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Anomalous electron-spin-resonance angular intensity variation in the two-chain compound N-ethyl-N-ethyl morpholinium tetracyanoquinodimethane [DEM(TCNQ)$_2$]

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The spin susceptibility and electron-spin-resonance (ESR) linewidths of the two inequivalent TCNQ sheets in DEM(TCNQ)$_2$ (N-ethyl-N-ethyl morpholinium tetracyanoquinodimethane) have been measured as a function of temperature and angle. The chains on one sheet undergo a spin-Peierls transition at 23 K. The other sheet remains paramagnetic down to 1.5 K. An anomalously large angular dependence of the ESR intensity for both sheets is observed. The intensity variation is such that the total susceptibility is isotropic. The g factors behave in a way typical for TCNQ with a small anisotropy. This behavior of the ESR intensity indicates either a large anisotropy of the subchain susceptibilities or a resonance involving a coupled mode in the paramagnetic region. The nature of such a coupled mode has to date eluded explanation.

I. INTRODUCTION

Recent interest in the morpholinium tetracyanoquinodimethane (TCNQ) salts stems from the identification of a spin-Peierls transition in N-methyl-N-ethyl morpholinium [MEM(TCNQ)$_2$].[1] In an effort to better understand the mechanism producing the spin-Peierls transition it was decided to study two other morpholinium TCNQ salts. HEM(TCNQ)$_2$ (HEM denotes N-ethyl-morpholinium) and DEM(TCNQ)$_2$ (DEM denotes N-ethyl-N-ethyl-morpholinium). In HEM(TCNQ)$_2$ the structure was found to exhibit tetramerized, i.e., $2k_F$ distorted, TCNQ chains already at room temperature.[2] A detailed study of the magnetic susceptibility has been reported.[3] Early bulk magnetic susceptibility measurements on MEM(TCNQ)$_2$ and DEM(TCNQ)$_2$ as a function of temperature ($4 < T < 300$ K) indicated that the two compounds were qualitatively analogous.[4]

Morssink and van Bodegom[5] have recently reported the detailed crystal structure of DEM(TCNQ)$_2$ at 294 K. They found that unlike the MEM- and HEM(TCNQ)$_2$ salts, DEM(TCNQ)$_2$ possesses two inequivalent TCNQ sheets, separated by the DEM$^+$ ions. One sheet, labeled B, is very similar to the stacking in MEM(TCNQ)$_2$ at 113 K (Ref. 6) and consists of parallel dimerized chains. The other sheet, labeled A, is quite different in that it appears more two dimensional (2D) like. An exploratory ESR study revealed two well-separated narrow lines identified with the inequivalent TCNQ dimers of the two sheets. This suggests that the interaction between the sheets is extremely small and facilitates a study of the spin susceptibility of each sheet.

This paper presents a detailed study of the spin susceptibilities of the two chains as functions of temperature ($1.5 < T < 300$ K) and angle. It is found that the spin susceptibility of the TCNQ chain which is structurally similar to the MEM(TCNQ)$_2$ also exhibits a spin-Peierls phase transition at 23 K compared to 19 K for the MEM(TCNQ)$_2$.[1] The other TCNQ chain does not possess such a phase transition down to 1.5 K. A most surprising and as yet unexplained feature of the spectra is the very large anisotropy of the separate spin susceptibilities.

II. STRUCTURE

A projection of the structure of DEM(TCNQ)$_2$ is given in Fig. 1. Clearly two groups of inequivalent TCNQ ions can be distinguished. The TCNQ-A's as well as the TCNQ-B's are stacked parallel to the ac plane and separated by sheets of diamagnetic DEM$^+$ ions, which makes interaction between A and B ions fairly small. The normal projection of the B sheet along the longest molecular axis is given in Fig. 2. B and B' form a dimer. The interdimer overlaps BB'' and BB''' are given in Fig. 3(a). Clearly the overlap BB'' is much larger than the overlap BB''' so this sheet can be considered as consisting of weakly interacting 1D chains.

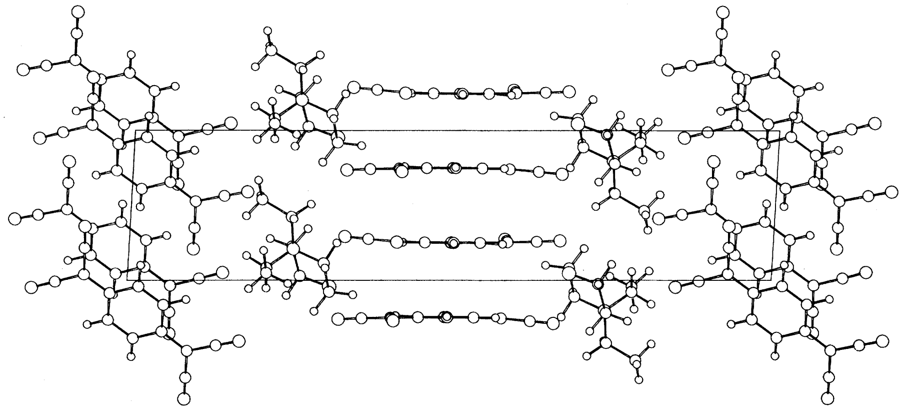

FIG. 1. Projection of the structure of DEM(TCNQ)$_2$ along [100] onto the plane perpendicular to [100].

The analogous overlaps AA'' and AA''' in the A sheet are given in Fig. 3(b). Though the overlap AA''' is probably larger than the overlap AA'' the difference may be small and in that case the A sheet should be considered as consisting of strongly interacting chains (i.e., a two-dimensional spin system).

III. SPIN SUSCEPTIBILITY

The bulk susceptibility of DEM(TCNQ)$_2$ is qualitatively similar to MEM(TCNQ)$_2$ but less structured. The susceptibility arises from electrons on the two inequivalent TCNQ chains. These two chains can be separately studied using ESR techniques.[7] Therefore the spin susceptibility was measured by comparison with a standard sample of Si(P) using a method previously described.[8] Two factors influenced the analysis of the data. First, even at maximum separation of the two ESR lines there still remained some overlap,[7] and secondly, the line shapes are in between Lorentzian and Gaussian. To overcome these problems the data were digitally recorded and computer fit with convoluted Gaussian-Lorentzian functions. These results were compared to a simpler method of numerically integrating the data to obtain the absorption spectrum and then separating the two

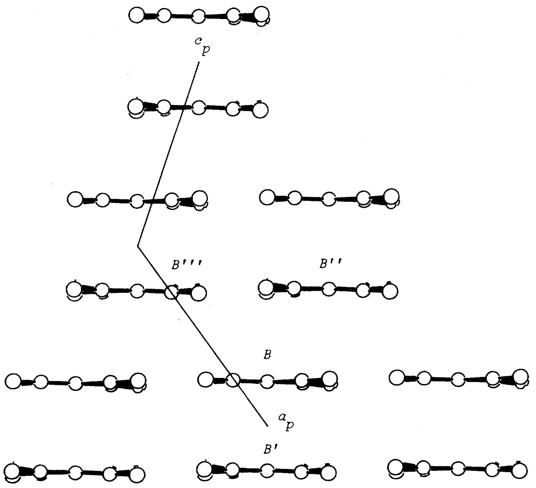

FIG. 2. Normal projection of the B sheet of TCNQ molecules in DEM(TCNQ)$_2$ along the longest molecular axis.

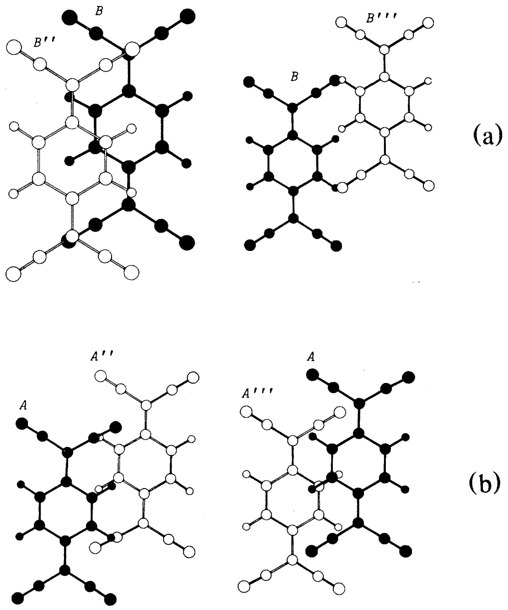

FIG. 3. Projection of two neighboring TCNQ molecules in DEM(TCNQ)$_2$ along the normal to the quinodimethane least-squares plane. (a) B-sheet molecules. (b) A-sheet molecules.

absorption peaks by assuming that they are symmetrical with negligible overlap on the outside halves. The two peaks were then cut and weighed to obtain the relative areas. The two methods agreed to within 5%.

Some typical ESR spectra at 9 GHz are shown in Fig. 4. A similar behavior is found at 35 GHz. The large variation of the relative intensity with orientation is indicative of a strong anisotropy of the susceptibility. Equally remarkable is the fact that the total susceptibility is isotropic as seen in Fig. 5 where the angular variation of the integrated ESR lines at 77 K is shown. The total ESR susceptibility agrees with the measured static susceptibility. This large apparent anisotropy is quite unexpected for TCNQ systems since the g values are nearly isotropic. In all TCNQ systems studies to date the spin susceptibility has been observed to be isotropic. Since the average susceptibility is also here isotropic the ESR spectra show that intensity is transferred from one line to the other and that this transfer of intensity is strongly angular dependent. This suggests that the ESR spectrum is that of some kind of coupled mode involving both subchains. This coupled mode must then exist even at temperatures much larger than the intrachain exchange interactions and certainly much larger than the interchain exchange interaction. Since the two lines observed occur at g values which have angular variations consistent with that expected for the two

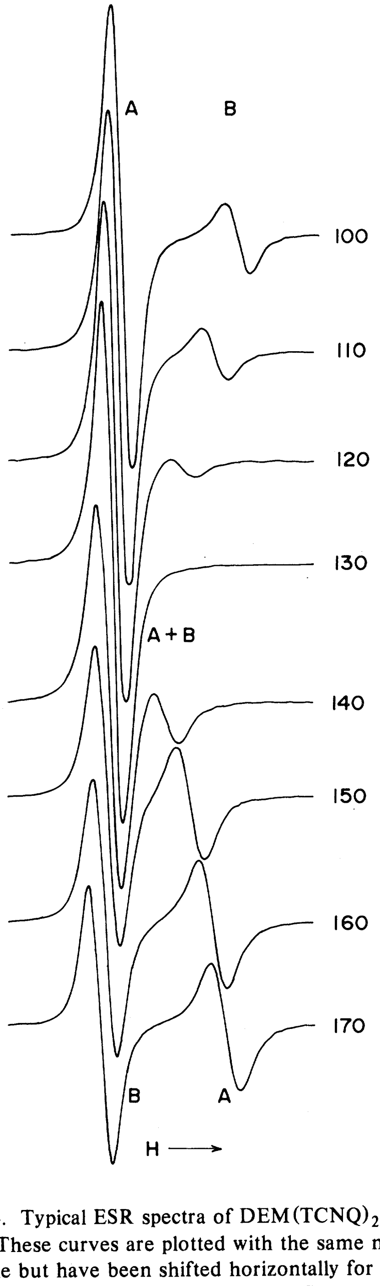

FIG. 4. Typical ESR spectra of DEM(TCNQ)$_2$ at various angles. These curves are plotted with the same magnetic field scale but have been shifted horizontally for clarification of the plot. The g values of both A and B vary as in Fig. 1 of Ref. 7.

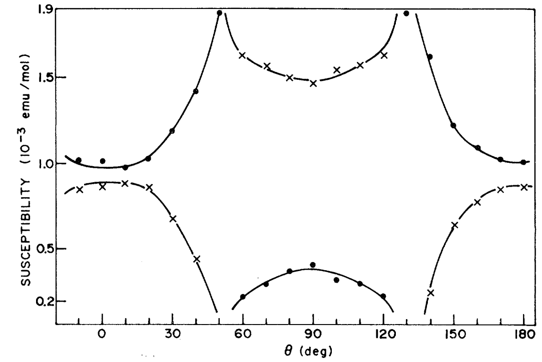

FIG. 5. Spin susceptibility determined from the area under the two integrated ESR lines as a function of angle. Crosses for sheet A and dots for sheet B.

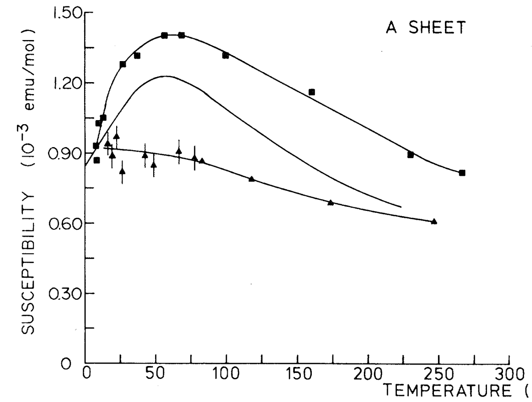

FIG. 6. Temperature dependence of the parallel and perpendicular spin susceptibilities for sheet B.

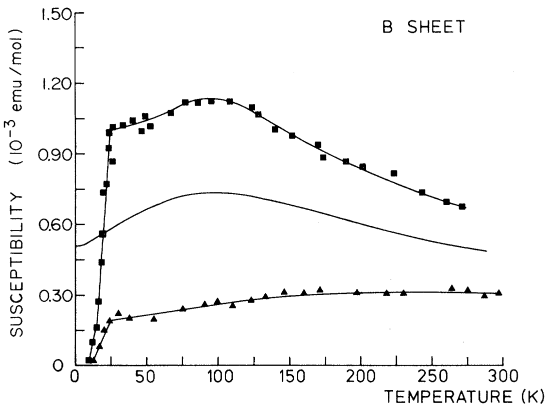

FIG. 7. Temperature dependence of the parallel and perpendicular spin susceptibilities for sheet *A*.

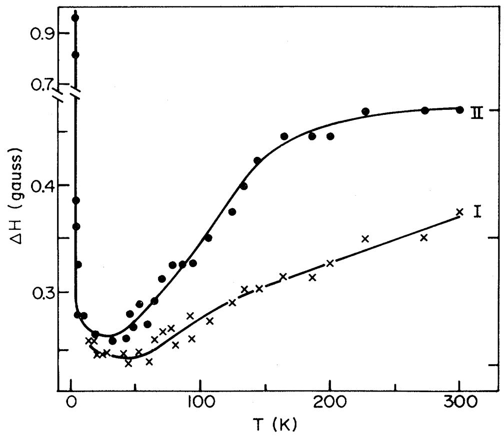

FIG. 8. ESR linewidth as a function of temperature. Dots for sheet *A* and crosses for sheet *B*.

separate chains, the coupled modes would have about the same frequency-field relation as the uncoupled chains but strongly differing intensities. The coupled modes must then have the experimentally observed properties: (1) exist high temperatures, (2) the same frequency-field dependence as the uncoupled chains, and (3) strongly angular-dependent intensities such that the total intensity is isotropic. Although we have tried various interaction couplings like Heisenberg anisotropic exchange ($d\vec{S}_1 \times \vec{S}_2$), which is possible for this crystal symmetry[9] and dipolar interactions, even a qualitative explanation of the data has *eluded* us to date.

In Figs. 6 and 7 the temperature dependence of the *A* and *B* sheet susceptibilities are shown. Also shown is the calculated Bonner-Fischer[10] susceptibility for exchange integrals of 45 and 75 K for the *A* and *B* chains, respectively. These values were taken to obtain the maximum at the correct temperature. From these data we see that the anisotropy in the susceptibility increases as the temperature decreases. This shows that the anisotropy is related to the correlation length within the sheets.

We also see that the *B* sheet chains undergo a spin-Peierls transition at 23 K below which the anisotropy in the *A* sheet rapidly decreases to zero. There is no phase transition observed for the *A* sheet down to 1.5 K. The temperature dependence of the *A* sheet linewidth, however (Fig. 8), is indicative for an approach to magnetic ordering of some kind below 1.5 K (Ref. 11).

IV. CONCLUSIONS

A detailed ESR investigation of DEM$(TCNQ)_2$ has shown that this system is composed of two very weakly coupled spin systems. One of these spin systems is one dimensional and exhibits a spin-Peierls transition at 23 K. The other system remains Heisenberg-like to 1.5 K showing some signs of an approach to magnetic ordering. This system is most likely two dimensional. We have also observed a strong anomalous anisotropy in the ESR intensity of the two systems which is probably a result of a weak coupling between them. The nature of the coupling required to result in the observed behavior is not yet understood. Recently a new system with four inequivalent chains connected by a four-fold screw axis has been found to also exhibit the anomalous ESR intensities much like that of DEM$(TCNQ)_2$. It appears therefore that this behavior is more general and may be characteristic for weakly coupled nonequivalent one-dimensional systems.

ACKNOWLEDGMENTS

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