Spin-Peierls transition in a Cu^{2+} linear chain

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We present susceptibility vs temperature and high-field (40 T) magnetization data on Cu-HTS. The data are interpreted in terms of a spin-Peierls transition at about 12 K in this antiferromagnetic $S = 1/2$ linear chain compound.

The Spin-Peierls (SP) transition |1,2| in an antiferromagnetic Heisenberg chain of spins $S = 1/2$ results from the magnetoelastic coupling between the magnetic chain system and the surrounding lattice (3-d phonon field). Below the transition temperature T_{SP} a "spontaneous dimerization" of the chains occurs, which increases progressively to a limiting value as $T \rightarrow 0$. Few experimental examples have been found so far |1|, and include $TTF^{+}-CuS_4C_4(CF_3)_4$ and related compounds (Cu $\rightarrow$ Au; S $\rightarrow$ Se), as well as $MEM-(TCNQ)_2$. These materials consist of large, planar, organic molecules, and the spins $S = 1/2$ responsible for the magnetism arise from unpaired electrons situated on the TTF^+ and the $(TCNQ)_2$ groups, respectively.

Interestingly, although numerous ionic Cu^{2+} compounds have been found |3| which closely approximate the $S = 1/2$ antiferromagnetic Heisenberg chain, none of these show a SP transition. Instead, long-range 3-d magnetic order is observed below a transition temperature T_c. Clearly, once a 3-d ordered structure is established the SP transition can no longer occur. Conversely, below the SP transition the ground state becomes non-magnetic, so that the interchain couplings are rendered ineffective. Thus T_{SP} excludes T_c and vice versa |1,4|.

Apparently, for the Cu^{2+} chains one has always had $T_c > T_{SP}$. We suggest the explanation to lie in the fact that the structure of these chains is usually quite rigid in crystallographic respect. To provide strong exchange along the chains, the Cu^{2+} ions are linked together by short (e.g. ionic) superexchange bonds, whereas the chains are separated as much as possible by bulky organic molecules, bonded by weak van der Waals forces. Consequently, the occurrence of the soft mode along the chain direction needed |5|, for the SP transition is very unlikely. By contrast the planar

molecules in the above mentioned SP compounds allow much more easily the small shifts needed to produce the spin dimerization (magnetic energy gain) without too much loss in lattice energy.

A possible test of this reasoning is provided by the compound Cu-HTS (catena-hexane-dionebis (thiosemicarbanonato) copper II). In this material |6,7| the Cu^{2+} ion is part of a planar molecule (cf. fig. 1), which molecules form linear stacks with Cu-Cu distances of about 3.5 Å. Therefore, the conditions for the occurrence of a soft mode would seem to be favourable.

Our powder susceptibility data, shown in fig. 2 as a function of temperature, may be fitted quite well to the prediction for the uniform antiferromagnetic $S = 1/2$ Heisenberg chain in the range $T > 20$ K, yielding $J/k_B \cong -19.6$ K and g = 2.26. Below 18 K the χ starts to deviate and appears to fall to zero, indicating a non-magnetic phase. Defining, as in ref. 8, T_{SP} as the temperature of maximum slope in the χ vs T plot, we find $T_{SP} = 12 \pm 2$ K. The low value of T_{SP} compared to 18 K indicates a considerable degree of short-range order to be involved in this transition.

The magnetization curve at 1.2 K up to 40 T has been measured in the pulsed field magnet of our Laboratory |9|. The result, shown in fig. 3, cannot be fitted satisfactorily with predictions for alternating chains, in contrast with our earlier studies of such systems |10,11|. This seems to confirm the assignment of a Spin-Peierls dimerization. The critical field needed to depin the dimerization vector can be calculated from T_{SP} according to the formula |1| : $\mu_B H_c \approx 0.7$ kT_{SP}. With $T_{SP} = 12$ K we obtain $H_c \approx 12$ T, in agreement with the data in fig. 3. In the same figure we show the magnetization curve for the uniform chain |12| calculated with the parameters found for
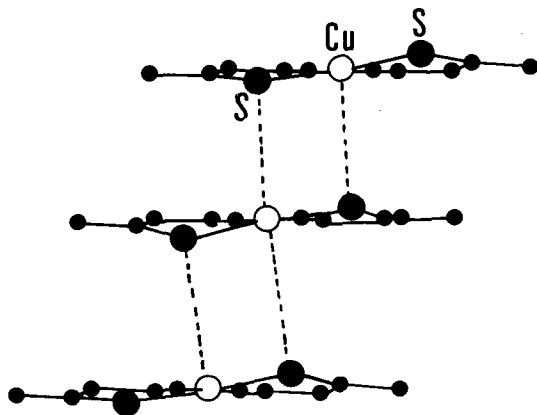

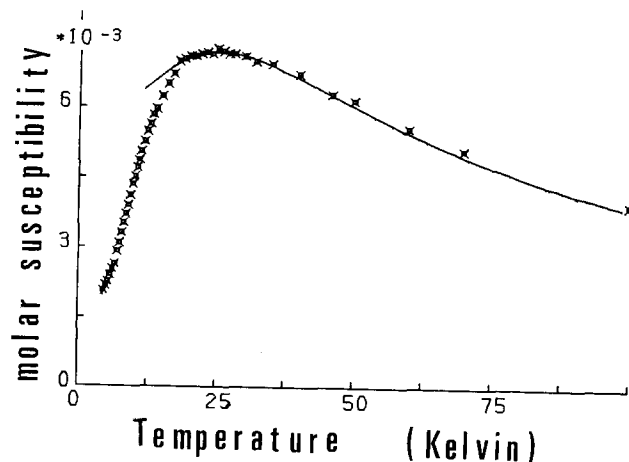Fig. 1 : Linear stacking of the Cu-HTS molecules (from ref. 6).

Fig. 2 : Powder-susceptibility of Cu-HTS. Solid curve is the susceptibility for the uniform chain.
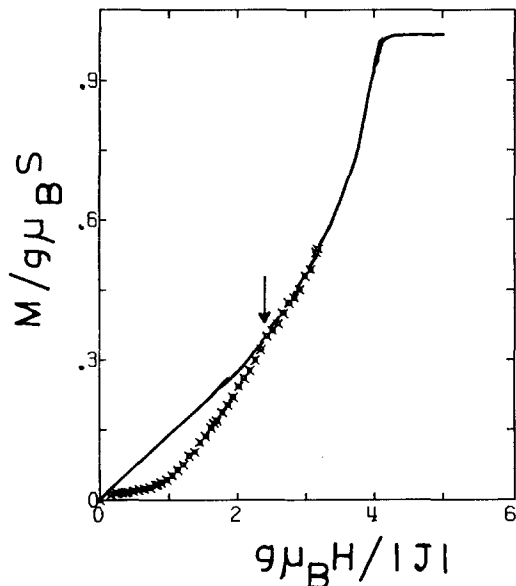
Fig. 3 : High-field magnetization of Cu-HTS. Solid
curve shows the magnetization for the uniform
chain ($|J|/g\mu_B$ corresponds to 13 T).

Fig. 5 : Attempt to fit the magnetization curve of Cu-HTS
with an alternating chain model.

T > 20 K from the susceptibility. One observes that
for H $\gtrsim$ 30 T the data coincide with this curve,
indicating that above this value the uniform phase is
retrieved (arrow in fig.3).
As noted already, we are unable to fit the susceptibi-
lity and magnetization data simultaneously to predic-
tions for the alternating S=1/2 antiferromagnetic Hei-
senberg chain. This is demonstrated in figs. 4 and 5.
Although the susceptibility data could be approximated
by an alternating chain curve with an alternation ra-
tio of say $\alpha \gtrsim 0.9$ (fig.4), such values are incompati-
ble with the behavior of the magnetization, as is evi-
dent from fig.5. In order to obtain a fit that approa-
ches the steep part of the lower half of the magneti-
zation curve, a value of $\alpha \lesssim 0.6$ is required, but even
then one is left with a quite unsatisfactory fit for
the other parts of the curve. In our opinion this ex-
cludes an explanation of our experiments in terms of
an alternating chain model.
We remark that our susceptibility data differ some-
what from previously published results by Hatfield
and coworkers |7|. We attribute this to differences
in preparation methods, since we have observed that
the magnetic properties of the endproduct are diffe-
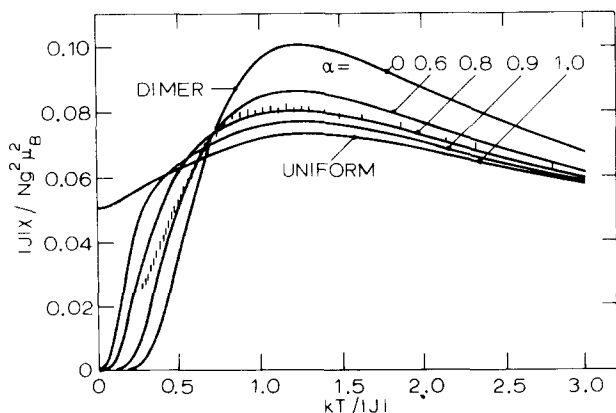rent depending on the solvent used.

The observed short-range order effects appear to
be more pronounced than in the hitherto studied SP
systems. This might be due to the fact that the ratio
$kT_{SP}/|J|$ is 3x larger in our present case. Another
explanation might be a low-dimensional character of
the phonon lattice in this material, which would
enhance the departures from mean-field behavior. Such
an anisotropy in the phonon spectrum would not be
unexpected in view of the crystallographic structure.

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Fig. 4 : Attempt to fit the susceptibility data of Cu-HTS
with an alternating chain model.

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