cal interest as a reducing mechanism for the boundary resistance as well as of fundamental interest for surface phenomena. In the references concerning the boundary resistance between liquid ^{3}He and CMN,[1,5,6,13] or between liquid ^{3}He and a metal containing magnetic impurity,[16] one sees the linearly temperature-dependent R_M effective in the very low-temperature region. However, the reduction in R_B through the contribution of R_M is still not large for practical use. It is worthwhile to emphasize here from the view point of the present investigation that the magnetic coupling is strongly enhanced under the condition of the synchronism between the motion of ^{3}He spins and of electron spins. As a natural consequence, it is suggested that by seeking the condition of synchronism in the critical-temperature region of CMN, a more effective reduction in R_B is probably obtained in the ^{3}He-CMN system. In the system, liquid ^{3}He may be cooled effectively during the demagnetization of CMN, for example, as the lowering field and CMN temperature are stopped at the point fulfilling the condition of the strong coupling. For ^{3}He cooling with metal, as a nuclear refrigerant, containing magnetic impurity, the same method might be expected too.

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Theory of the Structural Phase Transformations in Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ)*

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An order parameter theory is derived and used to explain the observed structural phase transformations in tetrathiafulvalene tetracyanoquinodimethane. It is shown that there should be three transitions. One set of chains orders at 54 K, the other at 47 K. The modulation wave vector in the $\vec{a}^*$ direction is equal to $a^*/2$ between 54 and 47 K, increases as $a^*/2+\lambda(47-T)^{1/2}$ between 47 and 38 K, and locks to a value of $a^*/4$ below 38 K as a consequence of Umklapp terms in the free energy.

X-ray[1] and neutron[2] scattering studies of tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ) have revealed structural phase transformations with a number of unusual features. In these experiments, it appeared that there were two transitions, one at 38 K, the other at 54 K. At low temperatures, there was a $4\vec{a}\times 3.4\vec{b}\times\vec{c}$ modulation relative to the undistorted lattice and, as the temperature was raised above 38 K, the modulation period in the $\vec{a}$ direction began to de-

crease, abruptly at first, then more gradually until it reached $2\vec{a}$ near 51 K. The purpose of this Letter is to propose an explanation of these observations. It proves possible to account for the detailed temperature dependence of the modulation period in the $\vec{a}$ direction and to show that there are in fact *three* transitions. This is confirmed by a reanalysis of the neutron scattering data[2] shown later in Fig. 1. The additional transition is of second order and takes place at 47 K. Between 47 and 54 K, the modulation in the $\vec{a}$ direction is constant and equal to $2a$. TTF-TCNQ consists of chains of TTF molecules and chains of TCNQ molecules arranged in sheets. It is shown that between 54 and 47 K only one set of chains is ordered although, at this point, the experiments do not tell if they are TTF or TCNQ. Below 47 K, the coupling between the distortions in the TTF and the TCNQ causes the second set of chains to order and, simultaneously, the modulation period to increase. Finally the transition at 38 K and the locking to a period of $4a$ is shown to be associated with phase locking to the lattice produced by Umklapp terms in the free energy.

The argument will be phrased in terms of a Peierls distortion of the lattice, since this is directly observed in the structural experiments. However, all of the equations could be reinterpreted as a charge-density-wave state in the electron gas, which goes along with the lattice distortion. The physical basis of the discussion is that, if the TTF and TCNQ chains have scale temperatures which are large compared to the transition temperature, their coherence lengths are long enough to suppress fluctuations, except in a narrow region close to the transition, and the static lattice distortions may be regarded as order parameters in terms of which the free energy may be expanded. This is similar to the justification of the Ginzburg-Landau theory[3] of a strongly coupled superconductor. It is important to realize that there is no need to assume the validity of mean-field theory applied to the system as a whole or to the coupling between the chains,[4,5] and the analysis will make use of general symmetry properties and a few phenomenological parameters, rather than a detailed theory of the dynamics of the chains.

Order parameters φ_{1q} and φ_{2q} for the two types of molecules are defined as

$$\varphi_{iq}=N^{-1}\sum_{\vec{r}_i}\psi(\vec{r}_i)\exp\{-i[(\tfrac{1}{2}a^*+q)x_i+q_by_i]\}\pm N^{-1}\sum_{\vec{r}_i'}\psi(\vec{r}_i')\exp\{-i[(\tfrac{1}{2}a^*+q)x_i'+q_by_i']\},$$

where $\vec{r}_i$ and $\vec{r}_i'$ are positions of molecules on the two sublattices of type i, respectively, so that $x_1, x_1' = 2\pi n/a^*$ and $x_2, x_2' = 2\pi(n+\frac{1}{2})/a^*$. Also $\psi(\vec{r}_i)$ is the component of the distortion in the $\vec{b}$ direction at $\vec{r}_i$, and $\vec{q}\equiv(q_a,q_b,0)\equiv(\frac{1}{2}a^*+q,q_b,0)$ is the ordering wave vector. The plus sign should be used in the case that the distortion modes are acoustic and the minus sign should be used in the case of optic modes. Coulomb forces between charge-density waves on one type of chain tend to favor optic modes and $q_a=\frac{1}{2}$, whereas the Coulomb forces between the different chains prefer $q_a=0$. It will be seen that the two order parameters do not vary in the same way, and at this point, the experiments do not tell us which refers to TTF and which to TCNQ so this will not be specified. The differences between the energy per molecule of the ordered and disordered phases will be denoted by $F(\varphi_{1q},\varphi_{2q},q)$ which has to be minimized with respect to φ_{1q}, φ_{2q}, and q. This free-energy functional of the complex order parameters must be real and invariant under translations, inversion, and the twofold screw-axis transformation, which are the symmetry elements of the high-temperature phase.[6]

Since the susceptibilities of the individual chains diverge as $T\to 0$ each set is expected to order. But, at the highest transition temperature $T_1=54$ K, it is found experimentally[1,2] that $q=0$, and it will be seen[7] that this implies that there is no coupling between distortions in the two types of chain. Hence, barring a coincidence, only one set will order at T_1. Suppose that it is type 1. Then to examine the question of when a transition is driven in the type-2 chains, $F(\varphi_{1q},\varphi_{2q},q)$ will be expanded in powers of φ_{2q}, keeping φ_{1q} exactly since it may not remain small over the whole region of interest. Under inversion, $\varphi_{i\vec{q}}\to-\varphi_{i-\vec{q}}=-\varphi_{i\vec{q}}{}^*$, so there should be an even number of order parameter factors in each term of the expansion. To second order in φ_{2q}, we have

$$F(\varphi_{1q},\varphi_{2q},q)=f(|\varphi_{1q}|^2,q)+A'(|\varphi_{1q}|^2,q)(\varphi_{2q}\varphi_{1q}{}^*+\varphi_{1q}\varphi_{2q}{}^*)+B(|\varphi_{1q}|^2,q)|\varphi_{2q}|^2. \quad (1)$$

When the twofold screw-axis transformation $(x,y,z)\to(-x,\frac{1}{2}+y,\frac{1}{2}-z)$ is applied to the order parameters, $\varphi_{1q}\to\pm\varphi_{1-q}\exp[-i\pi q_b/b^*]$ and $\varphi_{2q}\to\mp\varphi_{2-q}\exp[-i\pi q_b/b^*]$, so that $|\varphi_{iq}|^2\to|\varphi_{i-q}|^2$ and $\varphi_{1q}\varphi_{2q}{}^*\to-\varphi_{1-q}\varphi_{2-q}{}^*$. Therefore, f and B are *even* in q and A' is *odd* in q. Real order parameters ψ_{iq} and phases θ_i are de-

fined by $\varphi_{iq}=\psi_{iq}\exp(i\theta_i)$. Minimizing with respect to $\theta_1-\theta_2$ and expanding in powers of q to study the neighborhood of $q=0$, we find

$$F(\psi_{1q},\psi_{2q},q)=f(\psi_{1q}^2,0)+(aq\psi_{2q}+b\psi_{2q}^2+cq^2)+\cdots, \tag{2}$$

where a, b, and c are functions of ψ_{1q} and T but not of q, and a vanishes when $\psi_{1q}=0$. This equation is the starting point of the analysis of the transition. First, F has to be minimized with respect to ψ_{1q} to obtain

$$\psi_{1q}=\bar{\psi}_{1q}(T)+O(q^2,\psi_{2q}^2,q\psi_{2q}). \tag{3}$$

Here, $\bar{\psi}_{1q}(T)$ is the solution of $\partial f(\bar{\psi}_{1q},0)/\partial\bar{\psi}_{1q}=0$ and the usual Landau argument shows that, just below the transition temperature T_1, $\bar{\psi}_{1q}^2$ increases as T_1-T. If Eq. (3) is substituted into Eq. (2), ψ_{1q} is replaced by $\bar{\psi}_{1q}$ and, otherwise, only terms of higher than second order are modified.

Near T_1, the coefficients b and c are positive, otherwise the type-2 chains would already have ordered, contrary to assumption, or $q=0$ would not be a minimum contrary to experiment. The crucial feature of Eq. (2) is that the term linear in ψ_{2q} vanishes at $q=0$. If q remained zero, type-2 chains would order independently when b became zero, as it would, because the divergences of the susceptibilities of the individual chains cause b to decrease quite rapidly as the temperature is lowered. But it also may be energetically favorable for q to depart from zero and drive a transition in ψ_{2q} before $b=0$. To see that this does, in fact, happen, we minimize F with respect to q to find

$$q=-(a/2c)\psi_{2q}+O(\psi_{2q}^3), \tag{4}$$

and, when this is substituted into Eq. (2), F becomes

$$F=f(\bar{\psi}_{1q}^2,0)+(b-a^2/4c)\psi_{2q}^2+D\psi_{2q}^4 \tag{5}$$

to fourth order in ψ_{2q}. Equation (4) shows how the moving wave vector is associated with the development of order in the type-2 chains. When $D>0$, there is a second-order transition at the temperature T_2 for which $b-a^2/4c$ vanishes. This is higher than the temperature at which $b=0$, because $c>0$. Thus, the coupling helps to drive the transition of ψ_{2q}. Minimizing F in Eq. (5) with respect to ψ_{2q} gives

$$\psi_{2q}^2=-(b-a^2/4c)/2D=\alpha(T_2-T),\quad T<T_2, \tag{6}$$

after expanding about T_2. From Eqs. (4) and (7), the variation of q is given by

$$q^2=\begin{cases}0, & T_1\geq T\geq T_2,\end{cases} \tag{7}$$

$$q^2=\begin{cases}(a^2\alpha/4c^2)(T_2-T), & T<T_2.\end{cases} \tag{8}$$

To see if this result is consistent with the experiments, the data of Fig. 1 in Ref. 2 are replotted here in Fig. 1, where q_a is the measured wave vector in units of a^*, $q=(q_a-\frac{1}{2})a^*$. It can be seen that, within the experimental error, the data are consistent with Eqs. (7) and (8) and T_2 is found to be 47 ± 0.5 K. Since q^2 is approximately linear in T down to about 38 K, it appears that $\bar{\psi}_{1q}$ saturates fairly rapidly as T is reduced below T_1.

In summary, the picture which emerges is that, between 54 and 47 K, only one type of chain has ordered and q is constant and equal to zero ($q_a=\frac{1}{2}$). At 47 K, it becomes energetically favorable to adjust q and drive a transition in the second type of chain. It is desirable to search for other evidence of the 47-K transition. It may be possible to see directly the separate ordering of the chains in x-ray or neutron scattering experiments. There is an effect on the type-1 chains and Eqs. (3), (7), and (8) show that the amplitude ψ_{1q} has a discontinuous slope at T_2.

It remains to understand the transition at 38 K and the reason that q_a locks to a value of $a^*/4$ at

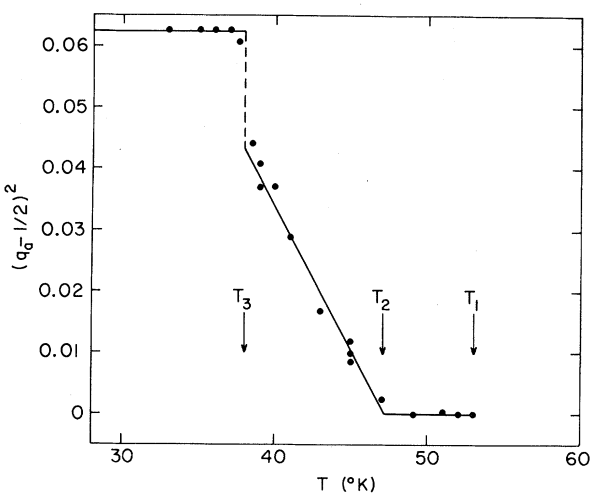

FIG. 1. Temperature dependence of the wave vector q_a in the a^* direction. The arrows indicate the three structural phase transitions.

low temperatures. All of the terms in Eq. (1) stem from exponential factors which have their total wave vector equal to zero. But the translational symmetry of the lattice also allows them to sum to integral multiples of the lattice vector. Then, when $q = a^*/4$, there are additional contributions of the form

$$\delta F = -V\psi_{1,a^*/4}{}^3\bar{\psi}_{2,a^*/4}\cos 4\theta + U\bar{\psi}_{2,a^*/4}{}^2. \quad (9)$$

Here, $\bar{\psi}_{2,a^*/2}$ is an order parameter with wave vector $(a^*/4, -3q_b, 0)$ and phase $\bar{\theta}$, and $4\theta \equiv 3\theta_1 + \bar{\theta}$. (To simplify the discussion, $\psi_{2,a^*/4}$ and $\bar{\psi}_{1,a^*/4}$ have been omitted since they should give smaller contributions.) There are similar terms in pth order of perturbation theory with wave vectors having components a^*/p in the $\vec{a}^*$ direction and phase factor $\cos p\theta$. For $V > 0$, $\theta = 0$ gives the lowest energy and, on minimization, $\bar{\psi}_{2,a/4} = V\psi_{1,a^*/4}{}^3/2U$ and $8F = -V^2\psi_{1,a^*/4}{}^6/4U$. Now suppose Q is the a^* component of $\vec{q}$ measured relative to $a^*/4$ and the rest of the free energy F is expanded to give a constant plus $\alpha(Q - Q_0)^2$, where $(a^*/4 - Q_0)^2$ is given by Eq. (8). Then, in the simplest theory in which only one a^* component of the wave vector is included, as Q_0 decreases, Q will jump from Q_0 to zero when $\alpha Q_0^2 = V^2\psi_{1,a^*/4}{}^6/4U$, and will stay there until $-Q_0$ exceeds this value. This is the transition at T_3 in TTF-TCNQ and the locking of q_a to $a^*/4$. No departure from $q_a = a^*/4$ has been observed below 38 K in TTF-TCNQ, possibly because Q_0 does not continue to decrease as shown in Eq. (8) but saturates when ψ_{2q} saturates.

This simple form of the theory is incomplete because when $Q \neq 0$, it is possible[8] to obtain a contribution from δF by allowing a more general lattice distortion in which θ depends upon x (the distance along the $\vec{a}$ direction) and it is necessary to see if this will give a lower energy than at $Q = 0$ and modify the transition. With Q replaced by $d\theta/dx$, the total free energy for length L may be written

$$F' = \alpha\int dx\{Y[1 - \cos p\theta] + (d\theta/dx)^2 - 2Q_0\, d\theta/dx\} + \alpha L Q_0{}^2 + \delta F(\theta = 0), \quad (10)$$

where $\alpha Y \equiv \psi_{1,a^*/4}{}^3\,\bar{\psi}_{2,a^*/4}$. Minimizing F', we find that $\theta(x)$ satisfies the time-independent sine-Gordon equation,[9] or pendulum equation. Its solutions consist of regions of constant phase separated by "solitons" in which θ increases by $2\pi/p$ over a short distance. For a constant Q, the change in phase in a distance L is QL and this could alternatively be achieved by having N solitons where $2\pi N/p = QL$. The solitons should be equally spaced at a distance $L/N = 2\pi/pQ$ to minimize the repulsive interaction[9] between them. With this form of $\theta(x)$, F' becomes

$$\frac{F'}{\alpha L} = \frac{8}{\pi}|Q|\left(\frac{Y}{2}\right)^{1/2}\left\{1 + 4\exp\left[-\frac{2\pi}{|Q|}\left(\frac{Y}{2}\right)^{1/2}\right]\right\} - 2Q_0Q + Q_0{}^2 + \frac{\delta F(\theta = 0)}{\alpha L}, \quad (11)$$

for $(2\pi/Q)(Y/2)^{1/2} \gg 1$. The first part of the equation consists of the energy of a single soliton[9] plus the large-distance interaction of a pair of solitons,[9] multiplied by their number. For large Q, if the interaction of a pair of close solitons[9] is used, the free energy becomes $(8/\pi)|Q|(Y/2)^{1/2} + (Q - Q_0)^2 + \delta F(\theta = 0)/\alpha L$. It is interesting to note that F' is formally independent of p. When $Q_0 = 1$, Eq. (11) agrees exactly with the result obtained by McMillan[8] from a numerical minimization of Eq. (10) with $p = 3$. From Eq. (11), it is clear that $Q = 0$ is stable when $(4/\pi)(Y/2)^{1/2} > |Q_0|$ and it is easily verified that this is satisfied at the transition indicated by the simple theory. It can also be shown that there is only one such transition in F', so the simpler theory is unmodified.

If Q_0 did not saturate, a locking to other commensurate values ($p \neq 4$) would be expected at lower temperatures. These locking regions would be quite narrow if harmonics of q_b were energetically unfavorable as, indeed, would be the case for the $p = 4$ transition if $3q_b$ were further away from $b^* - b^*/4$.

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[7]When the order parameters corresponding to $q_a = \frac{1}{2}$ ($q = 0$) are subject to the twofold screw axis, $\varphi_{10} \rightarrow \pm \varphi_{10} \times \exp(-i\pi q_b/b^*)$ and $\varphi_{20} \rightarrow \mp \varphi_{20} \exp(-i\pi q_b/b^*)$. Therefore, the order parameters transform like two different representations of the space group, and the most general real second-order term which can be formed is $F_2 = a_1(T)|\psi_{10}|^2 + a_2(T)|\psi_{20}|^2$ and there are no mixed terms.

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Conduction-Band Tunneling and Electron-Spin Polarization in Field Emission from Magnetically Ordered Europium Sulfide on Tungsten*

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We measured the temperature dependence of the current and spin polarization, and determined the work functions from Fowler-Nordheim plots. The current increases exponentially with decreasing temperature. Work-function data can be related directly to the height of the internal W-EuS barrier. This barrier is lowered by magnetic splitting of the EuS conduction band for one electron-spin state which should lead to a spin polarization of unity. The measured spin polarization, however, is equal to the polarization of the $4f^7$ electrons of europium.

At low temperatures europium sulfide is a ferromagnetic insulator.[1] Esaki, Stiles, and von Molnar[2] studied the internal field emission (Fowler-Nordheim tunneling) on metal-EuS-metal junctions at temperatures above and below the EuS Curie point, which is at 16.5 K for pure, annealed thin films. They discovered a decrease in the Schottky potential-barrier height due to magnetic ordering. In external field emission from metal-EuS-vacuum emitters additional information can be obtained by measuring the electron-spin polarization. The first field-emission studies and polarization measurements on EuS-coated tungsten tips were performed by Müller *et al.*[3] They found three different types of emission, two of which (*types I* and *II*) yielded high polarization; for *type I* ($P_{max} \sim 0.5$) conduction-band tunneling was assumed but no temperature dependence of the current was reported. In this Letter we report polarization and work function measurements on W-EuS emitters which exhibit the pronounced temperature dependence of the current as observed by Esaki, Stiles, and von Molnar for internal field emission.

The layout of our apparatus is shown in Fig. 1. Oriented tungsten tips[4] with ⟨111⟩ or ⟨110⟩ directions parallel to the axis and radii of typically 50 to 100 nm were coated at room temperature with EuS by *in situ* vacuum deposition. The EuS was evaporated from a tungsten oven which could be moved in front of the tip; the rate of deposition was 70 nm/min and evaporation times ranged from 0.5 to 2 min. The tip is cooled by a helium-flow system such as that described by Reed and Graham,[5] which in our case allows temperature variation in the range from 9 to 300 K. The tip can be heated by drawing a current through the filament to which the tip is spot welded. Above 600°C the thermal glow was observed through a telescope; at temperatures below 600°C the annealing process was controlled by monitoring the temperature-dependent heating current.

During field-emission studies a pressure of about 10^{-10} Torr was maintained at the tip. The tip was at a potential of -2 kV with respect to the grounded fluorescent screen, and the variable potential of the cylindrical anode determined the emission current. A longitudinal magnetic field variable from 0 to 0.5 T was used for imaging the emitting tip surfaces onto the screen. The emission pattern can be moved by electrostatic deflection and for electron-polarization analysis one point of the pattern was selected by

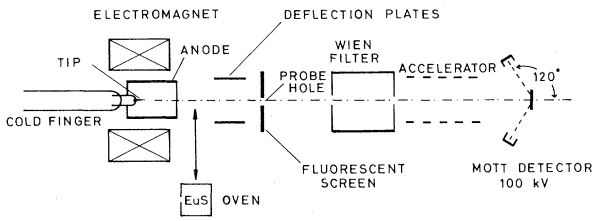

FIG. 1. Schematic diagram of the apparatus (not to scale).