a critical reading of the manuscript. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

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[1] J. J. Lander, Phys. Rev. 91, 1382 (1953).

[2] J. F. McGilp and P. Weightman, J. Phys. C 9, 3541 (1976); E. D. Roberts, P. Weightman, and C. E. Johnson, J. Phys. C 8, 2336 (1975); S. P. Kowalczyk, R. A. Pollak, F. R. McFeely, L. Ley, and D. A. Shirley, Phys. Rev. B 8, 2387 (1973); E. D. Roberts, P. Weightman, and C. E. Johnson, J. Phys. C 8, 1301 (1975).

[3] E. Antonides, E. C. Janse, and G. A. Sawatzky, Phys. Rev. B 15, 1669 (1977).

[4] E. Antonides, E. C. Janse, and G. A. Sawatzky, Phys. Rev. B 15, 4596 (1977).

[5] P. J. Feibelman, E. J. McGuire, and K. C. Pandey, Phys. Rev. Lett. 36, 1154 (1976).

[6] J. A. D. Matthew and Y. Komninos, Surf. Sci. 53, 716 (1975).

[7] S. Doniach and M. Šunjić, J. Phys. C 3, 285 (1970).

[8] D. N. Zubarev, Usp. Fiz. Nauk 71, 71 (1960) [Sov. Phys. Usp. 3, 320 (1960)].

[9] J. Hubbard, Proc. Roy. Roy. Soc. London, Ser. A 276, 238 (1963).

[10] J. C. Slater, H. Statz, and G. F. Koster, Phys. Rev. 91, 1323 (1953); see also Ref. 9.

X-Ray Scattering Study of Spin-Lattice Dimerization in a Quasi One-Dimensional Heisenberg Antiferromagnet

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X-ray measurements on the quasi one-dimensional Heisenberg antiferromagnet TTF-(tetrathiafulvalenium-)$CuS_4C_4(CF_3)_4$ reveal a new crystallographic phase below $T_0 = 11$ K in which spin-$\frac{1}{2}$ TTF^+ units are paired. The temperature dependence of the order parameter below 11 K is accurately given by the BCS gap equation. Unexpectedly, the pairing is found along a diagonal direction in the $\vec{b}_F$-$\vec{c}_F$ plane rather than along the molecular stacking axis $\vec{c}_F$. Furthermore, strong diffuse scattering dominates the x-ray cross section at the dimerization superlattice positions for temperatures as high as 225 K.

The instability of one-dimensional (1D) antiferromagnetic systems to spin-lattice dimerization has been anticipated for over a decade.[1] Furthermore, the Hamiltonian used for a 1D antiferromagnetic system and that used to describe the Peierls instability in 1D conducting systems[2] are quite similar.[3] In spite of enormous effort, no quantitative synthesis of theory and experiment has yet been achieved for the 1D conductors. It is therefore of substantial importance to investigate the behavior of lattice-unstable 1D spin systems with a view toward understanding the general Peierls problem. In this Letter, we report on the results of x-ray diffuse scattering experiments in tetrathiafulvalene *bis-cis*-(1,2-perfluoromethylethylene-1,2-dithiolato)-copper [or TTF-CuBDT]. Using x-ray techniques we have (a) studied the structural nature of dimerization, (b) measured the order parameter, and (c) probed the dimensionality and spatial extent of the fluctuations. As we shall discuss below, each of these is of considerable importance in the present problem.

Jacobs *et al.*[4] have recently completed a detailed study of the magnetic behavior of the insulating charge-transfer salt TTF-CuBDT. They have shown convincingly that there exist 1D chains of antiferromagnetically coupled spin-$\frac{1}{2}$ TTF^+ units with an exchange $J = 77$ K ($H = \sum_l J\vec{S}_l \cdot \vec{S}_{l+1}$). Using the Bonner-Fisher calculation[5] they fit the magnetic susceptibility, within experimental error, from about 230 to 12 K. Below 12 K a second-order phase transition occurs in which the susceptibility breaks below the Bonner-Fisher curve and decreases isotropically to zero as $T \to 0$. This behavior is well described by the mean-field spin-lattice-dimerization model of Pytte[3] using Bulaevskii's calculation[6] for the susceptibility of the alternating chain. Such agreement strongly suggests that the reduction in magnetic energy which results from dimerization is the driving force for the transition.

Our principal results may be briefly stated. We find that below $T_0 = 11$ K new Bragg peaks develop at the Brillouin-zone corner whose temperature dependence is accurately fitted by use of the BCS gap equation. The location of these peaks implies that TTF molecules along the stacking axis $\vec{c}_F$ remain equivalent, contrary to previous speculation,[4] while pairing occurs along a diagonal direction in the $\vec{b}_F$-$\vec{c}_F$ plane. We suggest that the first-order structural transition[4] which has been characterized by Stucky and Delker[7] at $T_s \approx 240$ K is important in establishing this diagonal axis as the 1D magnetic chain axis. Studies above $T_0 = 11$ K show that the diffuse scattering is not 1D in character and that it persists as the dominant feature in the $\vec{q}$-dependent scattering up to the structural transition at $T_s \approx 240$ K.

At temperatures above 11 K the structure of TTF-CuBDT is triclinic ($P\bar{1}$) with one formula unit per crystallographic unit cell. However, it may also be described in terms of an $F\bar{1}$ lattice with a cell containing four formula units.[8] In this representation the structure is similar to rocksalt, having alternate TTF^+ and CuBDT^- units along axes which are approximately orthogonal. The lattice constants for both the $P\bar{1}$ and the $F\bar{1}$ lattices at 20, 200, and 297 K are given in Table I. The transformation between the two reciprocal lattices is given by $\vec{Q}_F = T\vec{Q}_P$, where T is the matrix which relates the real lattice vectors:

$$\begin{pmatrix} \vec{a}_F \\ \vec{b}_F \\ \vec{c}_F \end{pmatrix} = \begin{pmatrix} -1 & -2 & -1 \\ -1 & 0 & 1 \\ 1 & 0 & 1 \end{pmatrix} \begin{pmatrix} \vec{a}_P \\ \vec{b}_P \\ \vec{c}_P \end{pmatrix}.$$

In Fig. 1 we show a projection of the TTF molecules on the $\vec{a}_P$-$\vec{c}_P$ or $\vec{c}_F$-$\vec{b}_F$ plane as determined by Stucky and Delker[7] at temperatures above and below the 240 K structural transition.

Our experiments were performed with a 50-kW, rotating-anode x-ray generator. Cu $K\alpha$ x rays were focused on the sample using a vertically bent pyrolytic graphite (PG) monochromator. A flat PG crystal was used as an analyzer after the sample to decrease the background due to extraneous scattering from the cryostat windows. This system combined moderate $\vec{Q}$ resolution (~ 0.01 Å^{-1}) with a high-intensity beam to provide generous thermal diffuse scattering signals from small crystals. The crystals used in this study were typically $6 \times 0.5 \times 0.1$ mm^3 in size; their preparation is described in Ref. 4.

TABLE I. The lattice constants of TTF-CuBDT at various temperatures for both the $F\bar{1}$ and $F\bar{1}$ cells. These data are taken from Ref. 7.

	Lattice parameters			
Temperature	$F\bar{1}$		$P\bar{1}$	
20 K	$a = 23.20$	$\alpha = 105.10$	$a = 8.51$	$\alpha = 83.4$
	$b = 13.29$	$\beta = 102.10$	$b = 11.43$	$\beta = 120.6$
	$c = 7.72$	$\gamma = 95.74$	$c = 6.76$	$\gamma = 101.8$
200 K	$a = 23.392$	$\alpha = 103.77$	$a = 8.467$	$\alpha = 84.72$
	$b = 13.293$	$\beta = 100.81$	$b = 11.609$	$\beta = 119.95$
	$c = 7.794$	$\gamma = 95.76$	$c = 6.858$	$\gamma = 102.10$
297 K	$a = 23.139$	$\alpha = 92.28$	$a = 7.801$	$\alpha = 92.67$
	$b = 13.150$	$\beta = 101.80$	$b = 11.435$	$\beta = 118.09$
	$c = 7.890$	$\gamma = 90.90$	$c = 7.532$	$\gamma = 95.44$

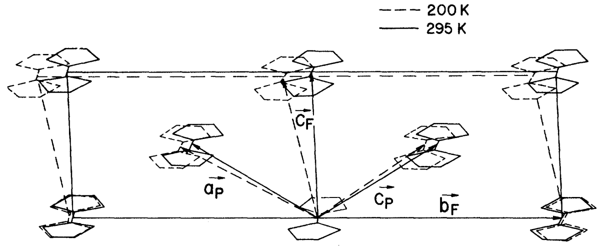

FIG. 1. A projection of the TTF molecules in TTF-CuBDT on the $\vec{a}_P$-$\vec{c}_P$ or $\vec{c}_F$-$\vec{b}_F$ plane shows the large structural distortion which occurs at $T_s \sim 240$ K. See Ref. 7.

Our initial x-ray observations were made in the $(hkh)_P = (h0l)_F$ zone. In the $P\bar{1}$ reciprocal lattice, Bragg peaks of the high-temperature structure occur with integer h, k, l coordinated with no absences, while in the $F\bar{1}$ description no mixed (both even and odd) h, k, l are allowed. Although the structural transition at 240 K causes a substantial change in lattice constants, the symmetry is unchanged,[7] and the mosaic spread usually remains narrow ($\sim 0.5°$). Our choice of the $(h0l)_F$ scattering zone was predicated on the suggestion of Jacobs *et al.* that $\vec{c}_F$ would be the 1D magnetic chain axis. A doubling of $\vec{c}_F$ would produce peaks at reduced wave vector $\vec{q} = (\zeta, 0, \frac{1}{2})_F = (\frac{1}{4}, -\zeta/2 - \frac{1}{4}, \frac{1}{4})_P$, where ζ would be determined by the interchain phasing. Our results, however, demonstrate that this is not the case. At the spin-lattice dimerization transition we find new peaks developing at $\vec{q} = (\frac{1}{2}, 0, \frac{1}{2})_P = (-1, 0, 1)_F$. One can conclude directly that alternate TTF molecules along both $\vec{a}_P$ and $\vec{c}_P$ become structurally inequivalent (see Fig. 1), while successive TTF's along $\vec{c}_F$ remain equivalent. Because the $\vec{c}_P$ axis is 1.8 Å shorter than the $\vec{a}_P$ axis, we suggest that the 1D magnetic axis is along $\vec{c}_P$. We emphasize that although the choice between $\vec{c}_P$ and $\vec{a}_P$ as the 1D axis is not a direct diffraction result, our data do explicitly eliminate all other possibilities. Here it is important to realize that the higher-temperature structural transition is responsible for the majority of the difference between the lengths of $\vec{c}_P$ and $\vec{a}_P$. This fact leads us to suggest that the system may be more nearly two-dimensional above 240 K. Furthermore, below 240 K the system may still retain some 2D character in contrast to other model 1D spin systems such as $(CH_3)_4NMnCl_3$ (TMMC).[9] However, because of the Heisenberg nature of the interaction in TFF-CuBDT, a weak 2D coupling is not sufficient to cause an ordered Néel state above 11 K.[10]

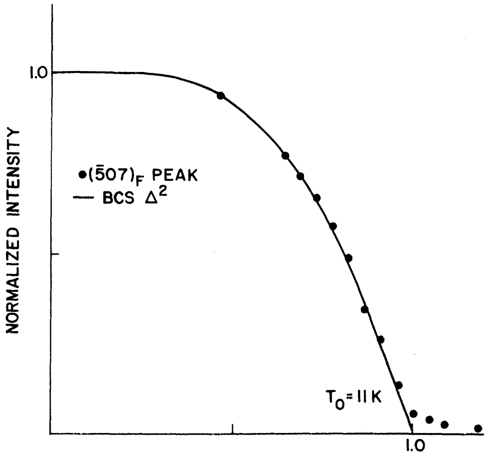

FIG. 2. The temperature-dependent intensity of the new Bragg peaks which develop upon dimerization is accurately fitted by the BCS gap function.

Figure 2 shows the temperature dependence of the intensity of the $(\bar{5}07)_F$ peak which, after normalization to unity at low temperatures, fits the square of the BCS gap function within experimental error.[11] The fit provides evidence for mean-field character of the transition for $|T/T_0 - 1| > 0.05$ in support of the analysis of the magnetic susceptibility by Jacobs *et al.* However, considerations based on the geometry and spatial extent of the critical fluctuations[12] lead us to expect deviations from mean-field behavior close to T_0.

We now consider the diffuse x-ray scattering above 11 K which provides a direct measure of the fluctuations preceding the transition. These data were obtained in the $(h0l)_P$ scattering zone. Remarkably, a strong peak is evident at $\vec{q} = (\frac{1}{2}, 0, \frac{1}{2})_P$ throughout the temperature range 11–225 K as shown in Fig. 3. Below 20 K, this scattering is approximately isotropic in $\vec{q}$ space.[13] This result implies that the lattice fluctuations are fully three-dimensional, in contrast to the magnetic fluctuations which one expects to be one-dimensional. The persistence of a pronounced peak to high temperatures indicates that a mode of very low frequency exists in this structure in the absence of substantial magnetic correlation. For example, at 225 K (20 times T_0 and 4 times J) the peak at $\vec{Q} = (\frac{5}{2}, 0, \frac{3}{2})_P$ is 50% greater than the phonon-plus-Compton background. This behavior is in marked contrast to that of TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane) where the thermal diffuse scattering at "$4k_F$" at 300 K

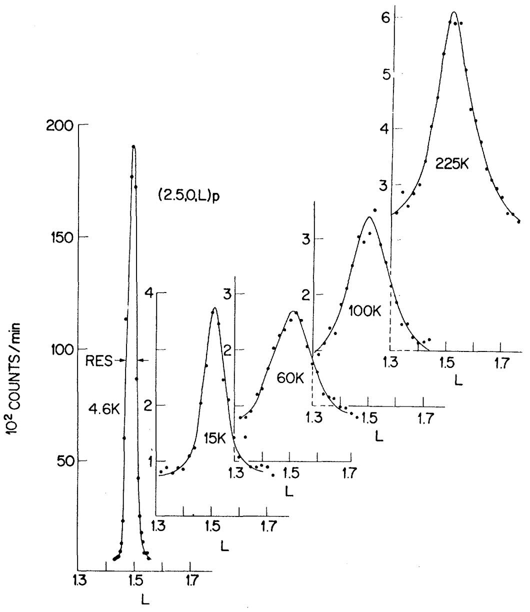

FIG. 3. Scans along $\vec{Q}=(2.5,0,l)_P$ at a number of temperatures above and below the spin-dimerization transition at $T_0 = 11$ K. A pronounced peak exists to temperatures as high as 225 K.

$\simeq 5T_0$ is less than 10% of the "background."[14]

We conclude by emphasizing the unique characteristics of TTF-CuBDT which appear to play an important role in the dimerization transition which we have observed. Firstly, a structural transition at 240 K gives rise to a 1D magnetic anisotropy in a system with no obvious concomitant structural one-dimensionality. Secondly, dimerization of TTF molecules along this axis is energetically favorable (i.e., these phonons are soft) even without magnetic interactions. To the extent that an extremely soft lattice is a prerequisite, it is not surprising that this type of phase transition has been found only rarely in nature. Clearly further detailed measurements in this model spin-dimerization system are required. Specifically, measurements of the critical behavior, a quantitative analysis of peak intensities to extract molecular displacements, and neutron-scattering studies of the lattice and spin dynamics would be valuable.

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[1] H. M. McConnell and R. Lynden Bell, J. Chem. Phys. 36, 2393 (1962); D. B. Chestnut, J. Chem. Phys. 17, 1198 (1949). See also the historical review in I. S. Jacobs, J. W. Bray, H. R. Hart, Jr., L. V. Interrante, J. S. Kasper, G. D. Watkins, D. E. Prober, and J. C. Bonner, Phys. Rev. B 14, 3036 (1976).

[2] A. J. Berlinsky, Contemp. Phys. 17, 331 (1976). See also P. A. Lee, T. M. Rice, and R. A. Klemm, Phys. Rev. B 15, 2984 (1977); W. D. Ellenson, S. M. Shapiro, G. Shirane, and A. F. Garito, Phys. Rev. B (to be published), and references therein.

[3] E. Pytte, Phys. Rev. B 10, 4637 (1974).

[4] Jacobs *et al.*, Ref. 1.

[5] J. C. Bonner and M. E. Fisher, Phys. Rev. 135, A640 (1967).

[6] L. N. Bulaevskii, Zh. Eksp. Teor. Fiz. 44, 1008 (1973) [Sov. Phys. JETP 17, 684 (1963)].

[7] G. D. Stucky and G. L. Delker, private communication. See also G. L. Delker, Ph.D. thesis, Department of Chemistry, University of Illinois, 1976 (unpublished).

[8] J. S. Kasper and L. V. Interrante, Acta Crystallogr., Sect. B 32, 2914 (1976).

[9] R. J. Birgeneau, R. Dingle, M. T. Hutchings, G. Shirane, and S. L. Holt, Phys. Rev. Lett. 26, 718 (1971).

[10] N. D. Mermin and H. Wagner, Phys. Rev. Lett. 17, 1133 (1966).

[11] Recent unpublished neutron-scattering experiments on deuterated crystals carried out by the present authors in collaboration with G. Shirane also show mean-field behavior. However, a higher transition temperature (11.9 K) and a 5% larger initial slope for the order-parameter intensity are found. These minor differences may derive from sample-to-sample differences (including deuteration) or slight x-ray damage effects.

[12] J. Als-Nielsen and R. J. Birgeneau, Am. J. Phys., 45, 554 (1977).

[13] Above 20 K the diffuse scattering remains isotropic in the $(h0l)_P$ zone. Accessible peaks in the $(hkh)_P$ zone, which would give the width normal to the $(h0l)_P$ plane, are not strong enough to measure above 20 K.

[14] S. Kagoshima, T. Ishiguro, and H. Anzai, J. Phys. Soc. Jpn. 41, 2061 (1976).