

The anisotropic exchange constant, D , as defined by Erdos¹⁸ includes both pseudo-dipolar D_{ex} and dipolar D_{dip} couplings:

$$D = D_{\text{ex}} + D_{\text{dip}} \quad (4)$$

Fig. 1 Schematic energy level diagram for two interacting electron spins when $J < 0$

The pseudo-dipolar contribution, according to the theory of Bleaney and Bowers⁵ consists of:

$$D_{\text{ex}} = -\frac{1}{8}J[\frac{1}{4}(g_{\parallel} - 2)^2 - (g_{\perp} - 2)^2] \quad (5)$$

The dipolar part is found to be equal to:²

$$D_{\text{dip}} = -(g_{\parallel}^2 + \frac{1}{2}g_{\perp}^2) \frac{\beta^2}{r^3} \quad (6)$$

Since J is negative (as defined), $D_{\text{ex}} > 0$. However, D_{dip} is always negative. From the experimental value of D derived from:

$$d_{\parallel} = \frac{2D}{g_{\parallel}\beta}; \quad d_{\perp} = \frac{D}{g_{\perp}\beta} \quad (7)$$

where $d_{\parallel}$ and $d_{\perp}$ are the parallel and perpendicular components of the separations, respectively, one can calculate a value for D_{ex} and deduce the J value from eqn. (5).

The inter-ion distance, r , in the pair can be calculated¹⁹ from the relative intensity I_{rel} between the signal observed at $\Delta m_s = 2$ (forbidden transition) and that obtained at $\Delta m_s = 1$ (allowed transition):

$$I_{\text{rel}} = \frac{I(\Delta m_s = 2)}{I(\Delta m_s = 1)} = \frac{A}{r^6} \left(\frac{9.1}{\nu} \right)^2 \quad (8)$$

In eqn. (8), A is a constant with a value of 21 ± 2 , r is the inter-ion distance in Å and ν is the measuring microwave frequency in GHz.

The isotropic exchange interaction constant, J , which can be deduced from the pseudo-dipolar equation, can also be calculated with more precision by studying the variation of the dimeric spectrum intensity vs. temperature. The popu-

lation of the triplet state will be governed by the Boltzmann distribution and the Curie law following eqn. (9):

$$\frac{3}{T} \exp(-J/k_B T) \quad (9)$$

Thus, the J value can be deduced from a study of the temperature dependence of the EPR intensity.

In addition, when $J \gg A_{\text{iso}}$, the hyperfine splitting observed in the EPR spectrum of the single ion responsible for the formation of the ion pairs must be exactly double that observed in the dimer spectrum.²⁰

Results and Discussion

Fig. 2 illustrates the EPR spectrum (X band) of CuCe oxide (Cu : Ce = 0.01) obtained after calcination of the solid under a flow of dried air at 1173 K.²¹ The spectrum consists of two peaks separated by ca. 700 G on each side of a complex central signal composed of several narrow lines and centred at ca. $g = 2$. Apparently, on the low-field side of the lowest of these peaks there is a resolved six-line group, whereas a five-line group is observed near the strong, high-field peak.

The spectrum can be compared to those observed in different samples containing isolated Cu^{2+} ions²²⁻²⁴ and/or copper(II) ion pairs,²⁵⁻²⁷ but it is much more resolved. In order to obtain more information about the EPR spectrum, Q-band analysis of the solid was performed (Fig. 3). The X and Q-band EPR spectra clearly evidence the presence of three signals: Two signals, A_1 and A_2 , which are more resolved in the Q band than in the X band, are formed by sets of four narrow lines, suggesting the presence of isolated Cu^{2+} ions in ceria. One signal, K, is attributed to copper(II) ion pairs. Indeed, the seven components with relative intensities 1 : 2 : 3 : 4 : 3 : 2 : 1 of the hyperfine splittings with two identical nuclei of spin 3/2 clearly visible for $g_{\parallel}$ and $g_{\perp}$ and the weak signal observed at just half the normal magnetic field intensity are characteristic of the existence of copper(II) ion pairs. The weak signal corresponds to the forbidden transition ($\Delta m_s = 2$), whereas the signal observed at the normal magnetic field corresponds to the allowed transition ($\Delta m_s = 1$).

A_1 and A_2 Signals

The EPR parameters determined for signals A_1 and A_2 are given in Table 1. The observed lineshapes are typical of a polycrystalline sample containing Cu^{2+} ions in sites of axial symmetry.

The narrow lines observed for A_1 suggest that this signal corresponds to isolated Cu^{2+} ions in CeO_2 . The g and A anisotropic tensor values deduced from the signal can be correlated with copper(II) ions in octahedral sites with a tetragonal distortion.^{28,29} A comparison with signals obtained in CuTh oxide²² (Cu : Th = 0.01) which have been attributed to Cu^{2+} ions in substitutional sites either in the bulk or on the surface, has shown that the EPR parameters of the A_1 signal are very different despite the fact that the structures of ceria and thoria are similar. The copper(II) ions in CeO_2 were accessible to different reactants (H_2 , CO , C_2H_2 etc.),³⁰

Table 1 EPR parameters of Cu^{2+} ions in CuCe oxide (Cu : Ce = 10^{-2})

signal	$g_{\parallel}^a$	$g_{\perp}^a$	g_{iso}^a	$A_{\parallel}^b$	$A_{\perp}^b$	A_{iso}^b
A_1	2.2079	2.0403	2.0962	170 (0.0176)	27 (0.0026)	74.6 (0.0074)
A_2	2.1233	2.0758	2.0916	82 (0.0081)	40 (0.0039)	54 (0.0053)
K ^c	2.2079	2.0403	2.0962	85 (0.0088)	13.5 (0.0013)	37.3 (0.0037)

^a ± 0.0005 . ^b $\pm 0.0001 \text{ cm}^{-1}$, in G and values in parentheses in cm^{-1} . ^c $D = 0.066 \text{ cm}^{-1}$, $D_{\text{dip}} = -0.081 \text{ cm}^{-1}$, $D_{\text{ex}} = 0.147 \text{ cm}^{-1}$, $J = -52.5 \text{ cm}^{-1}$, $r = 3.4 \text{ Å}$, A (half field) = 80.6 G, g (half field) = 4.5.

Fig. 2 (a) X-band EPR signal (9.3 GHz) observed at 77 K in a CuCe oxide sample (Cu : Ce = 0.01); (b) expanded scale

whereas in ThO_2 they were inert, so the Cu^{2+} ions in the former are probably localized on the solid surface and not in the lattice sites.

The A_2 signal is characterized by much broader and more intense lines compared with the A_1 signal. The EPR parameters are close to those given for square-planar copper(II) complexes.^{31,32} It has been shown³⁰ that the Cu^{2+} ions attributed to the A_2 signal are localized at the substitutional surface sites of CeO_2 , since these species remained inert towards different reactants.

K Signal

After theoretical consideration of the dimeric spectra, it is now possible to explain the K signal illustrated in Fig. 2 and 3. The spin Hamiltonian EPR parameters which have been measured are given in Table 1. From Fig. 2, the values of $g_{\parallel}$ and $g_{\perp}$ were determined by measuring the magnetic field H at the centre of the two perpendicular and parallel components,

respectively. The separation of the two perpendicular components is $d_{\perp} = D/g_{\perp}\beta$ and for the parallel components $d_{\parallel} = 2D/g_{\parallel}\beta$. To our knowledge, no EPR spectrum corresponding to the dimeric Cu^{2+} ions has been observed to date with such well resolved perpendicular components. The hyperfine splitting constants of the perpendicular and parallel components are 13.5 and 85.0 G, respectively. The seven hyperfine lines of the parallel components may be clearly observed in the Q band (Fig. 3).

The intensities ratio, I_{rel} , has been measured by double integration of the signals observed at $\Delta m_s = 2$ and $\Delta m_s = 1$. In our case, $I_{\text{rel}} = 0.0133$ and therefore r may be calculated from eqn. (8) to be 3.4 Å. $D_{\text{dip}} = 0.081 \text{ cm}^{-1}$, as determined from eqn. (6), the zero-field splitting constant is derived from eqn. (7) ($D = 0.066 \text{ cm}^{-1}$), and therefore $D_{\text{ex}} = 0.147 \text{ cm}^{-1}$. From eqn. (5), the isotropic exchange interaction constant has been deduced ($J = -52.5 \text{ cm}^{-1}$).

Furthermore, the five hyperfine lines observed for the $\Delta m_s = 2$ transition at 77 K became six and seven lines (theoretical value) when the EPR spectrum was recorded at

Fig. 3 Q-band EPR signal (35 GHz) observed at 77 K in a CuCe oxide sample (Cu : Ce = 0.01)

293 and 423 K, respectively (Fig. 4). This high resolution of the half magnetic field signal has also been observed when the atomic ratio Cu : Ce in CuCe oxide increases from 0.01 to 0.02. The centre of the hyperfine lines has a g value of 4.5 and the splitting constant is 80.6 G. If α is the angle between the symmetry axis of the Cu^{2+} ions of the pair and the static magnetic field, and assuming a value of $\alpha = 25^\circ$, the latter splitting constant agrees very well with the calculated one fol-

lowing the equation:

$$A(\alpha) = [g_{||}^2 A_{||}^2 \cos^2 \alpha + g_{\perp}^2 A_{\perp}^2 \sin^2 \alpha]^{1/2} / g \quad (10)$$

where

$$g = [g_{||}^2 \cos^2 \alpha + g_{\perp}^2 \sin^2 \alpha]^{1/2} \quad (11)$$

Kottis and Lefebvre³³ made a detailed calculation for the naphthalene triplet and found that the probability for the $\Delta m_s = 2$ transition reached a maximum at $\alpha = 30^\circ$. Chao and Lunsford³⁴ found the same value ($\alpha = 30^\circ$) for identical Cu^{2+} ion pairs in the zeolite powder sample.

A series of computed EPR spectra (Fig. 5) due to the axial copper(II) dimer which illustrate the behaviour of the spectra from $D = 0.05$ to 0.5 cm^{-1} with $|J| > 0$ and $r = 3.5 \text{ \AA}$ for $\Delta m_s = 1$ and $\Delta m_s = 2$ have been plotted by Smith and Pilbrow.³ The g values chosen were very close to those corresponding to the K signal. For the zero-field splitting constant obtained above ($D = 0.066 \text{ cm}^{-1}$), the computed spectrum is similar to that plotted in Fig. 2.

In order to confirm the J value obtained above, the variation of the copper(II) ion pair spectrum with temperature has been studied. In contrast to the previous observation in CuTh oxide of a higher copper content,³⁵ the EPR parameters of the A_1 , A_2 and K signals did not change with temperature. By comparison of the intensities of the EPR spectra recorded at 77, 293 and 473 K (Table 2), J has been calculated from eqn. (9). This value ($J = -52.0 \text{ cm}^{-1}$) was very close to that obtained above.

Fig. 4 X-band EPR signals observed at $\Delta m_s = 2$ (forbidden transition): (a) 77, (b) 293, (c) 473 K

Table 2 Relative intensity of K signal vs. the EPR measuring temperature (referred to 77 K)

T/K	$I_{\text{rel. calc.}}^a$	$I_{\text{rel.}}^b$
77	1	1
293	0.2627	0.43
473	0.1627	0.37

^a Theoretical variation of relative intensity with Curie law only.

^b Measured relative intensity of K signal.

Fig. 5 Calculated EPR spectra for $g_{\parallel} = 2.36$, $g_{\perp} = 2.09$, $\nu = 9.16$ GHz for the axial dimer (hyperfine interaction is not included).

Since this J value was much larger than A_{iso} (37.33 G or 0.0037 cm^{-1}) of the K signal, and the Cu^{2+} single ion corresponding to A_1 has hyperfine splitting constants ($A_{\parallel} = 170$ G and $A_{\perp} = 27$ G) exactly double those corresponding to the K signal ($A_{\parallel} = 85$ G and $A_{\perp} = 13.5$ G), then the single ion must be the precursor of the copper(II) ion pairs in ceria. The same effects are seen in $\text{Cu}_2(\text{CH}_3\text{CO}_2)_4 \cdot 2\text{H}_2\text{O}$,³⁶ where the average Cu hyperfine splitting is *ca.* half that in $(\text{Cu/Zn})_2(\text{CH}_3\text{CO}_2)_4 \cdot 2\text{H}_2\text{O}$ responsible for a single copper signal and in copper-doped zinc formate,³⁷ where for 0.5% Cu, A_{iso} is 100 G, but for 3.4% Cu, $A_{\text{iso}} = 49$ G.

In addition, it has been shown^{20,38} that if the two ions of a dimer are equivalent and if the pair axis is the same as the principal axis of the single ion, and $J \gg A_{\text{iso}}$, the spectra corresponding to those species should have the same g tensor values and the A tensor values of the dimeric spectrum should be half that of the single ion. Obviously, one sees from Table 1 that this is the case. This indicates that the two Cu^{2+} ions of the pair must be equivalent and that their axis must be the same as that of the single ion g tensor. In contrast, for ThO_2 ,^{25,35} it has been shown that the copper(II) ion pairs are formed from two non-equivalent Cu^{2+} ions and no EPR correlation was found between the single ion signal and the dimer spectrum.

It is now possible to discuss the relative positions of the Cu^{2+} ions for the pair involved in the CeO_2 structure. The Cu^{2+} pair cannot occur between two substitutional ions or between two interstitial ions since the inter-ion distance calculated (3.4 Å) is smaller than the ceria lattice parameter (5.41 Å) and the copper(II) ion pairs are sensitive to reduction. It is thus reasonable to suggest that the copper(II) ion pairs are present on the ceria surface as supported species.

The coupling *via* an oxygen between the electrons on the two Cu^{2+} ions is probably responsible for the high resolution of the K signal, in particular, the perpendicular components. Indeed, when the calcination of the CuCe oxide solids is carried out under a flow of dried helium only, instead of dried air, the resolution of the perpendicular components disappears and that of the parallel components decreases (Fig. 6).

Fig. 6 EPR spectra of CuCe oxide (Cu : Ce = 0.01) calcined at 1173 K for 3 h: (a) under dried air atmosphere; (b) under helium atmosphere

Then the EPR spectrum obtained in the presence of helium is similar to that observed in the presence of air but calcined only up to 973 K. Consequently, it seems that calcination under a flow of dried helium is not enough (as in the case of air) to diffuse or disperse the copper(II) ion pairs on the surface of the ceria lattice. In addition, in thoria²⁵ which had been calcined under a flow of dried air (as for the ceria sample), the perpendicular components of the dimer spectrum were not resolved, as in the case of the K signal. This difference may be due to the distance between the two Cu^{2+} ions of the dimer which is larger in the case of thoria (5.1 Å) than for ceria (3.4 Å). Furthermore, the two Cu^{2+} ions of the dimer in ceria are equivalent, whereas in thoria they are non-equivalent,²⁵ this difference is probably correlated to the high resolution obtained in the K signal, in particular, for the perpendicular components.

Conclusion

This work evidences a well resolved EPR spectrum of copper(II) ion pairs in CuCe oxide. High resolution of the perpendicular components of a dimer spectrum has been observed. This resolution suggests the formation of a pair from two equivalent Cu^{2+} ions separated by one oxygen atom. The inter-ion distance of 3.4 Å is small compared with those observed for other dimers. Monomer and dimer signals exhibit the same g values while hyperfine splittings are two times smaller for the dimer than for the monomer. This indicates that the corresponding Cu^{2+} ions are very probably located in the same type of environment. However, the inter-ion distance of 3.4 Å is smaller than the Ce–Ce distance of 5.41 Å in the ceria lattice, indicating that one cannot have two Cu^{2+} ions at two nearby substitutional lattice positions. Moreover, such dimers may be easily reduced. One may then suggest that copper dimers are present as surface species like

very small clusters (two Cu nuclei only) stabilized by the surface. These results will be discussed in a future article.³⁰

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