

$S = 1$ and $S = 2$ EPR signals in modified CuO and BaCuO₂

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EPR spectra of (i) CuO annealed in air at different temperatures up to 900°C and (ii) CuO reacted with BaO in the ratio 3:2 at different temperatures up to 900°C were studied. In (i), evidence for the formation of monomers, dimers, and tetramers of copper ions was found. In (ii), in addition to those spectra obtained in (i), aggregates of four copper ions coupled through cyclic exchange with resultant electronic spin $S = 2$ and affected by the immediate barium neighbors were obtained. It is found that these copper aggregates giving the EPR signals are magnetically isolated from the main CuO cluster.

INTRODUCTION

CuO exhibits complex magnetic properties,¹ many of which are still unresolved. Moreover, it constitutes one of the essential starting materials of the high-temperature superconductors. We undertook the electron paramagnetic resonance (EPR) study of this compound as copper is a 3*d* transition element. BaO is another starting material for the high- T_c superconductors, and we extend our EPR study to the CuO+BaO system also. Both CuO and CuO+BaO systems have been studied earlier by many workers,²⁻⁸ but the results and their interpretations were not convergent.

EXPERIMENT

High-purity samples of CuO (Sigma-Aldrich), CuO (S.d. fine), CuCO₃Cu(OH)₂H₂O (S.d. fine), BaO (Sigma-Aldrich), and BaCO₃ (S.d. fine) were used as starting materials. CuO and CuCO₃Cu(OH)₂H₂O were annealed at different temperatures ranging from 100–900°C at intervals of 100°C, for 24 h. The CuO+BaO system was studied by reacting intimately mixed combinations of BaO or BaCO₃ with CuO or CuCO₃Cu(OH)₂H₂O in the atomic ratio of Cu:Ba=3:2 (which is the same ratio required for the preparation of high- T_c materials), at temperatures ranging from 100–800°C, with intervals of 100°C, and at 850, 875, and 900°C for 24 h. Different types of crucibles were used for the annealing of samples and the results were not found to be dependent upon crucible material. Spectra of the samples were recorded when they were furnace cooled to room temperature. Weight loss suffered by CuO was estimated by precisely weighing the sample before and after each annealing. Oxygen contents of the CuO samples were determined by chemical analysis using standard iodometric titration procedures. EPR spectra were recorded on a JEOL, JES-RE2X ESR spectrometer working in the X band with 100 kHz field modulation. X-ray-diffraction (XRD) patterns of the samples were recorded on a Philips, PW 1050 x-ray diffractometer using monochromatic Cu $K\alpha$ radiation.

RESULTS AND DISCUSSION**A. CuO**

There was no EPR signal at the lower annealing temperatures. The spectrum made its first appearance at the annealing temperature of 500°C and consisted of a broad low-field and a narrow high-field signal [shown in Fig. 1(a)]. The nature of the spectrum remained unaltered until 700°C. Results of these investigations have already been reported.^{9,10} On further raising the annealing temperature, a many-line complex EPR spectrum appeared.

It has been suggested by various workers^{1,2,11-14} that CuO should not give an EPR signal above its Néel temperature (230 K), because of the strong magnetic exchange interaction present. This exchange interaction is found to persist up to much higher temperatures, as seen from magnetic-susceptibility^{1,12} and neutron-diffraction studies.¹⁵

After repeatedly preparing new samples and taking different amounts of samples in the sample tube, the mystery of the spectra could be solved. For larger amounts of sample (≈ 0.2 g), the spectra were usually complex. It was found that when the sample amount is reduced, the signal strength is not reduced in the same proportion. When the sample amount is gradually reduced, the spectrum becomes simpler and at one stage consists of a maximum of three signals [Fig. 1(b)], one in the region of $g \approx 3.12$, the other two in the neighborhood of $g \approx 2$, one of these two being quite broad and the other sharp. On further subdividing the sample, the signals may appear singly or in combination of 2's or 3's [see Figs. 1(c)–1(f)]. At this stage, the sample became just a speck of matter, which can barely be seen by the naked eye. These specks were examined by optical microscope and their end-to-end dimensions were of the order of 150 μm . There were many subdivisions of the starting sample which did not give any signal. On repeated experimentation and meticulous recording of the sample under different conditions of sweep width, receiver gain, chart speed, and modulation width, it was revealed that the $g \approx 3.12$ signal consists of seven lines and the broad signal at $g \approx 2$ consists of 13 lines, while the other $g \approx 2$ sharp signal remains unsplit. The signals at $g \approx 3.12$ and $g \approx 2$ giving 7 and 13

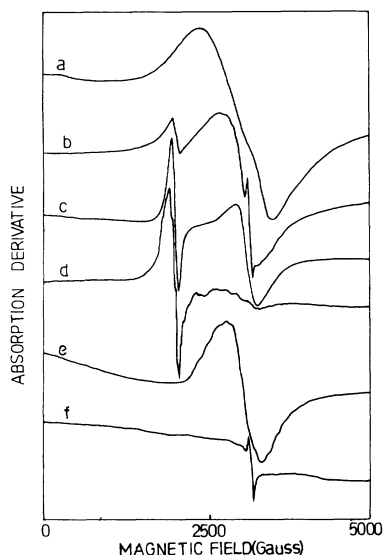


FIG. 1. EPR spectra of CuO: (a) annealed at 500° (b-f) spectra obtained from samples annealed at 700°, (b) showing three signals, one at $g \approx 3.12$ and other two at $g \approx 2$, (c) spectrum showing two signals at $g \approx 3.12$ and $g \approx 2$, (d) single signal at $g \approx 3.12$, the weak lines at high field are due to the broad $g \approx 2$ signal, (e) single broad signal at $g \approx 2$, (f) single sharp unsplit signal at $g \approx 2$.

lines, respectively, are illustrated in Figs. 2 and 3. The single sharp signal at $g \approx 2$ is shown in Fig. 1(f). Seeing the splitting of the $g \approx 3.12$ signal into seven components, it may be assigned to a pair of Cu²⁺ ions coupled by superexchange through the intervening oxygen ion. The exchange-coupled ion pair may give a resultant electronic spin of $S=1$ and the resultant nuclear spin of $I=3$, and can split the signal into seven hyperfine components.¹⁶ This signal may be assigned to the $\Delta m = \pm 1$ transition of the $S=1$ system, obtained through the exchange coupling between a pair of copper ions and the deviation of g from the $g \approx 2$ value may be explained as due to a larger l admixture in the wave function. The broad signal at $g \approx 2$ with 13 components (shown in Fig. 3) may be attri-

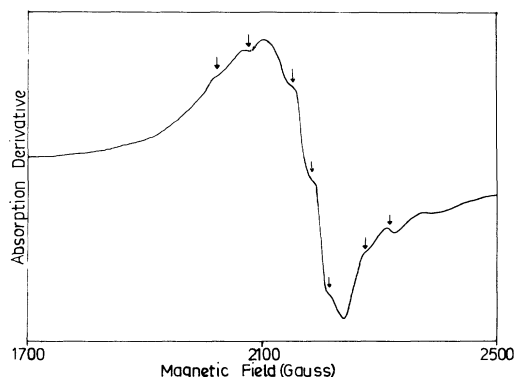


FIG. 2. EPR spectrum of the CuO annealed at 700°C showing a single signal at $g \approx 3.12$ with seven hyperfine splittings.

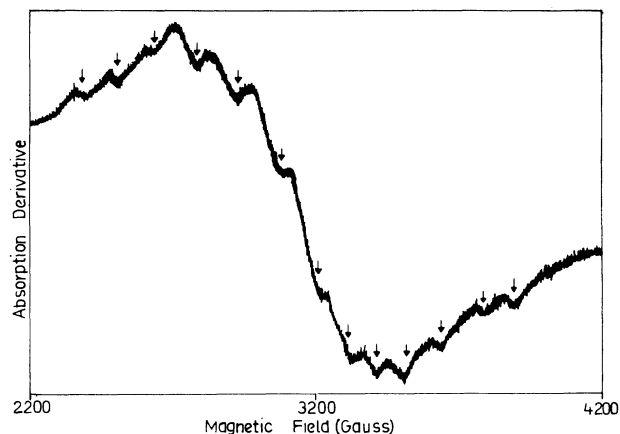


FIG. 3. EPR spectrum of CuO annealed at 800°C showing a single broad signal at $g \approx 2$, showing 13 components.

buted to ferromagnetically coupled aggregates of four copper ions coupled through cyclic superexchange via the intervening oxygen.¹⁷⁻¹⁹ Such an aggregate can give a resultant electronic spin of $S=2$ and the resultant nuclear spin of $I=6$, and can split the signal into 13 hyperfine components. The observed signal is assigned to the $\Delta m = \pm 1$ transition of the $S=2$ system obtained through the exchange coupling of four copper ions and the value of $g=2.12$ for this transition seems to be equal to the average of the four individual g factors; $1/4(g_1 + g_2 + g_3 + g_4)$, each g being ≈ 2 .

The single sharp line at $g \approx 2$ without any hyperfine structure [Fig. 1(f)] may be attributed to the usual $\Delta m = \pm 1$ transition of Cu²⁺ monomers. These Cu²⁺ monomers, dimers, and tetramers seem to be magnetically isolated from the main CuO cluster or appear as islands in the bulk CuO network. Their occurrence in small regions of the sample, the separation of the signals upon subdivision of the sample, and the presence of hyperfine structure in $S=1$ and $S=2$ signals, all indicate the magnetic isolation of these systems from the main CuO cluster. The complex spectra which were seen in the beginning with larger sample amounts were due to the occurrence of several specks at different orientations.

The cause of formation of these aggregates may be losses in oxygen content of the sample when annealed at elevated temperatures. On heating the sample at higher temperatures, these aggregates are formed in localized sites and the removal of oxygen around them may be responsible for their magnetic isolation from the bulk.²⁰ Below 500°C, the oxygen loss is not sufficient to produce enough such aggregates to be detected. As the annealing temperature is increased, their number also increases, as seen from the overall increase in signal intensity.

To verify the possibility of oxygen loss, the sample was weighed precisely after each annealing and the progressive weight loss was registered. The weight loss of the sample after each annealing is given in Table I. The weight loss of the sample is attributed to the oxygen loss by the sample. This was further confirmed by the oxygen-content determination of the sample after each

TABLE I. Data showing the percentage weight loss of CuO with annealing temperature.

Annealing temperature (°C)	Percentage weight loss at each temperature	Cumulative percentage weight loss
100	0.0184	0.0184
200	0.0411	0.0595
300	0.0698	0.1293
400	0.0978	0.2271
500	0.1414	0.3685
600	0.2167	0.5852
700	0.4514	1.0366
800	0.0878	1.1244
900	0.0588	1.1832

annealing, using the standard iodometric titration procedure, and was found to be in good agreement with the data of the weight-loss measurement.

X-ray-diffraction studies were performed on CuO and $\text{CuCO}_3\text{Cu}(\text{OH})_2\text{H}_2\text{O}$ after each annealing to check whether, on annealing, any phase transformation has taken place or not. The x-ray-diffraction pattern of untreated $\text{CuCO}_3\text{Cu}(\text{OH})_2\text{H}_2\text{O}$ is shown in Fig. 4(a) and that of the same compound annealed at 700°C is shown in Fig. 4(b). The XRD pattern of $\text{CuCO}_3\text{Cu}(\text{OH})_2\text{H}_2\text{O}$ annealed at any temperature between 300–900°C was found to be the same as shown in Fig. 4(b) and resembles the diffraction pattern of CuO annealed at any temperature. It shows that the materials studied here are CuO only.

B. CuO + BaO

In this system, the spectra at the lower annealing temperatures were of the same nature (one broad low-field

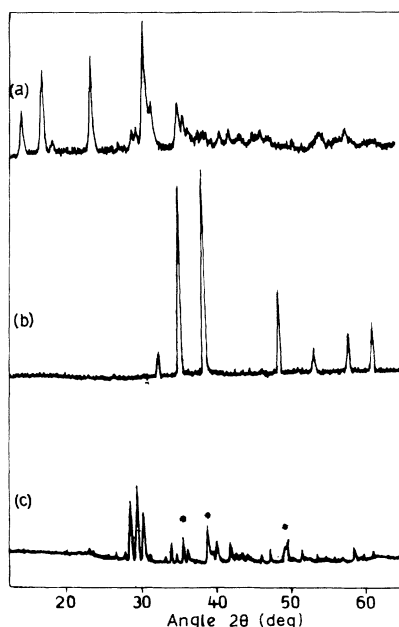


FIG. 4. XRD of (a) untreated $\text{CuCO}_3\text{Cu}(\text{OH})_2\text{H}_2\text{O}$, (b) $\text{CuCO}_3\text{Cu}(\text{OH})_2\text{H}_2\text{O}$ annealed at 700°C, and (c) CuO + BaO heated at 875°C (* shows line due to CuO).

and one sharp high-field signal) as that for CuO and the explanation is the same. The only difference noted was that here the spectrum made its first appearance at 300°C, earlier in comparison to CuO, which may be due to the dilution effect of BaO molecules in the CuO chains. After the first appearance of the signal on raising the annealing temperature, the pattern of the spectrum undergoes marginal changes, but presumably of not much significance. A preliminary account of this investigation has been reported previously.^{21,22} On annealing the sample only in the small temperature interval of 850–900°C, very complex spectra are generally produced and with little variation in appearance from sample to sample. It was observed that all the spectra that were obtained in CuO appeared here also, either singly or in combinations of 2's or 3's. The signals which were seen both in CuO and in CuO + BaO will not be shown here again. In the CuO + BaO system, the 13-component signal appeared in two forms; one as in CuO and the other where it was overlapped by another very strong signal (at $g \approx 2$) as shown in Fig. 5. The whole pattern could be seen together only when the spectrum was recorded on very low gain [Fig. 5(a)]. At reduced gain and due to the domineering presence of the stronger signals, it was difficult to decipher all the 13 components clearly. Eight components may be seen on the left-hand side [Fig. 5(b)] and three components on the right-hand side of the strong signal [shown in Fig. 5(b')], if these portions are recorded separately on higher gain. The position of the rest two lines superimposed on the stronger signal can also be guessed from the minute changes seen in the gradients of the much stronger signal.

The additional feature obtained here was the occurrence of an eight-line pattern starting from near-zero field to the $g \approx 2$ region plus two strong signals near $g = 2$ (as also seen in Fig. 5). The latter two signals are attributed to BaCuO_2 formed due to the solid-state reaction at this temperature.^{7,8} This spectrum is illustrated in Fig. 6. The eight-line pattern can be interpreted as parallel and

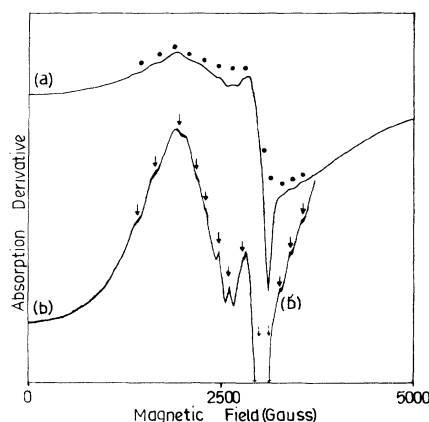


FIG. 5. EPR spectrum of CuO + BaO reacted at 875°C, (a) showing the 13 component broad signal plus the strong signal at $g \approx 2$, (b,b') spectrum taken partially at higher gain showing clearly the lines. ↓ Indicates the two signals which could not be accommodated in the figure.

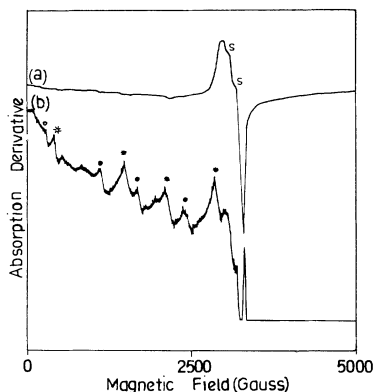


FIG. 6. EPR spectrum of CuO + BaO reacted at 875°C showing the eight signal pattern. (S) shows the two strong additional signals at $g \approx 2$. (*) and (●) indicate the two sets of four lines.

perpendicular components of a species with resultant electronic spin $S = 2$. As the single crystal of the specimen could not be prepared, the detailed analysis could not be done. It is plausible to assume that the electronic spin $S = 2$ is obtained here by the cyclic exchange among four copper ions, and these aggregates are under the influence of neighboring barium ions.

An x-ray-diffraction pattern of the sample is also carried out and shown in Fig. 3(c). All the lines reported in the XRD of BaCuO₂ (Refs. 6 and 23) are present here with the same relative intensity. It contains the main lines of CuO also [shown by * in Fig. 3(c)]. It shows that the sample mainly contains BaCuO₂ and a small amount of CuO. Therefore, the persistence in the CuO + BaO system of all those spectra, seen in pure CuO, is justified. BaCuO₂ is the main constituent here and it shows its stronger presence in almost all the spectra. Rarely, a spectrum can be obtained where the strong EPR signal at $g \approx 2$ due to BaCuO₂ is not seen. It seems that in the CuO + BaO system also, copper aggregates are formed in scattered patches and are magnetically isolated from the main lattice.

While looking for the mechanism of high- T_c superconductivity, four-spin exchange among copper ions may be considered as a suitable candidate as has also been suggested by some workers.^{24–29} However, CuO, in which four-spin cyclic exchange has been seen presently, is not a superconductor and its structure,³⁰ is different from those of high- T_c superconductors and much more work is needed to establish any connection between four-spin cyclic exchange and the true mechanism of high- T_c superconductivity.

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