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Electron paramagnetic resonance studies of some ternary oxides of copper(II)

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Abstract. The electron paramagnetic resonance (EPR) of ternary oxides of Cu(II) has been studied between 4.2 and 300 K. The systems include those with 180° Cu–O–Cu interactions (such as Ln_2CuO_4, $Sr_2CuO_2Cl_2$, Sr_2CuO_3 and Ca_2CuO_3) or 90° Cu–O–Cu interactions (such as $Y_2Cu_2O_5$ or $BaCuO_2$) as well as those in which the Cu^{2+} ions are isolated (such as Y_2BaCuO_5, $La_{1.8}Ba_{1.2}Cu_{0.9}O_{4.8}$ and Bi_2CuO_4). The change in the EPR susceptibility as a function of temperature is compared with that of the DC magnetic susceptibility. Compounds with extended 180° Cu–O–Cu interactions which have a low susceptibility also do not give EPR signals below room temperature. For compounds such as Ca_2CuO_3 with one-dimensional 180° Cu–O–Cu interactions a weak EPR signal is found the temperature dependence of which is very different from that of the DC susceptibility. For Y_2BaCuO_5 as well as for $La_{1.8}Ba_{1.2}Cu_{0.9}O_{4.8}$ the EPR susceptibility as well as its temperature variation are comparable with those of the static susceptibility near room temperature but very different at low temperatures. Bi_2CuO_4 also shows a similar behaviour. In contrast, for $Y_2Cu_2O_5$, in which the copper ions have a very distorted non-square-planar configuration, the EPR and the static susceptibility show very similar temperature dependences. In general, compounds in which the copper ions have a square-planar geometry give no EPR signal in the ground state (0 K) while those with a distortion from square-planar geometry do give a signal. The results are analysed in the light of recent MS X_α calculations on CuO_4^{6-} square-planar clusters with various Cu–O distances as well as distortions. It is suggested that in square-planar geometry the ground state has an unpaired electron in anionic orbitals which is EPR inactive. Competing interactions from other cations, an increase in Cu–O distance or distortions from square-planar geometry stabilise another state which has considerably more Cu 3d character. These states are EPR active. Both these states, however, are magnetic. For isolated CuO_4^{6-} clusters the magnetic interactions seem to involve only the states which have mainly anionic character.

1. Introduction

The recent discovery of high-temperature superconductivity in ternary oxides of copper (Bednorz and Müller 1986, Wu *et al* 1987) has preceded greatly a proper understanding of the properties of the non-superconducting oxides of copper including CuO itself. In order to fill this void, we have embarked on a programme to understand the physical properties of ternary copper oxides which form a fascinating array of complex structures (Muller-Buschbaum 1977, Raveau 1986).

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A recent study (below 300 K) on the magnetic susceptibility of some of these oxides (Sreedhar and Ganguly 1987) showed that all the oxides in which there are long-range 180° Cu–O–Cu interactions have a very low susceptibility ($\sim 100 \times 10^{-6}$ emu mol^{-1} for copper) indicative of a high antiferromagnetic ordering temperature. These compounds include those in which there are one-dimensional Cu–O–Cu interactions involving short (less than 1.98 Å) Cu–O linkages as in Sr_2CuO_3, Ca_2CuO_3 or even $SrCuO_2$, or two-dimensional square-planar interactions as in $Sr_2CuO_2Cl_2$ and Ln_2CuO_4 (Ln ≡ Pr, Nd, Sm, Eu, Gd, etc) (see Muller-Buschbaum (1977), and references therein). Compounds in which there are only 90° Cu–O–Cu interactions as in Li_2CuO_2 (Hoppe and Rieck 1970) or even $BaCuO_2$ (Kipka and Muller-Buschbaum 1977) show a Curie–Weiss-like behaviour with well defined μ_{eff} values typical of an $S = \frac{1}{2}$ system. In oxides such as Y_2BaCuO_5 (Michel and Raveau 1982), $La_{1.8}Ba_{1.2}Cu_{0.9}O_{4.8}$ (Michel *et al* 1981) (henceforth referred to by its nominal composition 'La_2BaCuO_5') and Bi_2CuO_4 (Boivin *et al* 1973, Arpe and Muller-Buschbaum 1976) in which the copper ions are isolated with no Cu–O–Cu linkages but with only Cu–O–O–Cu interactions, there is some indication (Sreedhar *et al* 1987, Sreedhar and Ganguly 1987) of magnetic ordering in the sense that there is a maximum in the magnetic susceptibility or the appearance of field-dependent susceptibility at around 30–50 K. These temperatures are close to the temperatures at which superconductivity is found in the copper oxides. This fact may be more than just a coincidence since the CuO_2 planes in La_2CuO_4 or the Cu_2 planes in the $YBa_2Cu_3O_{7-d}$ compounds are separated by Cu–O–O–Cu linkages (Longo and Raccah 1973, Siegrist *et al* 1987, David *et al* 1987). The next-nearest-neighbour interactions in a square-planar lattice also involve Cu–O–O–Cu interactions. There have been theories proposed (see, e.g., Anderson and Zou 1987, Hirsch and Scalapino 1985) which link the superconducting transition to the appearance of three-dimensional correlations.

There is also the question of whether a d^9 state of a Cu^{2+} ion in an oxide matrix is itself a ground state. This is because of the possibility that the one-electron Cu^{2+} energy level is below that of the O^{2-} ion so that there may be a charge transfer from the oxide ion to the copper ion, resulting in the formation of strongly covalent bonds or in the formation of Cu^+ and O^- ions. It is therefore of paramount importance to understand the nature of the magnetic ground state of such insulating ternary copper oxides. One of the means of probing magnetic states in Cu(II) systems is to employ electron paramagnetic resonance (EPR) techniques.

In this paper, we report our results of the low-temperature EPR investigations on some of these copper oxides with special emphasis being on the compounds in which the copper ions are isolated. The compounds studied include those with extended 180° and 90° Cu–O–Cu interactions, those in which the copper ions are isolated in the sense that there are only Cu–O–O–Cu interactions, those in which there are direct Cu–Cu interactions, etc. The studies include a comparison of the temperature dependence of the EPR susceptibilities of these compounds with that of the static DC magnetic susceptibility reported earlier (Sreedhar and Ganguly 1987). These studies are especially important since it enables first of all an identification of the EPR centres unequivocally especially when the EPR susceptibility is comparable with the bulk susceptibility. Such precautions have not been taken in the recent studies on the high-temperature superconductors. Secondly, a transition from one magnetic state to another may be probed if these states differ in their response to radio-frequency absorption especially when one of these state become EPR inactive for some reason. In our studies on some concentrated systems containing isolated Cu(II) ions in the paramagnetic state the EPR susceptibility at room temperature is quite comparable with the bulk susceptibility, indicating that the EPR centres in these cases correspond to those in the bulk. However, a large discrepancy is seen between the temperature dependences of the EPR and DC susceptibility in some of these cases. Copper ions in square-planar coordination do not give EPR signals in the ground state. In antiferromagnetically ordered systems the EPR signal is absent or is weak as in the one-dimensional Ca_2CuO_3. This behaviour is similar to that in the high-temperature superconductors.

In order to understand this behaviour, we compared our results with the recent MS X_α calculations (Sarma and Sreedhar 1987) on $[CuO_4]^{6-}$ square-planar clusters for various Cu–O distances as well as for various charges of the Watson sphere (thereby simulating competing interactions) and for slight distortions from square-planar geometry. Our results are consistent with the assumption that the unpaired electron in square-planar coordinated copper ions is EPR inactive, probably because the highest occupied molecular orbital (HOMO) has a large-anion character. A distortion from square-planar geometry makes the HOMO have more Cu 3d character and the unpaired electron may then be both EPR and magnetically active.

2. Experimental details

The compounds were prepared by the standard ceramic methods and has been described earlier (Sreedhar and Ganguly 1987, Muller-Buschbaum 1977, Raveau 1986). Thermogravimetric analysis (TGA) in a hydrogen atmosphere was carried out on these compounds to determine the oxygen stoichiometry. The TGA results are in agreement with the nominal compositions so that it may be assumed that the copper ions in these cases are nominally in the divalent state. X-ray diffraction studies were also carried out to ensure a single-phase character.

A Brucker ER200 X-band spectrometer was used for the measurements of the EPR signal.

3. Results

3.1. *Compounds with 180° Cu–O–Cu interactions*

Several compounds such as Ln_2CuO_4 ($Ln \equiv$ La, Pr, Nd, Sm, Eu, Gd), $Sr_2CuO_2Cl_2$, Sr_2CuO_3, Ca_2CuO_3 and $SrCuO_2$ which have extended 180° Cu–O–Cu linkages (Muller-Buschbaum 1977) show very small and nearly temperature-independent magnetic susceptibility (Sreedhar and Ganguly 1988) which is indicative of high antiferromagnetic ordering temperatures higher than 300 K). All these compounds do not give strong EPR signals representative of the bulk of the copper ions, as is indeed expected for antiferromagnetically ordered ions. The oxides with one-dimensional 180° Cu–O–Cu interactions such as Sr_2CuO_3 (which is easily hydrolysed in humid atmospheres) and Ca_2CuO_3 gives a weak EPR signal (figure 1(*a*)) which is about 1% of the total Cu^{2+} concentration as estimated by comparison of the EPR signal intensity with that from $CuSO_4.5H_2O$. A freshly prepared sample usually does not give an EPR signal. The temperature dependence of the EPR susceptibility (see figure 1) has a ferromagnetic intercept. This behaviour is quite different from the static magnetic susceptibility behaviour (figure 1) which is nearly temperature independent. The discrepancy between the EPR and the static susceptibility is reminiscent of the behaviour found (Drent *et al* 1975)

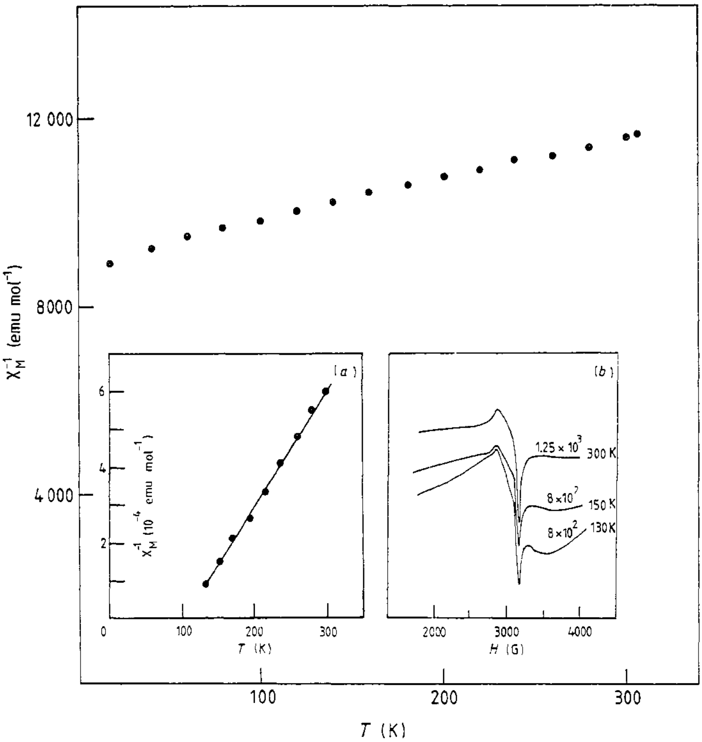

Figure 1. Plot of inverse molar magnetic susceptibility against temperature for Ca_2CuO_3. The insets show (*a*) a plot of inverse χ_{EPR} against T and (*b*) EPR signals as a function of temperature.

for $TiCl_3$, which is also a one-dimensional antiferromagnetic system. Such a behaviour for $TiCl_3$ has been attributed to surface states (Drent *et al* 1975).

It should be noted that in Ca_2CuO_3 the EPR susceptibility at low temperatures becomes comparable with that of the static susceptibility, which is intriguing. It is possible that in the time scales of the EPR experiment there exists a well defined EPR active paramagnetic moment on a small fraction of the copper ions. The magnitude of these moments becomes averaged out to nearly zero on a larger time scale. These moments may exist at the surface as proposed for $TiCl_3$ or at the sites where the one-dimensional antiferromagnetic chain is broken. In the latter case there could be ferromagnetic interactions between nearest-neighbour spins at these sites. It should be noted that there seems to be no *a priori* reason for surface EPR states to show ferromagnetic interactions.

3.2. Compounds with isolated CuO_4 units

3.2.1. Y_2BaCuO_5 and 'La_2BaCuO_5'. The environment of the Cu^{2+} ions in these compounds is best visualised by consisting of edge-shared square-planar CuO_4 units in which every alternate copper site is vacant. Such chains are present parallel to the *c* axis. In Y_2BaCuO_5 the copper ions are in a distorted square-pyramidal coordination (Michel and Raveau 1982) just as the Cu^{2+} ions in $YBa_2Cu_3O_7$ while in 'La_2BaCuO_5' the copper ions are believed to be in square-planar coordination (Michel *et al* 1981). The average Cu–O distance in the plane is larger (2.09 Å) for the compound derived from yttrium compared with that (1.855 Å) for the compound derived from lanthanum.

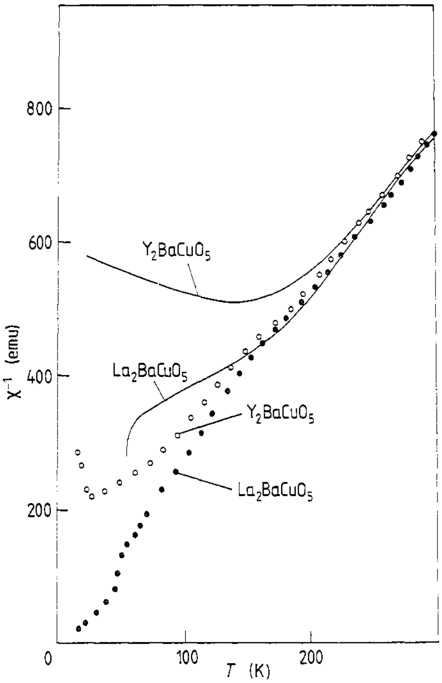

Figure 2. Inverse molar magnetic susceptibility of Y_2BaCuO_5 and 'La_2BaCuO_5': ——, χ_{EPR}^{-1}; ○, ●, χ_{DC}^{-1}. χ_{EPR} has been normalised to the χ_{DC} value at 300 K.

In figure 2(*a*), we show the temperature dependence of the static molar magnetic susceptibility of these two compounds. The static magnetic susceptibility of Y_2BaCuO_5 shows a sharp maximum at 30 K indicative of antiferromagnetic ordering. At high temperatures, however, the behaviour is Curie like as expected for isolated ions and as observed by other researchers (Michel and Raveau 1982). The μ_{eff} obtained from the χ_M^{-1} plot is close to 1.73 μ_B as expected from the spin-only value of one unpaired electron. 'La_2BaCuO_5' also shows a similar behaviour in the static susceptibility at high temperatures when the susceptibility is calculated per gram atom of copper. At low temperatures, there is an abrupt increase in the susceptibility at around 40 K with the simultaneous appearance of a field dependence. The susceptibility below this temperature shows considerable hysteresis on heating and cooling cycles. The nature of the susceptibility plot at low temperatures suggests that there could be an antiferromagnetic ordering with canting of spins or even perhaps the possibility of the formation of a spin-glass state arising out of competing interactions (Sreedhar and Ganguly 1987).

The EPR spectra of Y_2BaCuO_5 and its solid solution with Y_2BaZnO_5 were first studied by Michel and Raveau (1983). These workers reported the room-temperature spectra which is typical of Cu^{2+} ions in square-pyramidal environments but did not report the temperature dependence of the EPR signals. The EPR spectra of Y_2BaCuO_5 and La_2BaCuO_5 at 300 K are shown in figure 3. The EPR spectra of the Y_2BaCuO_5 is similar to that reported earlier (Michel and Raveau 1983). The EPR signal from La_2BaCuO_5 at room temperature seems to be similar to that (Alger 1968) of $CuSO_4.5H_2O$ in which the Cu^{2+} are believed to be in compressed octahedra. There is a weak feature, however, at around $g = 2.23$ which is very close to the value of $g_\parallel$ for Y_2BaCuO_5 (see figure 3). Indeed

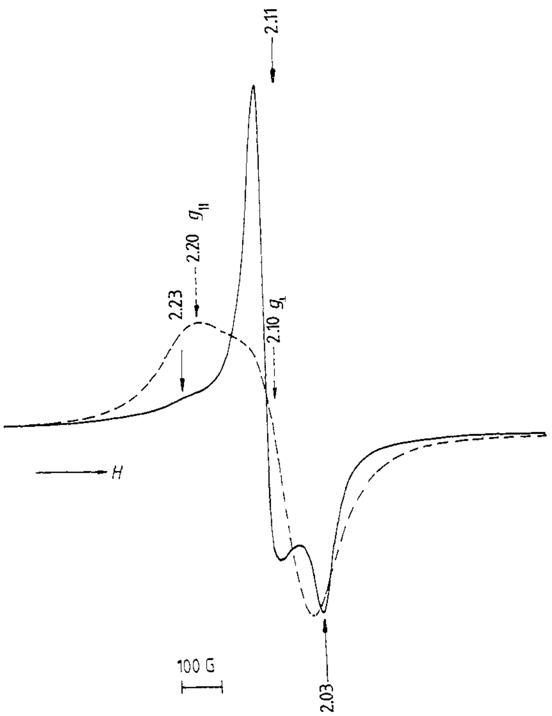

Figure 3. EPR signals from Y_2BaCuO_5 (---) and 'La_2BaCuO_5' (———) at 300 K.

the EPR signal of La_2BaCuO_5 seems to show a splitting of the $g_{\perp}$ line of Y_2BaCuO_5, indicating that the basal CuO_4 unit is not perfectly square-planar in the former despite the fact that structural studies (Michel *et al* 1981) show it to be square-planar. In contrast, Y_2BaCuO_5, which has a strong distortion in the basal plane, shows an EPR spectra more typical of square-planar Cu^{2+} complexes. The average value of the two low-g-value lines in La_2BaCuO_5 is very close to that of the $g_{\perp}$ line in Y_2BaCuO_5.

The temperature dependences of the EPR spectra are shown in figures 4 and 5. For Y_2BaCuO_5, the features associated with the $g_{\parallel}$ line seem to be absent at 4.2 K. The EPR signal is broadened at the wings relative to the spectra at 250 K. The most important point is that the EPR signal in both the compounds seems to show features typical of isolated ions even at 4.2 K which is much below the temperatures at which anomalies in magnetic susceptibility are seen ($T < 30$–40 K). There does not seem to be therefore any EPR evidence for long-range antiferromagnetic order at 4.2 K. In our opinion, such a behaviour is remarkable and symptomatic of the peculiar properties associated in general with copper oxides.

In figure 2, we have also shown the variation in the susceptibility calculated from the area of the EPR lines at various temperatures and compare it with the temperature dependence of the DC magnetic susceptibility. The susceptibilities have been normalised to be equal at 300 K for the two cases. The EPR susceptibility of these compounds calculated at room temperature using $CuSO_4.5H_2O$ as the standard (Alger 1968) is within a factor of 2 of that of the static magnetic susceptibility. The calculation of EPR susceptibility using relative methods is fraught with errors, as is well known. Nevertheless the relative magnitude of the susceptibility does suggest that the EPR susceptibility is

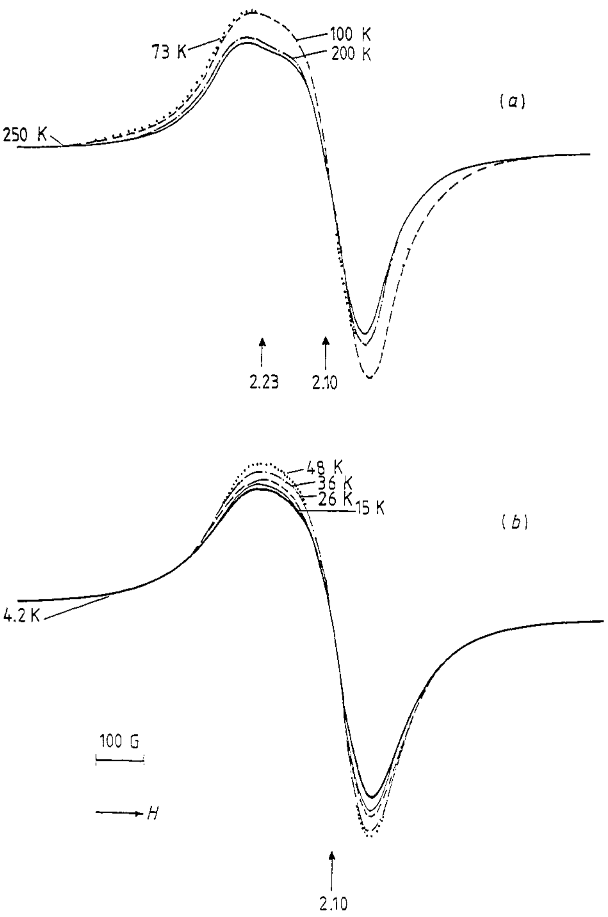

Figure 4. Temperature dependence of the EPR signal from Y_2BaCuO_5: (*a*) 300–70 K; (*b*) 50–4.2 K.

representative of the bulk and not due to surface or defect centres. What is remarkable in figure 2 is the marked deviation of the EPR susceptibility from that of the static susceptibility at low temperatures. For Y_2BaCuO_5, χ_{EPR} shows a maximum at around 78 K instead of 30 K. For La_2BaCuO_5, χ_{EPR} also shows irreproducible behaviour in heating and cooling cycles below $T \simeq 40$ K, mimicking in this sense the behaviour of the static magnetic susceptibility. To the best of our knowledge, this type of marked discrepancy (especially in the temperature dependence) between the EPR susceptibility and the static susceptibility seems to be without precedence in the literature.

3.2.2. Bi_2CuO_4. The structure of this compound (Boivin *et al* 1973, Arpe and Muller-Buschbaum 1976, Kakhan *et al* 1981) may be visualised in terms of a staggered stacking of isolated CuO_4 units in a one-dimensional chain along the *c* axis. The Cu–Cu separation along the axis is only 2.92 Å and there are no Cu–O–Cu interactions. This compound shows a near-Curie–Weiss type of behaviour (there is always a curvature which is convex towards the temperature axis in the plots of χ_M^{-1} against *T*) in the static magnetic susceptibility (figure 4) at high temperatures with a positive paramagnetic Curie tem-

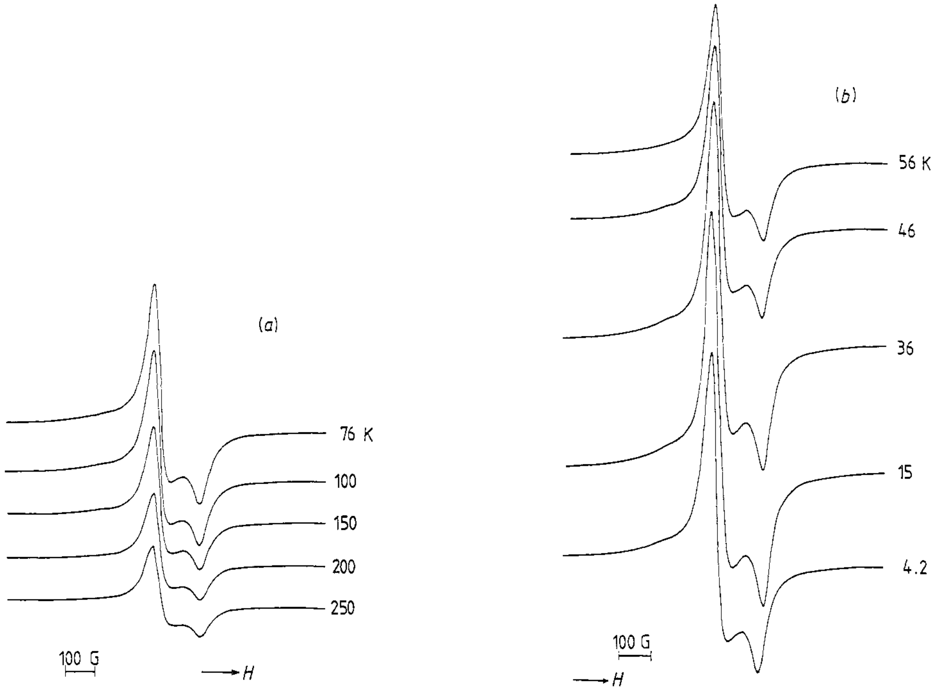

Figure 5. Temperature dependence of the variation in the EPR signal from 'La_2BaCuO_5': (*a*) 300–70 K; (*b*) 60–4.2 K.

perature indicative of antiferromagnetic interactions ($\theta = 40$ K). At low temperatures, it shows a broad maximum at around 50 K (figure 6). The susceptibility behaviour at high temperatures (above the maximum) is fitted well (Sreedhar *et al* 1987, Sreedhar and Ganguly 1987) by a Heisenberg $S = \frac{1}{2}$ one-dimensional antiferromagnetic chain model (Bonner and Fisher 1964). The deviation from this model is seen just below the temperature at which the maximum in the magnetic susceptibility is seen. This could be attributed to the onset of three-dimensional antiferromagnetic ordering or to a spin–Peierls type of transition. It has been observed that the susceptibility is fitted extremely well between 12 and 500 K by a modified Bleaney–Bowers (1952) expression of the type

$$\chi = C^*/T + (C/T)[1 + \tfrac{2}{3}\exp(2J/kT)]^{-1}$$

with $C^* = 0.042$ emu K^{-1}, $C = 0.57$ emu K^{-1} and $2J/k = 100$ K. The above expression is different from the Bleaney–Bowers (1952) expression by the factor $\frac{2}{3}$ in the denominator. In the Bleaney–Bowers expression this factor is $\frac{1}{3}$ and is the ratio of the number of singlet to triplet states of copper dimers. The factor $\frac{2}{3}$ implies the presence of two singlet states. The additional singlet state may be attributed to a charge disproportionation of Cu^{2+} dimers to Cu^+ and low-spin Cu^{3+} states. Such a disproportionation may be favoured from crystallographic considerations since there is some crystallographic evidence (Arpe and Muller-Buschbaum 1976) for the existence of two inequivalent copper sites with different Cu–O distances. A second consideration is that Coulomb repulsion energy between two copper ions in a chain may be reduced by such a disproportionation without affecting significantly the cation–anion attractive energies. Such a factor would be especially important when the transfer integral is small.

The EPR signal from Bi_2CuO_4 is very broad (figure 7). The EPR susceptibility is again

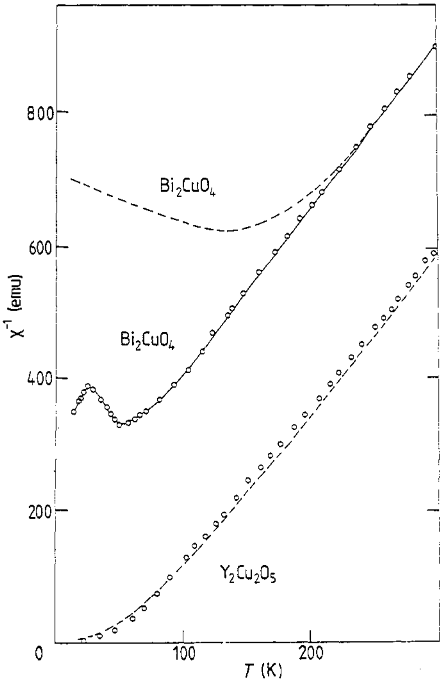

Figure 6. Comparison of the inverse static DC susceptibility and χ_{EPR}^{-1} for Bi$_2$CuO$_4$ and Y$_2$Cu$_2$O$_5$: —O—, experimental inverse DC susceptibility points; - - -, experimental χ_{EPR}^{-1} which has been normalised to the χ_{DC} value at 300 K.

comparable with the bulk susceptibility at room temperature. There is no definitive evidence for the presence of triplet copper dimers. This is perhaps not to be expected because of the concentrated nature of the system. There is, however, some evidence for a very weak shoulder on the broad main peak at around g = 4.1–4.2. The main peak

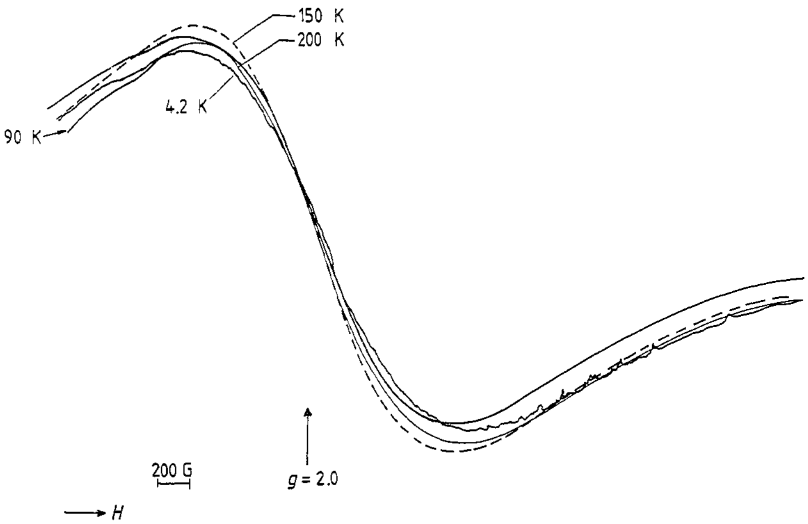

Figure 7. Variation in the EPR signal from Bi$_2$CuO$_4$ as a function of temperature.

itself has a g-value close to 2.09. Neither the linewidths (see figure 7) nor the g-values show much change as a function of temperature. The changes in the EPR intensity is also a weak function of temperature (see figure 7). Between 50 and 4.2 K the EPR signals are almost superimposable. The EPR results therefore do not seem to support the possibility of long-range antiferromagnetic ordering at low temperatures since this should normally be accompanied by a broadening and eventual disappearance of the EPR line in the antiferromagnetically ordered state. Such a behaviour is observed in $Y_2Cu_2O_5$, as we shall see later.

The temperature dependence of the EPR susceptibility calculated from the area of the curve is shown in figure 6 after normalising with the DC magnetic susceptibility at room temperature. Here again we note the large discrepancy between the temperature dependence of the static susceptibility and the EPR susceptibility.

3.3. *Compounds with 90° Cu–O–Cu interactions*

3.3.1. $Y_2Cu_2O_5$. This compound has a structure (Freund and Muller-Buschbaum 1978, Bergerhof and Kasper 1968) which may be best visualised in terms of the edge sharing of two CuO_4 units to form dimeric Cu_2O_6 units with 90° Cu–O–Cu linkages. These dimeric units are linked through corners to other dimeric units in a chain through an oxide ion, the Cu–O–Cu angle in these linkages being close to 135°. These linking oxide ions are out of the plane of the other bridging oxide ions in the dimeric units. The CuO_4 units do not have square-planar coordination in this structure. The plot of inverse magnetic susceptibility against temperature (figure 6) shows a Curie–Weiss behaviour at high temperatures with a C-value of 0.57 emu K^{-1} per gram atom of copper which is too large for an $S = \frac{1}{2}$ system. At high temperatures the value of θ is about 40 K indicative of ferromagnetic interactions but at low temperatures the susceptibility does not diverge. This behaviour has been attributed (Sreedhar and Ganguly 1987) to the formation of $S = 1$ units in the dimers which at low temperatures starts to couple antiferromagnetically.

The change in the EPR spectra as a function of temperature are shown in figure 8. The EPR susceptibility is again almost exactly that of the DC magnetic susceptibility at room temperature. The change in χ_{EPR} as a function of temperature is compared with the change in the static susceptibility in figure 6. It can be seen from these figures that unlike the previous examples the change in χ_{EPR} reflects extremely well the change in the static susceptibility. As the temperature is decreased to 50 K from room temperature, the g-value remains virtually unchanged. Below 30 K the lines start to broaden and the g-value shifts to 2.00. The large increase in the linewidths at low temperatures indicates the onset of long-range magnetic ordering.

3.3.2. $BaCuO_2$. This compound has a complex structure (Kipka and Muller-Buschbaum 1977) with the majority of the copper ions being in square-planar units which share edges. There is therefore 90° Cu–O–Cu interactions which according to the superexchange rules should give rise to ferromagnetic interactions. Accordingly, the plot of inverse magnetic susceptibility against temperature for this compound (Sreedhar and Ganguly 1987) has a positive intercept on the temperature axis indicative of ferromagnetic interactions. The C-value calculated from the slope is 0.37 μ_B emu K^{-1}, as expected for an $S = \frac{1}{2}$ system. There is, however, no measurable EPR signal intrinsic to $BaCuO_2$ even at the lowest temperatures investigated (80 K). Similarly, Li_2CuO_2 also shows no EPR signal intrinsic to the sample at all temperatures examined although this compound exhibits

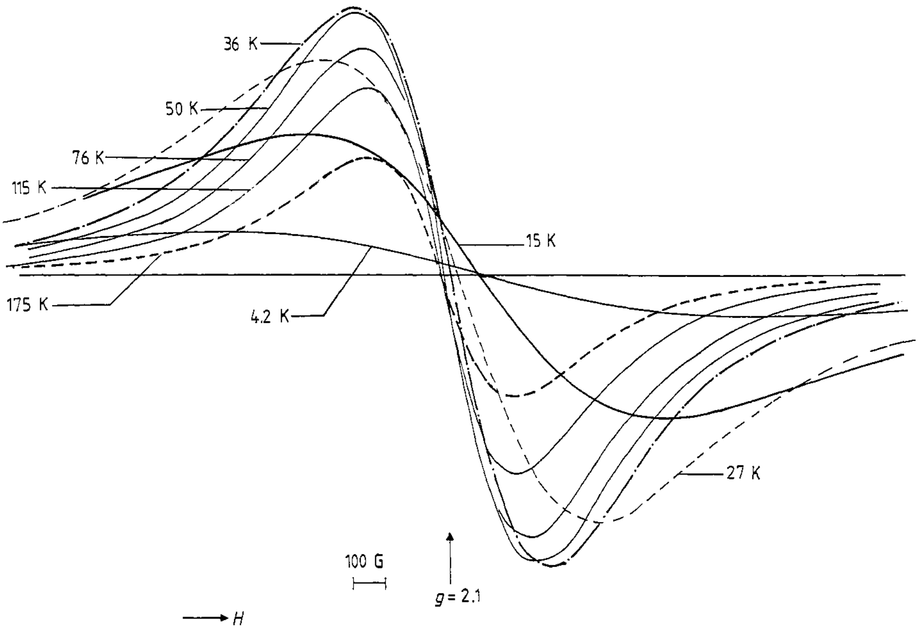

Figure 8. Variation in the EPR signal from $Y_2Cu_2O_5$ as a function of temperature.

a well-defined Curie–Weiss behaviour in the magnetic susceptibility (Sreedhar and Ganguly 1987) with the Curie constant value being close to that expected. This compound has the copper ions in perfectly square-planar CuO_4 units which are edge shared (Hoppe and Rieck 1970) to form one-dimensional chains with 90° Cu–O–Cu interactions along the chains.

4. Discussion

The above results seem to indicate that all the compounds with perfect square-planar coordination give no EPR signal in the ground state while those which show a slight distortion from the perfect square-planar symmetry seem to do so. The magnetic susceptibility of compounds with copper ions in square-planar coordination is small when there are extended 180° Cu–O–Cu interactions. In all other cases the susceptibility is strongly temperature dependent and in most cases obeys the Curie–Weiss law.

The dramatic differences between the static DC magnetic susceptibility and the EPR susceptibility especially in Y_2BaCuO_5 and 'La_2BaCuO_5' is perhaps the most significant and revealing result. It seems to us that the best way that these results may be qualitatively accounted for is to consider the relative location of the Cu $3d^9$ levels relative to the O^{2-} level (or to the top of the valence band). In CuO itself, photo-electron spectroscopy studies (Hufner and Wertheim 1973) have shown the Cu $3d^9$ manifold to be located well within the O 2p band. A strong overlap between the copper and oxygen ions probably decreases the relaxation time and broadens the EPR signal so as to render it non-observable. The changes in the EPR lineshapes as a function of temperature (in figures 4 and 5) do not indicate a gradual broadening as a function of temperature. It is unlikely, therefore, that the changes in EPR susceptibility are due to relaxation time changes.

Another possibility is that a triplet state involving copper ions are formed at intermediate temperatures and that these states are converted into singlet states at still lower temperatures. The absence of any EPR evidence for a triplet state in Y_2BaCuO_5 or La_2BaCuO_5 suggests that the formation of a triplet state is not likely.

We may instead have the following scenario.

(i) There are two states both of which are magnetic with one unpaired electron; the relative populations of these states are determined by the temperature.

(ii) One of these states is EPR active and is not involved in antiferromagnetic interactions at least in the temperature ranges studied; this would account for the fact that the isolated-ion nature of the EPR signal persists down to lowest temperatures.

(iii) The other state is EPR inactive but may participate in antiferromagnetic interactions which would account for the change in the susceptibility of Y_2BaCuO_5.

(iv) For 'La_2BaCuO_5' the situation is more complicated and probably involves changes in the relative populations of the two states brought about perhaps by subtle structural changes.

In order to look for such states, we examine the results of the MS X_α studies recently carried out (Sarma and Sreedhar 1987) on isolated CuO_4 units as a function of Cu–O distance, as a function of the charge of the Watson sphere which mimics the competition of the counter cations for covalency with oxygen and finally as a function of a slight tetrahedral distortion. It was found by these workers that in the square-planar CuO_4 units with Cu–O distance equal to 1.90 Å (the distance for example (Longo and Raccah 1973) in La_2CuO_4) the HOMO and the lowest occupied molecular orbital are $4A_{1g}$ and $3B_{1g}$ states, respectively, for such clusters. The relative orderings of these two orbitals are easily affected by the changes represented in the other calculations. Thus an increasing Cu–O distance is found to lower the energy of the $3B_{1g}$ orbital much more rapidly relative to that of the $4A_{1g}$ orbitals, although the latter is always the HOMO. On increasing the Watson sphere charge to +8 (from the neutralising +6) in these calculations the ground state of the cluster appears to have both $4A_{1g}$ and $3B_{1g}$ fractionally occupied. A tetrahedral distortion stabilises the $3B_{1g}$ state below the $4A_{1g}$ state.

More insight is obtained from the spin-polarised MS X_α calculations on these clusters. It has been found that the spin polarisation within the copper atomic sphere is only 0.03 when the $4A_{1g}$ orbital is occupied and increases to 0.51 when the $3B_{1g}$ orbital is occupied. By summing the $l = 2$ component of the orbital changes within the copper atomic sphere, it is found that the number of d orbitals present in both cases is nearly 9.0. In terms of the l-component analysis of the orbital charges in different regions, it turns out that, while the $3B_{1g}$ orbital is formed via the hybridisation of $d_{x^2-y^2}$ orbital with the oxygen p_x (and p_y) orbitals, $4A_{1g}$ orbitals have negligible Cu d character (less than 10% for all the clusters).

In summary, we conclude that the $4A_{1g}$ state is mainly anionic in character with a very small Cu 3d character while the $3B_{1g}$ orbital has in most cases close to 50% Cu 3d character. Under suitable conditions, these two states may be degenerate as when the distortion is increased. From the above discussion, it may be postulated that the occupation of the $4A_{1g}$ orbital does not give rise to detectable EPR signals while the occupancy of the $3B_{1g}$ orbital may give EPR signals typical of Cu^{2+} ions.

It is interesting to note that all the compounds in which the copper ions are in perfect square-planar coordination show no EPR signal in the ground state. In such compounds the $4A_{1g}$ orbital is expected to have the lowest energy. In compounds such as Y_2BaCuO_5, La_2BaCuO_5 and Bi_2CuO_4 the copper ion is slightly displaced from the plane of the oxygen ions. Such a distortion should make the $3B_{1g}$ orbital lower in energy. At high temperatures, these latter orbitals may be occupied, giving rise to strong EPR signals. In $Y_2Cu_2O_5$ the strong distortion from the square-planar arrangement may stabilise strongly the $3B_{1g}$ orbital so that the $4A_{1g}$ orbital is relatively inaccessible at ordinary temperatures. In such a case the EPR susceptibility is expected to be comparable with the DC susceptibility.

We note that the above discussion does not account for the peculiar field dependence or the hysteresis behaviour of the susceptibility in La_2BaCuO_5. Since both the EPR and the static susceptibility show similar dependences in terms of the irreproducibilities below 40 K, the behaviour should be intrinsic to the sample. It would be necessary to carry out a full structural study in order to understand the low-temperature behaviour.

The magnetic susceptibility and EPR results obtained by us suggest that there is a condensation of spins into non-magnetic states probably by the dimerisation of $S = \frac{1}{2}$ spins into $S = 0$ singlets without long-range magnetic order. Such a reluctance to order over long range in $S = \frac{1}{2}$ spin systems may be of importance from the point of view of resonating valence bond theories (Anderson 1987, Baskaran *et al* 1987).

An interesting conclusion may perhaps be drawn from the above. For square-planar CuO_4 clusters which are connected by corners the strength of the magnetic interactions may be high. However, for isolated CuO_4^{6-} clusters in which there are no direct Cu–O–Cu linkages, magnetic interactions involving states such as $3B_{1g}$ may be very weak. These states are occupied at higher temperatures. It is only when the mainly anionic $4A_{1g}$ states are occupied to a large extent (as at low temperatures) that there can be antiferromagnetic interactions. This is evident from the fact that in oxides it is anions which are in close proximity to one another. In a sense therefore the magnetic anomaly seen at low temperatures in isolated CuO_4^{6-} clusters may be attributed to the antiferromagnetic ordering of spins on anionic states. It should be noted, however, that the geometry of the orbitals involved in considering the interactions between clusters is also important. Thus, clusters which share edges show very low magnetic ordering temperatures. This aspect is being further investigated.

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