Instability of the quasi-one-dimensional atomic chain in TlHF₂

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The methods of steady state and pulsed NMR spectroscopy are used to study the behavioral features of the quasi-one-dimensional chains in TlHF₂, which consist of alternating metallic and nonmetallic atoms with overlapping electron shells. Superexchange interactions are detected between the thallium nuclei in the chain, taking place through the electron shell of the HF₂⁻ ion. A structural instability is detected in the quasi-one-dimensional system, leading to a phase transition involving a doubling of the period. A pair interaction between thallium atoms in the chain (through the difluoride ion), with a convex dependence on the separation, is discussed as a possible mechanism for the instability.

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Structures with low dimensionality (chains or sandwich structures) are of significant interest in modern condensed-matter physics. One of the characteristic features of such systems is the appearance of various types of structural instability.[1,2] In this paper we use the methods of steady state and pulsed NMR spectroscopy to study the behavioral features of the quasi-one-dimensional chains in TlHF₂, which consist of alternating metallic and nonmetallic atoms with overlapping electron shells; we detected a structural instability in the system that leads to a transition involving a doubling of the period. According to the data of Hassel and Krinstad,[3] the structure of TlHF₂ (Fig. 1) belongs to the cubic system (space group $T_h^7 - Ia3$, $a = 8.58 \pm 0.01$ Å, $Z = 8$). The thallium atoms are arranged at the vertices of the octants, and the linear, symmetric HF₂⁻ ions are located along the body diagonals of the octants in such a way as to form nonintersecting infinite chains of atoms $\cdots$–Tl–F–H–F–Tl–$\cdots$ with overlapping electron shells [the F–F distance (2.32 Å; Ref. 4) and Tl–F distance (2.52 Å) are substantially smaller than the corresponding sums of the ionic radii of F⁻ (1.33 Å) and Tl⁺ (1.36 Å)].

Measurements of the specific heat of TlHF₂ in the temperature range 7–298 K have not revealed any anomalies.[5] The NMR data on ¹H and ¹⁹F indicate that there is a first-order (close to second-order) phase transition in TlHF₂ at $T = 356$ K, accompanied by a dynamic disordering of the difluoride ions with respect to the four body diagonals.

EXPERIMENTAL RESULTS

The NMR spectra of ¹H, ¹⁹F, ²⁰³Tl, and ²⁰⁵Tl ($I = 1/2$ for all these nuclei) in polycrystalline samples of TlHF₂ were recorded in a field of 9.6 kOe in the temperature range 152–380 K (it is difficult to record the spectra at lower temperatures because of the rapid growth of the spin–lattice relaxation time T_1). The times T_1 were measured at frequencies of 18 MHz for the nuclei ²⁰³Tl and ²⁰⁵Tl and at 26 MHz for the nuclei ¹H and ¹⁹F at temperatures in the range 210–350 K.

The temperature dependence of the second moments M_2 of the ¹H and ¹⁹F spectra (Fig. 2) were determined by a partial averaging of the dipolar interactions of the ¹H and ¹⁹F nuclei upon approach to the phase transition and were found to correlate completely with the nuclear interaction constants given by Zil'berman *et al.*[4] for the linear three-spin system ¹⁹F–¹H–¹⁹F. For the spectra of ²⁰³Tl and ²⁰⁵Tl the values of the second moments are more than an order of magnitude larger than the values calculated for a dipolar interaction of the spins ($M_2^{dip} = 2.2$ Oe²). Over the entire range of temperatures studied, the ratio of the second moments of the thallium isotopes, $M_2(^{203}Tl)/M_2(^{205}Tl)$, was approximately 2.32, i.e., was practically inversely proportional to the ratio of the natural abundances of these isotopes (29.5% for ²⁰³Tl and 70.5% for ²⁰⁵Tl). This means that the decisive contribution to the formation of the NMR spectra of ²⁰³Tl and ²⁰⁵Tl (unlike the ¹H and ¹⁹F spectra) is from superexchange interactions between the spins of the different thallium isotopes.[6]

The second moments M_2 in the low-temperature phase are comparable in order of magnitude to the values obtained for Tl₂O₃ and metallic thallium by Bloembergen and Rowland[7] and Karimov and Shchegolev.[8] The distances between a given thallium atom and the thallium atoms closest to it in these compounds are from 3.35 to 3.48 Å for Tl₂O₃ (6 atoms) and from 3.4 to 3.45 Å for the metal (12 atoms). It must be assumed that for the six nearest neighbors in the TlHF₂ at a
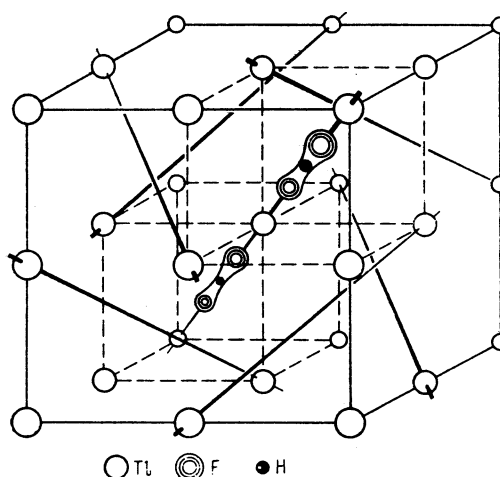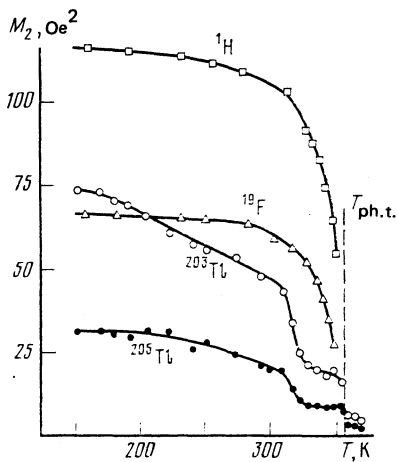

FIG. 1. The unit cell of the TlHF₂.

FIG. 2. Temperaure dependence of the second moments of the NMR spectra in TlHF$_2$.
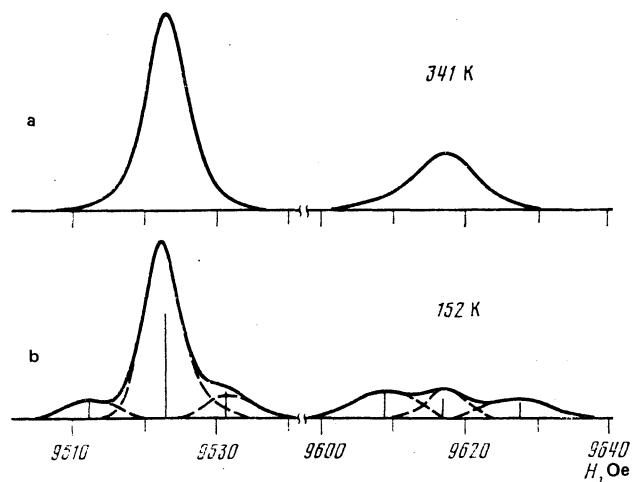

FIG. 3. NMR absorption spectra of ^{203}Tl and ^{205}Tl in polycrystalline TlHF$_2$ in a field of 9.6 kOe. The vertical lines are the calculated spectrum of a system of exchange-coupled pairs of spins of the two isotopes for J = 46.2 kHz.

distance of 4.29 Å the overlap of the electron shells of the thallium atoms cannot lead to such high values of M_2. Apparently, in our case the superexchange comes about through the electron shell of the dumbbell-shaped HF$_2^-$ ion and thus involves only the thallium atoms belonging to a single chain. This assumption is also supported by the change in the values of M_2 for the isotopes^{203}Tl and ^{205}Tl in the region of the phase transition. In fact, for the proposed superexchange mechanism the dynamic disordering of the HF$_2^-$ ions with respect to the four directions of the body diagonals upon the transition to the high-temperature phase should lead to a time-averaged superexchange constant of $\langle J \rangle \simeq J/4$ (J is the interaction constant in the low-temperature phase). Considering that at the same time the number of nearest neighbors effectively quadruples, one expects that upon the transition to the dynamically disordered phase the values of $M_2 \simeq \Sigma_i \langle J_i \rangle^2$ should decrease by about a factor of four (with allowance for the additional contributions to the second moment, such as that due to the small interchain exchange interaction, the decrease should be somewhat smaller). Comparison of the moments for $T = 358$ K (the high-temperature phase) and $T = 345$ K (the plateau in the low-temperature phase near the point of the phase transition) yields a ratio of 3.3 for ^{203}Tl and a ratio of 3.1 for ^{205}Tl, in good agreement with the estimates made above. A particular feature of the $M_2 (T)$ curve for the thallium nuclei is a sharp increase in M_2 (as the temperature is lowered) in the range ~ 310–320 K, in the existence region of the low-temperature phase (Fig. 2). This anomalous behavior of M_2 cannot be a consequence of a partial orientational disordering of the HF$_2^-$ ions, since no anomalies appear in the smooth curves of the temperature dependence of M_2 for ^{1}H and ^{19}F, which in both cases is directly related to the dynamics of the difluoride ions (the rms deviation of the ion axis from the [111] direction as estimated from the ^{1}H and ^{19}F spectra is 7.3° at 305 K and 10° at 325 K). On the basis of the results we are therefore compelled to suppose that the phase transition in the TlHF$_2$ is preceded by an additional structural rearrangement which radically alters the character of the electronic overlap along the one-dimensional chain $\cdots$–Tl–F–H–F–

Tl– $\cdots$. This rearrangement is accompanied by the appearance of fine structure in the spectra of ^{203}Tl and ^{205}Tl (Fig. 3), with the splitting of the lines increasing somewhat and the resolution improving as the temperature is lowered further.

The data of Hassel and Krinstad[3] imply that all the HF$_2^-$ ions are structurally equivalent in the low-temperature phase of TlHF$_2$. This assertion, however, is at odds with our present measurements of the spin–lattice relaxation time of the nuclei ^{1}H, ^{19}F, ^{203}Tl, and ^{205}Tl. As is implied by earlier results[9–11] for the case of MHF$_2$ crystals (M = K, Rb, Cs), the temperature dependence of T_1 observed here is due to the activation of a flip (a 180-degree reorientation) of the HF$_2^-$ ions, which modulates the "interionic" dipole interaction of the nuclear spins. In the case when the difluoride ions are structurally equivalent, as in crystals of the MHF$_2$ type, the condition for a minimum to occur on the $T_1(T)$ curves $[\tau_c(T) \sim \omega_0^{-1}$, where $\tau_c(T)$ is the flip correlation time and ω_0 is the resonant frequency of the given nucleus] is satisfied simultaneously for all the ions in the crystal. As a result, the corresponding curves show a single-minimum behavior.[9–11] At the same time, however, the spin–lattice relaxation measurements in TlHF$_2$ reveal the presence of two minima of T_1 for each nucleus (Fig. 4). If one assumes that all the atomic
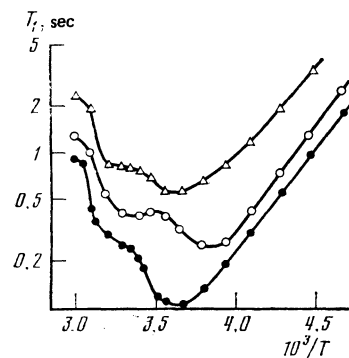

FIG. 4. Temperature dependence of the relaxation time of the ^{1}H, ^{19}F, ^{203}Tl, and ^{205}Tl nuclei in the TlHF$_2$ (O–Tl, ●–F, △–H).

chains in cubic TlHF$_2$ are equivalent, it follows that for temperatures in the region of the minima in T_1 there are at least two structurally nonequivalent HF$_2^-$ ions in each of the chains, having different barriers against the flip process.

To explain the character of the observed structural rearrangement, let us turn now to an analysis of the shape of the NMR spectra of ^{203}Tl and ^{205}Tl. Neglecting the relatively small dipole and pseudodipole interactions, and taking into account only the exchange interactions between nearest neighbors, we can write the Hamiltonian for the system of thallium nuclei in the form

$$H_{exch} = \sum_i \left[\omega_0{}^i I_i{}^z + J_{i,i+1} I_i{}^z I_{i+1}{}^z \right.$$
$$\left. + \frac{1}{2} \delta_{\alpha_i, \alpha_{i+1}} J_{i,i+1}(I_i{}^+ I_{i+1}{}^- + I_i{}^- I_{i+1}{}^+) \right], \quad (1)$$

where $\omega_0{}^i$ is the Larmor frequency of the given isotope, $\delta_{\alpha_i, \alpha_{i+1}}$ is equal to 1 or 0 depending on whether the spins are of like or different species. For a uniform chain of spins, all the exchange interaction constants $J_{i,i+1}$ are equal. The disorder of the chain with respect to the position of the isotopes does not permit the use of the formalism of Engelsberg et al.[12] to solve for the shape of the spectrum, as that formalism was developed for a uniform chain of identical spins coupled by the dipole interaction. We can assume, however, that the calculation will yield quasicontinuous spectra (of the type shown in Fig. 3a) in the frequency region $\omega_0{}^i \pm 2J$, with a different intensity distribution for each isotope.

At the same time, as we have already mentioned, when the temperature is lowered ($T \lesssim 315$ K) a fine structure appears in the ^{203}Tl and ^{205}Tl spectra (Fig. 3b), and they become triplets which differ only in the intensity of their central components. The lateral components of the ^{203}Tl and ^{205}Tl spectra, which are located symmetrically with respect to the centroid of the whole spectrum, practically coincide for the two isotopes.

We believe that the only possible explanation for the observed spectral shape lies in the assumption that a modulation of the exchange interaction constants ($J_{i-1,i} \succ J_{i,i+1}$) arises in the one-dimensional system, with the result that the continuous chain can be looked on as a set of exchange-coupled pairs of spins. The spectrum[13] of such a system (Fig. 3b) in fact consists of two triplets, whose central components (at the Larmor frequency of each isotope) correspond to pairs of spins of the same kind and have intensities of c^2 and $(1 - c)^2$, where c and $1 - c$ are the natural abundances of the isotopes. The lateral satellites of the triplets have intensities of $(1 \pm J/\Delta\omega)c(1 - c)$ and differ from the Larmor frequencies by $\pm J/2 \mp J^2/(4\Delta\omega)$. They correspond to pairs containing the two different isotopes. Good agreement is seen between the values of J determined in this model from analysis of the characteristic spectral splittings and from the difference in the second moments of the two isotopes (the contributions from the dipole interactions and anisotropy of the chemical shift cancel each other). For example, the values of J at $T = 152$ K as determined from the two methods are 46.2 ± 0.5 kHz and 50.1 ± 2.2 kHz.

Modulation of the spin–spin interaction can only be the

direct consequence of an alternating variation of the Tl–Tl separation in the one-dimensional chain. Another consequence of this effect should be the presence of two nonequivalent (in terms of the immediate environment) HF$_2^-$ ions, and this is manifested here in the presence of two minima on the curves of T_1 versus temperature, which are due to the flips of these ions. Evidently, an equilibrium chain of atoms exists in TlHF$_2$ only in the narrow temperature interval 328–355 K, preceding the phase transition (the "intermediate" plateau in Fig. 2), and loses stability as the temperature is lowered further (a transition involving a doubling of the period).

DISCUSSION OF THE RESULTS

Since TlHF$_2$ is a dielectric, the doubling of the period along the chain is not due to the well-known Peierls instability mechanism.[1] On the other hand, the often used model of a dielectric chain in which each atom is found in a double-minimum potential and interacts with its neighbors by harmonic forces[14] also fails to describe our problem. A possible cause of the doubling is suggested by the fact that the difluoride ion is somewhat elongated in the TlHF$_2$ structure in comparison with other compounds[15] of the MHF$_2$ type, so that its dimension approaches that of a free difluoride ion. As a result, we can assume that an attractive interaction is felt through the difluoride ion in rather distant regions, where the corresponding potential has a convex profile with a curvature that diminishes with distance.

Without going into the specifics of such a potential (although the main contribution here is due to covalent forces), we shall show that the shape of the interaction indicated above, which is rather natural at large distances, can actually be the cause of the doubling of the period. To do this it is sufficient to consider a model of the chain in which each atom is found in a harmonic potential well due to the lattice and interacts with its nearest neighbors along the chain through a potential of the required shape, which is specified by the Hamiltonian

$$H = \sum_i \left[\frac{\varepsilon}{2} u_i{}^2 - \frac{g}{2}(u_i - u_{i-1})^2 \right.$$
$$\left. + \frac{f}{3}(u_i - u_{i-1})^3 + \frac{h}{4}(u_i - u_{i-1})^4 \right]. \quad (2)$$

where u_i is the displacement of the i-th atom along the chain from its equilibrium position in the undistorted chain, ε and g are force constants, and the last two terms with constants f and h describe the nonparabolicity of the pair potential; the sum is taken over all the atoms of the chain. A consequence of expression (2) is that for $\varepsilon < 4g$ an instability arises in the chain, leading to a doubling of the period.

The temperature at which the system of interaction chains undergoes a phase transition to the state with the doubled period is determined by the relation

$$kT_c = \Lambda \exp(U/kT_c), \quad (3)$$

which is of a typical form.[16] Here Λ is the energy of interaction (per unit length) of the ordered part of the chain with the

surrounding chains, U is the energy of a domain wall in the chain, and k is the Boltzmann constant. The energy Λ is governed by the dipole–dipole interaction of the displaced atoms, with the main contribution coming from the interaction between crossing chains. As a result, a state in which the displacements of the closest atoms on nonparallel chains in the $TlHF_2$ structure are directed at an acute angle to one another should become stable. Assuming that $T_c = 315$ K, $g/\varepsilon = 1/2$, and $\varepsilon/a \sim 10^{12}$ dyn/cm^2, where $a = 4.29$ Å is the lattice constant for one formula unit, and estimating U with formulas (2) and (3), one can easily determine the average displacement of the atoms along the chain. In particular, for $T \sim 300$ K we obtain the value $\bar{u} \sim 0.06$ Å, which is comparable to the difference between the Tl–F separation and the sum of the ionic radii of F^- and Tl^+. Thus the superexchange interaction between the spins of the thallium nuclei in the elongated Tl–Tl link being exponentially dependent on the separation, is predicted to be small, in agreement with experiment.

In conclusion, it should be pointed out that additional careful structural studies of the $TlHF_2$ must be carried out in the temperature region below the critical point for the doubling of the period.

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