

EPR as a necessary complement of magnetic measurements in exchange coupled systems

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Abstract. Several examples are shown in which the complementary use of temperature dependent magnetic susceptibility measurements and EPR spectroscopy has provided information which neither technique alone could have given in the study of exchange coupled systems. For instance it is shown how EPR can help in determining the exchange pathways whose existence is observed from magnetic susceptibility measurements and more applications to monitoring weak exchange interactions determining the magnetic dimensionality, disclosing the nature of paramagnetic impurities, looking in detail into the multiplet structure of exchange coupled systems.

Keywords. EPR spectroscopy; magnetic susceptibility; exchange interactions; paramagnetic impurities; exchange coupled systems.

1. Introduction

In the study of the exchange interactions between paramagnetic centers, two techniques are most useful, namely magnetic susceptibility measurements and EPR spectroscopy. It is well-known that the information provided by them is largely complementary, the former giving an average answer from all the magnetic centers possessing different energies, while the latter can give, and in most cases it does give, the response of each individual set of centers characterized by one energy level. For instance, if we consider the case of a pair of spins $S_1 = 1/2$, $S_2 = 1$ which are strongly coupled, the total spin $S = S_1 + S_2$ is a good quantum number, yielding a quartet and a doublet. Magnetic susceptibility depends on the relative population of the two multiplets, and measuring it as a function of the temperature usually yields the energy separation between the two spin states. On the other hand EPR spectra, in the most favourable case, can show separately the doublet and the quartet, giving precious information on the details of the g tensor and of the zero field splitting tensor D , which can be obtained with difficulty through magnetic susceptibility measurements, and further on the hyperfine and superhyperfine tensors which the latter technique cannot provide. EPR is also extremely useful in monitoring weak exchange interactions, which can be obtained by magnetic susceptibility measurements only by going to extremely low temperatures, and in revealing the nature of paramagnetic impurities which can be present in the lattice. Finally using EPR it is often possible to obtain unequivocal answers on the magnetic dimensionality, which in many cases may not correspond to the structural dimensionality.

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From the above considerations one might conclude that EPR is a much stronger tool for the analysis of the magnetic coupling than the temperature dependent susceptibility measurements, but this is simply not true, since, for instance, the former can generally yield with only a low accuracy the energy separation between the thermally populated multiplets. The reason for this is that the method for determining the relative energies of the multiplets through EPR is that of measuring the signal intensities as a function of the temperature and comparing these with that of a Curie paramagnet standard. Intensity measurements in EPR are never very accurate because they are obtained by double integration of the observed signal and the possibility of overlap of different lines makes it a difficult problem even for modern spectrometers equipped with fast computers.

The conclusion of this introduction is therefore that magnetic susceptibility measurements and EPR spectroscopy are largely complementary techniques, which should always be combined in order to obtain the required knowledge of the thermally populated energy levels of exchange coupled systems. A statement like this might be conclusive, but in order not to be axiomatic, it is important to show its validity through examples, which we will take from our own experimental work on di-, tri-, tetra- and polynuclear exchange coupled systems.

In order to avoid confusion we state here that throughout this paper the exchange hamiltonians will be of the form:

$$H = \sum_{i,j} J_{ij} S_i \cdot S_j.$$

2. EPR helps in finding lost exchange pathways

We recently reported (Laugier *et al* 1986) the structure and the magnetic properties of a complex of formula $\text{CuCl}_2(\text{NITPh})_2$, where NITPh is the radical 2-phenyl-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxide whose formula is sketched below.

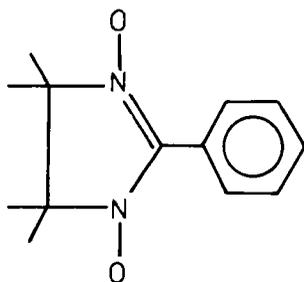


Chart 1.

The two N–O groups are completely equivalent by resonance, a result which is confirmed by the solution EPR spectra of the radical. The X-ray structure of the complex showed that two nitroxides are bound to a copper ion(II), each through one oxygen atom. The coordination of the metal ion is square planar CuO_2Cl_2 as shown in figure 1. The magnetic moment at room temperature corresponds to one unpaired electron *per* CuO_2Cl_2 unit, showing that the three spins $1/2$ are strongly coupled in an antiferromagnetic fashion to yield a ground doublet well-separated from other excited multiplets. The polycrystalline powder EPR spectra at room temperature give a *g* value in agreement with this view. However, on cooling, the

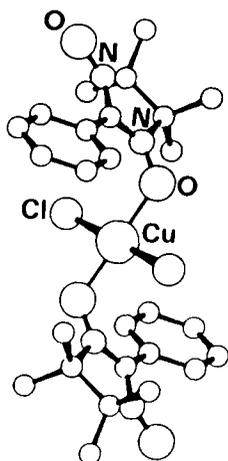


Figure 1. View of the molecular structure of dichloro-bis-(2-phenyl-4,4,5,5-tetramethyl imidazoline-3-oxide-1-oxyl) copper(II), $\text{CuCl}_2(\text{NITPh})_2$. (After Laugier *et al* 1986.)

magnetic susceptibility goes through a maximum at ~ 15 K, showing that some intermolecular antiferromagnetic interaction must be operative. In principle this interaction might be given by dimerization of the $\text{CuCl}_2(\text{NITPh})_2$, by a chain structure, or by three-dimensional order. The experimental points could be reasonably well-fitted with the chain model (Bonner and Fisher 1964), and not with the dimer model (Bleaney and Bowers 1952), but the problem of where the chain was remained. Looking more carefully at the structure one could find two reasonably short contacts, one between the hydrogen atom of the phenyl group of a NITPh radical with the chlorine of another CuO_2Cl_2 moiety, 284.4 pm, and another one between the N–O groups of two nitroxides belonging to two different $\text{CuCl}_2(\text{NITPh})_2$ molecules, at 394 pm. Although the latter would seem more reasonable for an effective exchange, the former could not be excluded a priori. Single crystal EPR spectra provided a definitive answer because they showed two signals corresponding to the two magnetically non-equivalent sites of the monoclinic cell. This means that the exchange pathway connects equivalent CuO_2Cl_2 moieties, therefore the H–Cl contact must be ruled out, as this is relative to a pair of magnetically non-equivalent sites in the unit cell. On the other hand the N–O contact connects $\text{CuCl}_2(\text{NITPh})_2$ molecules which are related by a translation parallel to c . This connection yields chains parallel to the c axis which are totally compatible with the EPR results.

3. EPR is sensitive to weak exchange interactions

A beautiful example of the sensitivity of EPR to weak exchange interactions is provided by the magnetic properties (Journaux *et al* 1985) of $\text{Cu}(\text{salen})\text{Ni}(\text{hfac})_2$ (salen = N,N'-ethylenebis(salicylaldiminato); hfac = hexafluoro acetyl acetonato). The crystal structure of this complex showed that it comprises the units of figure 2 and the magnetic susceptibility in the range 1–300 K was satisfactorily fit with a coupling constant $J = 23.6 \text{ cm}^{-1}$. This means that of the two states which

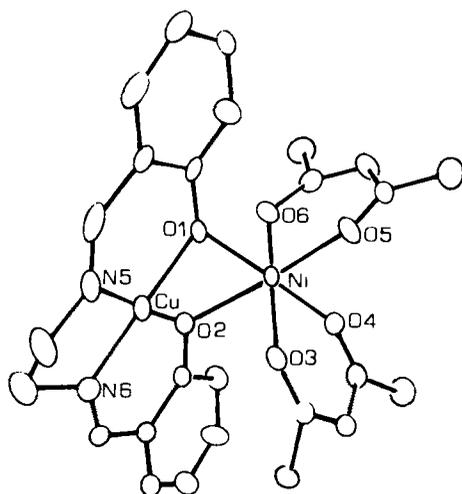


Figure 2. Perspective view of the $\text{Cu}(\text{salen})\text{Ni}(\text{hfac})_2$ unit (salen = N,N' -ethylenebis(salicylaldiminato)); hfac = hexafluoro acetyl acetonato). (After Journaux *et al* 1985.)

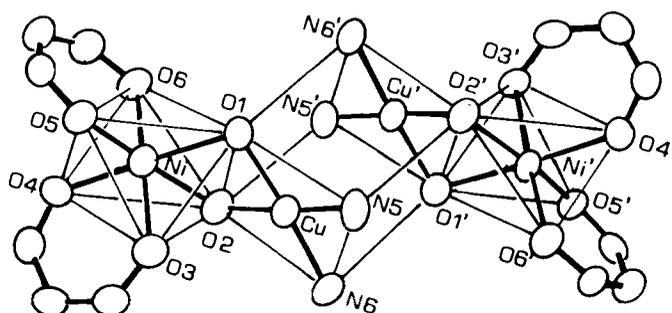


Figure 3. Schematic representation of the bis heterobinuclear entity $[\text{Cu}(\text{salen})\text{Ni}(\text{hfac})_2]_2$. (After Journaux *et al* 1985.)

are obtained by coupling $S_{\text{Cu}} = 1/2$ and $S_{\text{Ni}} = 1$ the doublet is 35.4 cm^{-1} below the quartet. However, the EPR spectra do not correspond either to a doublet or a quartet, but to a triplet! This result can be rationalized only by assuming that each $\text{Cu}(\text{salen})\text{Ni}(\text{hfac})_2$ is actually dimerized in the cell in such a way that the two $S = 1/2$ states couple to give a singlet and a triplet. Indeed a closer look to the crystal structure showed that each copper ion is related to another one, at $343.2(1) \text{ pm}$, by an inversion center, as shown in figure 3. The combined use of the magnetic susceptibility and of the EPR data allowed us to suggest the order of levels shown in figure 4. It must be stressed that only the use of the two techniques together could yield such a detailed knowledge of the nature of the low lying energy levels of $\text{Cu}(\text{salen})\text{Ni}(\text{hfac})_2$.

Also smaller values of exchange interactions can be monitored through studies of the linewidths seen in the EPR spectra (Huang and Soos 1974; Hughes *et al* 1975; Kuppersamy and Manoharan 1985).

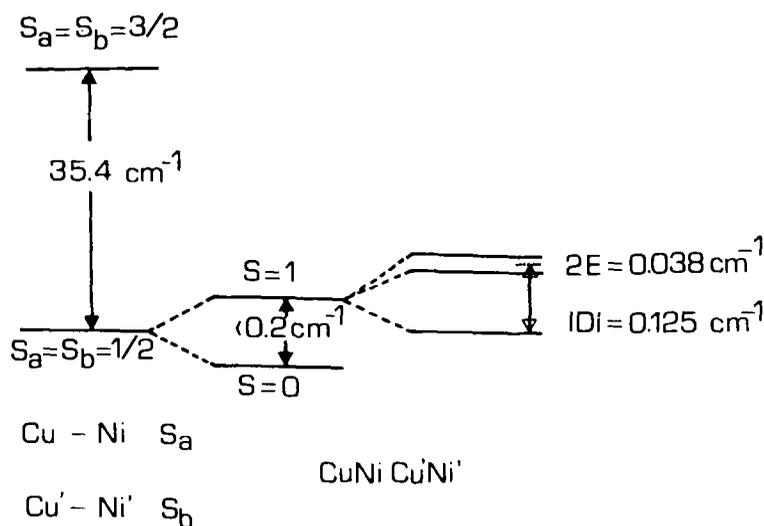


Figure 4. Low-lying states in $[\text{Cu}(\text{salen})\text{Ni}(\text{hfac})_2]_2$. (After Journaux *et al* 1985.)

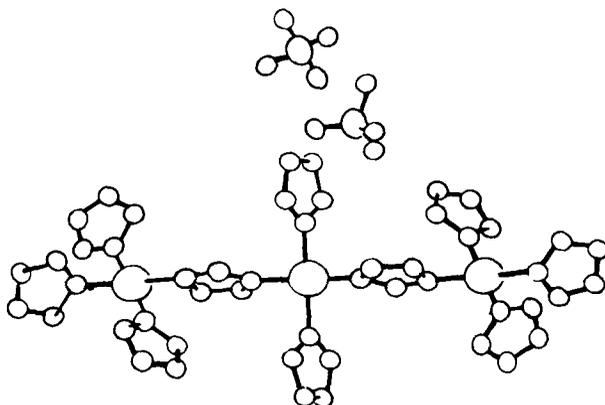


Figure 5. Sketch of the trinuclear unit of catena-*bis*(μ -perchlorato)-[*bis*(μ -imidazolato)-*bis*(perchlorato) *octakis* (imidazole) tricopper(II)], $[\text{Cu}_3(\text{iz}^-)_2(\text{iz})_8](\text{ClO}_4)_4$. (After Benelli *et al* 1984.)

4. EPR helps defining the magnetic dimensionality

One of the well-known problems encountered in the interpretation of the magnetic properties of polynuclear compounds is whether from the arrangement of the paramagnetic species obtained from the X-ray structure it is immediately possible to decide the magnetic dimensionality, i.e., whether magnetically the compound behaves as a cluster, a one-, two- or three-dimensional magnet. This problem has been discussed often (Jansen *et al* 1978; Willett 1978; Snit *et al* 1979; Hall *et al* 1981; Hatfield 1981) and we have found some cases where it could be solved complementing magnetic susceptibility measurements with EPR spectra.

Catena-*bis*(μ -perchlorato)-[*bis*(μ -imidazolato)-*bis*(perchlorato) *octakis* (imidazole)tricopper(II)] comprises trinuclear units $[\text{Cu}_3(\text{iz}^-)_2(\text{iz})_8]^{4+}$ ($\text{iz} = \text{imidazole}$), whose structure (Ivarsson *et al* 1972) is shown in figure 5, bridged by perchlorate

groups to yield a chain. The magnetic susceptibility, which shows evidence of an antiferromagnetic coupling, might in principle fit the formula appropriate to isolated trinuclear species or to an alternating chain (Benelli *et al* 1984). Indeed the EPR spectra revealed a hyperfine splitting due to the interaction of the unpaired electron with the copper nuclei, showing that intermolecular exchange interactions in this compound must be smaller than 0.013 cm^{-1} . No attempt was made therefore to fit the experimental magnetic data to the chain model, and indeed a satisfactory agreement was found to a trinuclear model.

Another interesting example is provided by $\text{Cu}(\text{hfac})_2(\text{TEMPOL})$, where TEMPOL is 4-hydroxy-2,2,6,6-tetramethylpiperidyl-N-oxyl, which is formed (Anderson and Kuechler 1980) by chains schematically indicated in figure 6. Again the problem is whether magnetically the compound behaves as an alternating chain, the two different coupling constants corresponding to the interaction of the nitroxide group with the closer and the farther copper ion respectively, or if a two-spin model is sufficient. The EPR spectra at room temperature are clearly indicative of a triplet state (Bencini *et al* 1984), suggesting that the interaction with the farther copper ion is negligible, at least in a first approximation. Indeed magnetic susceptibility measurements down to 2 K could be interpreted within a Bleaney-Bowers approximation with a ferromagnetic J value of -13 cm^{-1} , but extending (Benelli *et al* 1985) the measurements down to 40 mK a maximum in the susceptibility could be observed at $\sim 80 \text{ mK}$, which was attributed to an antiferromagnetic interaction of 0.054 cm^{-1} between the nitroxide and the farther copper ion.

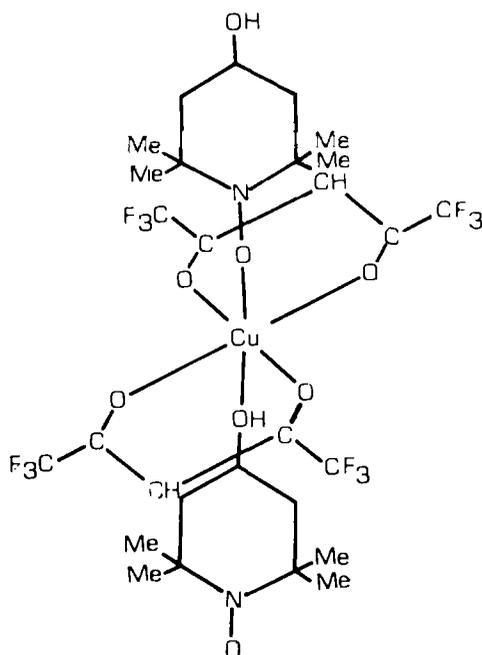


Figure 6. Sketch of the chain structure of *bis*(hexafluoroacetylacetonato)(4-hydroxy-2,2,6,6-tetramethyl piperidiny-N-oxyl) copper(II), $\text{Cu}(\text{hfac})_2\text{TEMPOL}$. (After Bencini *et al* 1984.)

5. EPR helps in revealing the nature of paramagnetic impurities

One of the most common problems encountered in the analysis of the magnetic data of antiferromagnetically coupled dimers, is that at low temperatures the magnetic susceptibility goes through a maximum and then decreases, but eventually, on further lowering the temperature, increases again. This result is usually interpreted as due to the presence of a paramagnetic impurity, which can give important effects at low temperature when the lattice becomes essentially diamagnetic.

EPR spectra can substantiate this assumption, by disclosing the nature of the impurity. A classical example is provided by copper acetate type complexes, in which the dinuclear species are antiferromagnetically (Abe and Shimada 1953) coupled. At a low temperature a spin doublet spectrum is readily observed, which must be assigned to isolated copper (II) ions. The g values of this species are identical to those of the dinuclear species, while the A values are twice as large. These results are generally justified as due to the presence of monomeric copper impurities, most probably associated with defective sites in which the second copper ion of the dimer is missing.

Recently we observed a more unusual impurity in an asymmetric dinuclear species (Bencini *et al* 1986) $[(\text{dien})\text{Cu}(\text{ox})\text{Cu}(\text{tmen})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (dien = N,N',N''-diethylene triamine; ox = oxalato; tmen = N,N,N',N'-tetramethylethylenediamine). Magnetic susceptibility measurements (Julve *et al* 1983, 1984) revealed that the inequivalent copper ions, which are bridged by an oxalato group, with an overall geometry as shown in figure 7, are antiferromagnetically coupled with a singlet-triplet separation of 75.5 cm^{-1} . Below 25 K the magnetic susceptibility increases rapidly, suggesting the presence of a paramagnetic impurity. Extending to this asymmetric dinuclear species the interpretation given for symmetric dimers above, two different kinds of "monomeric" impurities could be expected, one in which copper is in the dien environment and the other in which copper is in the tmen environment. The EPR spectra at low temperatures, however, showed the presence of a triplet species containing two equivalent copper ions. Since the spectra could be detected down to 4.2 K in this symmetric dinuclear species the two copper ions must be weakly coupled. The comparison with previous literature data (Felthouse *et al* 1977) suggested that the species responsible for the EPR spectra is $[(\text{dien})\text{Cu}(\text{ox})\text{Cu}(\text{dien})]^{2+}$.

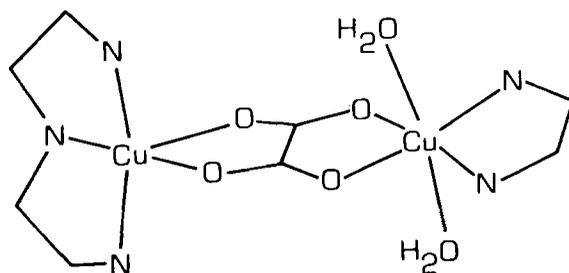


Figure 7. Overall geometry coordination in $[(\text{dien})\text{Cu}(\text{ox})\text{Cu}(\text{tmen})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (dien = N,N',N''-diethylene triamine; ox = oxalato; tmen = N,N,N',N'-tetramethyl ethylenediamine). (After Bencini *et al* 1986.)

From this it is apparent that in molecular lattices also there is a possibility of hosting molecules which are largely different from the building blocks of the parent lattice and that it might be desirable to investigate in more detail the nature of the "impurities" which can be formed in the normal synthetic procedure.

6. EPR looks in detail into the multiplet structure

This is the most obvious application of EPR spectroscopy, that of measuring the spectra of each individual multiplet generated by the exchange interaction which is thermally populated, in order to characterize it fully. Beyond the simple case of two $S = 1/2$ states, in the last few years many more examples have been worked out for a variable number of coupled spins of variable multiplicity (Gatteschi and Bencini 1985; Kahn 1985). It is in this field that much work remains to be done in order to understand which are the factors making the observation of the EPR spectra of some multiplets easy, and much more difficult for other ones. For instance, several Cu-Ni pairs have been characterized (Kokozsha *et al* 1967; Bencini *et al* 1980; Buluggiu 1980; Banci *et al* 1981a, b, 1982; Bencini and Gatteschi 1985; Gatteschi and Bencini 1985; Journaux *et al* 1985), which yield a quartet and a doublet, but to our knowledge, in no case have both been characterized in the same compound by EPR spectroscopy. Indeed, in general the doublet spectra are rather easily observed, but the spectra in the quartet state has to our knowledge been reported only in one case in which the coupling is ferromagnetic (Bencini *et al* 1980). Probably it is relaxation factors which are dominant: for an antiferromagnetic couple the lines of the quartet at high temperatures are broad, and at low temperatures, where presumably relaxation might be slow enough, the quartet is depopulated.

More interesting results could be obtained in the case of copper-manganese pairs where the spectra of both the $S = 2$ and $S = 3$ states were observed. $\text{Cu}(\text{prp})_2\text{enMn}(\text{hfac})_2$ (Hall *et al* 1981), where $(\text{prp})_2\text{en}$ is the Schiff base formed by 2-hydroxypropiophenone and ethylenediamine, hfac is hexafluoroacetyl-acetonato, contains dinuclear species (O'Connor *et al* 1979) in which the copper(II) ion is in a square planar environment and manganese(II) is octahedral, as shown in figure 8. Magnetic susceptibility measurements showed that the $S = 2$ state lies 78 cm^{-1} lower than the $S = 3$ state. EPR spectra showed (Banci *et al* 1981c) that the g values of the two multiplets are different, as expected (Gatteschi and Bencini 1985), and also that the zero-field splitting tensors differ. This result should also be kept in mind for the interpretation of the magnetic data, allowing for different g values in the various multiplets.

Things become more complicated for three- and tetranuclear species, where the number of thermally populated states increases. EPR spectra of both the ground $S = 3/2$ and of an excited $S = 5/2$ state were observed for $\text{Mn}(\text{hfac})_2$ (TEMPO)₂ and $\text{Mn}(\text{hfac})_2$ (PROXYL)₂ (TEMPO = 2,2,6,6-tetramethyl piperidinil-N-oxy; PROXYL = 2,2,5,5-tetramethylpyrrolidinil-1-oxy) (Benelli *et al* 1986a). In these complexes the metal ion ($S = 5/2$) is octahedrally coordinated to two nitroxides and two hexafluoroacetylacetonate ions (Dickman *et al* 1986). The coupling was found by magnetic susceptibility measurements to be antiferromagnetic, $J = 158 \text{ cm}^{-1}$ and $J = 210 \text{ cm}^{-1}$ for the TEMPO and PROXYL derivative

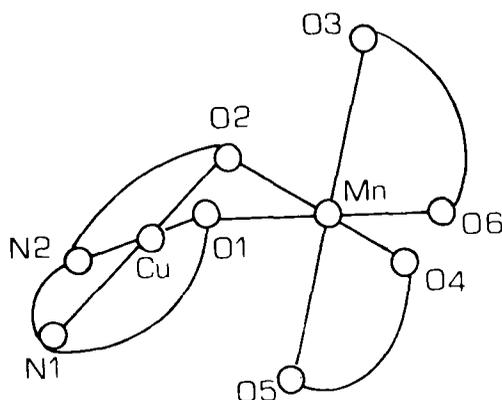


Figure 8. Sketch of the $\text{Cu}(\text{prp})_2\text{enMn}(\text{hfac})_2$ complex ((prp)₂en = Schiff base formed by 2-hydroxypropiophenone and ethylenediamine. hfac = hexafluoroacetylacetonato). (After Banci *et al* 1981c.)

respectively. The possible total spin states are $S = 3/2, 5/2, 5/2$ and $7/2$ and the EPR spectra helped in confirming the order of the two different sextuplet states. Indeed the spin hamiltonian parameters of the different multiplets are different and an analysis of the zero field splitting tensors allowed us to identify the $S = 5/2$ of which we observed the EPR spectra.

It is perhaps useful to mention here that although we have studied the EPR spectra of several trinuclear species containing three $S = 1/2$ spins we never observed (Banci *et al* 1983a, b; Bencini *et al* 1985a; Benelli *et al* 1986b; Gatteschi *et al* 1987) the spectra of the quartet and of the two doublets which are generated by the exchange interactions, and generally only one averaged signal is observed. The reason for this is not clear, although intermolecular exchange can be considered to be important.

7. Conclusions

We hope to have shown the many different kinds of information that can be obtained from the analysis of the EPR spectra of exchange coupled systems. Due to the limit of space we had to confine the treatment to our own work, but many more might be found in the literature. Perhaps the most important examples might be those relative to one- and two- dimensional magnets, where the analysis of the EPR spectra yielded unvaluable information on the spin dynamics (Drumheller 1982). Also in the study of biological compounds, in which a magnetic coupling is present, EPR spectra have been of fundamental importance for recognizing the nature of the centers (Palmer 1983; Solomon and Wilcox 1985; Bencini *et al* 1985b, c). We feel that this technique, which is now slightly older (Zavoisky 1945) than forty years, is still young and vital, and has still many important results to provide.

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