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MODIFICATION OF ELECTRONIC STRUCTURE BY CHARGE TRANSFER AND MOLECULAR MOTION IN TITANIUM DISULFIDE-ETHYLENEDIAMINE INTERCALATION COMPOUND

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Abstract—An attempt at modifying the electronic conduction mechanism by guest-host charge transfer and thermally excited molecular motion is reported. Ethylenediamine was intercalated into a semiconducting layered material, titanium disulfide, and a significant increase in charge carriers was evidenced by metallic conductivity, Pauli paramagnetism, and conduction electron spin resonance. Rotational motion of the guest molecule was evidenced by the proton spin-lattice relaxation measurement. However, no anomalous behaviors were found on the electronic properties which are attributable to motion-induced modification of the electronic state. © 1997 Elsevier Science Ltd

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1. INTRODUCTION AND STRATEGY

In this paper we report on an attempt to modify the electron conduction mechanism by thermally excited molecular motion in an intercalation compound through motion-induced change in charge transfer and hydrogen bonding interactions.

Transition metal dichalcogenides assume a number of structural polytypes, and they exhibit a variety of electronic properties such as magnetic ordering, superconductivity, or commensurate/incommensurate transition related to the formation of a charge-density wave, depending on delicate balances between electron correlation, electron-phonon interaction, and lattice deformation energies [1]. They are also interesting because of their ability to incorporate various guest species into the galleries of the layers, among which are alkali metals, transition metals, or organic molecules [2-4]. Enhancement of the superconducting transition temperature by intercalation of organic electron donors in TaS₂ and NbS₂ are known well [5, 6], and the $T_{\rm c}$ enhancement has been attributed to the increase in electronic density of states at the Fermi energy, $N(E_{\rm F})$.

There is another interesting possibility related to intercalation with this class of materials. If molecular motion of the organic guest species modifies the guest-host charge transfer and hydrogen-bonding interactions, it may also modify the electrical conduction. To realize this situation, the thermally excited state of the guest molecule must be some metastable trapped state where the molecule stays for a time comparable to the time spent in the ground state, and also the electronic interaction with the host is significantly different from that in the ground state. The requirement for the host lattice is that the electronic structure is affected sensitively by a small change



Fig. 1. Crystal structure of 1T-TiS₂.

in charge transfer. To this end we selected titanium disulfide (TiS₂) as host material. TiS₂ assumes the hexagonal structure (1T form) shown in Fig. 1, with $a_0 = 3.4048$ Å and $c_0 = 5.6904$ Å at room temperature [7]. Every titanium atom is surrounded by six sulfur atoms octahedrally, and the S-Ti-S triple atomic layers form a two-dimensional polymer network in the ab-plane. Since the bonding interaction between the polymer sheets is very weak, guest species can be intercalated in the so-called van der Waals gap between the sheets. Electronic structure calculation with a self-consistent layer method [8] revealed a narrow bandgap of 0.3 eV between the valence band having mainly the character of the sulfur 3p state and the conduction band having mainly the character of the titanium 3d state. However, recalculation with an augmented plane wave method [9] showed the existence of $N(E_{\rm F})$. Experimentally a small bandgap was suggested by ultraviolet photoelectron spectroscopy [10, 11], while the temperature dependence of in-plane resistivity showed $\rho \propto T^2$ behavior [12]. Anomalous behavior in thermoelectric power was observed at high pressure [13], and was interpreted in terms of pressure-induced p-d band crossing. Though the electronic structure of TiS2 has not been fully understood, it is clear that TiS₂ has a nature very close to that of a zero-bandgap semiconductor and must be very sensitive to a small change in charge transfer.

As an electron-donating guest molecule we chose ethylenediamine (en; $NH_2-(CH_2)_2-NH_2$). En is expected to donate partial charge from the lone electron pair on the amino nitrogen, and possibly form weak hydrogen bond $N-H\cdots S$. The van der Waals gap in TiS₂ is expected to offer a pretty flat potential onto the guest molecule compared to the intermolecular potential in the pristine solid state of

Table 1. Chemical compositions of $TiS_x(en)_v$

Specimens	x	у
Pristine TiS ₂ powder	1.994	0
Pristine TiS ₂ planar crystal	2.028	0
Powder TiS _x (en) _y	1.761	0.296
Planar crystal $TiS_x(en)_y$	1.385	0.274

the guest compound, so that molecular motion is expected to take place. Considering that the N-C bond of en has weak π character, the most easily accessible molecular motion will be rotation about the central C-C bond (anti-gauche isomerization). A recent gas phase electron diffraction study [14] revealed that the degenerate \pm gauche conformers with the N-C-C-N dihedral angle ϕ at $\pm \pi/3$ are more stable than the anti-conformer with $\phi = \pi$, the energy difference being 2.8 kJ mol⁻¹. Theoretical calculation [15] supported this, and estimated the height of the anti-gauche potential barrier at ca. 20 kJ mol^{-1} . These energy values suggest the existence of rotational motion in the intercalated solid compound. If the energetic difference between the two isomeric states is less than a few hundred kelvins (a few $kJ mol^{-1}$) in the solid state, temperature-dependent modification of the electrical conduction is expected because the charge transfer and hydrogen bonding interactions of the amino group with the host are different between the ground and the first excited isomeric states.

Reaction of en with TiS_2 was reported previously by Boller and Blaha [16]. They confirmed the intercalation reaction by observing thermogravimetric change and powder X-ray diffraction. In this paper we report the synthesis of the TiS_2 -en intercalation compound and a number of physical properties such as electrical resistivity, magnetic susceptibility, and electron spin resonance (ESR). We also report experimental results



Fig. 2. Temperature dependence of in-plane resistivity ρ_a for planar crystal TiS_{1.385}(en)_{0.274}.

	$\rho_a(T) = A_0 + A_1 T + A_2 T^2$			
	$A_0 (\Omega \text{ cm})$	$A_1 (\Omega \mathrm{cm} \mathrm{K}^{-1})$	$A_2 (\Omega \mathrm{cm} \mathrm{K}^{-2})$	
TiS ₂ †	1.95×10^{-4}	0.00	2.00×10^{-8}	
TiS _{1.385} (en) _{0.274}	9.99×10^{-5}	2.60×10^{-6}	1.81×10^{-8}	

Table 2. Temperature dependence of electrical resistivity $\rho_a(T)$ for pristine TiS₂ and TiS_x(en)_y

on solid state high resolution NMR spectroscopies of ¹³C, ¹⁵N, and ¹H, and the ¹H spin-lattice relaxation in a wide temperature range, 1.6 K to room temperature.

2. EXPERIMENTAL

The host material, TiS₂, was prepared by a temperature-gradient method. Titanium and sulfur powders were mixed and sealed in evacuated quartz tubing of 20 $\phi \times$ 300, and placed in an electric furnace for three weeks with the temperatures kept at 600 and 900°C at each end of the tubing. According to the gradient in the gaseous sulfur concentration within the tubing, three different products were obtained simultaneously: polycrystalline TiS₂ powder and needles of TiS₃ at the high and low temperature ends, respectively, and planar crystallites of TiS₂ in the intermediate region. The appearance of the crystals of TiS₂ was yellow-green with a metallic luster resembling gold, while those of TiS₃ had a silver luster. Powdered TiS_2 was bronze green. The sulfur content was analyzed with gas phase adsorption method: TiS_2 was burned in an oxygen flow, and the sulfur trioxide gas was reacted with lump silver to form silver sulfate. The weight uptake by silver was then measured. The sulfur content, x, in TiS_x was determined to be 1.944 for powder and 2.028 for planar crystal. It is known [17-19] that in many of the samples of TiS_2 the stoichiometry is usually titanium rich due to selfintercalation of the small titanium ions in the van der Waals gap, and these defects affect transport properties seriously and give metallic conductivity. In the present compound, however, the extent of nonstoichiometry was very small, so that the small deviation from x = 2 is neglected and the compound is hereafter denoted as TiS₂ in this paper.

A commercial ethylenediamine (en) reagent was purified to remove possibly dissolved carbon dioxide and water: the en was shaken vigorously with sodium hydroxide for three hours. After distillation it was refluxed for three hours with 3 Å molecular sieves, and redistilled. An excess amount of purified en was poured into a Pyrex tube with TiS_2 . After sealing *in vacuo*, the tube was heated to 120°C. As the intercalation proceeded the color of the TiS_2 changed to dark brown. It took 44 days to complete the reaction for planar crystals of TiS₂ whereas 20 h was enough for the powder sample. The products were washed with ether until the alkaline nature was lost, then dried in vacuum to remove the ether. Elemental analyses were performed for C, H, and N in addition to the sulfur described above. If the intercalated compound is expressed by the formula $TiS_x(en)_y$, the composition was revealed to be $TiS_{1.761}(en)_{0.296}$ for powder, and $TiS_{1.385}(en)_{0.274}$ for planar crystals. Sulfur contents are clearly less than the pristine TiS₂, suggesting partial decomposition. C, H, and N analyses gave good agreement with the formula of en, and proved that the cationic form $-NH_3^+$ does not exist. X-ray microanalysis revealed that the valence state of titanium is Ti⁴⁺ with trace amounts of Ti³⁺. Chemical compositions are summarized in Table 1.

X-ray diffraction was measured for powder and planar TiS₂ and their intercalated compounds. Electrical resistivity perpendicular to the *c*-axis of the planar TiS_{1.385}(en)_{0.274} was measured from 1.17 K to room temperature with a four-probe method. Magnetic susceptibility was measured with an MPMS-2 (Quantum Design) SQUID magnetometer. An ESR experiment was conducted with an E112 (Varian) spectrometer at an X-band frequency and temperatures from 4.2 K to 298 K. The ESR intensity was calibrated with a CuSO₄ · 5H₂O single crystal and 2,2diphenyl 1-picryl hydrazyl (DPPH).

Solid state high resolution NMR spectra were recorded at room temperature with an ASX-300



Fig. 3. Temperature dependence of static magnetic susceptibility χ_s for TiS_{1.761}(en)_{0.296} (\bigcirc) and pristine TiS₂ (\spadesuit).

(Bruker) spectrometer. To avoid the screening effect, powdered TiS_{1.761}(en)_{0.296} was mixed with dry sodium chloride in a mortar, and sealed in a sample container. ¹³C and ¹⁵N NMR were performed with magic-angle sample spinning combined with cross-polarization from protons (CP/MAS method). Chemical shifts were measured with respect to tetramethylsilane (TMS) for ¹³C and to nitromethane for ¹⁵N, with positive values on the less shielded side. Typically the ¹³C linewidth for the methylene signal of adamantane was 5 Hz. ¹H NMR was performed with a quadrature-detection version of the Burum-Rhim 24 pulse sequence [20] combined with sample rotation of 1.5 kHz (CRAMPS) at room temperature. Spectral resolution was checked by glycine: two methylene peaks were resolved, with a half-value width of ca. 220 Hz for each. Scaling in the frequency domain was done by observing a water signal. ¹H NMR spin-

(a)

lattice relaxation rates were measured with a laboratory-made spectrometer [21] at 11 MHz and 62 MHz, at temperatures from 1.3 K to room temperature. The temperature was controlled to within 1 K with a continuous liquid helium flow and a PID control system.

3. RESULTS AND DISCUSSION

3.1. Structures of TiS_2 and $TiS_x(en)_y$

X-ray study of the host material TiS₂ revealed lattice parameters, $a_0 = 3.406 \text{ Å}$ and $c_0 = 5.681 \text{ Å}$, consistent with the literature values of the 1T-TiS₂ [7]. Although structural analysis has not been completed due to difficulty in preparing a good single crystal, reflections from (001) and $(hkl; h \neq 0, k \neq 0)$ were distinguished by comparing the diffractograms of the planar and powder samples. Our structure

4.9 K

71.2 K 116 K 217 K 287 K 1000 G derivative absorption spectra, (b) asymmetry ratios, and (c) peak-to-peak linewidths.

Fig. 4. Temperature dependence of conduction electron spin resonance (CESR) spectra for TiS_{1.761}(en)_{0.296}: (a) selected first



Fig. 4. Continued.

analysis showed that the hexagonal space group of 1T-TiS₂ was maintained after intercalation, and the lattice parameters became $a_0 = 6.812$ Å and $c_0 =$ 9.598 Å. The c-axis repeat distance was lengthened by 3.917 Å, and cell doubling took place along the a-axis. In this hexagonal unit cell containing four formula units of TiS₂, four octahedral sites and eight tetrahedral sites are found. Though nonstoichiometry of the compounds makes it difficult to determine the limiting structure, a plausible limiting concentration will be $TiS_2(en)_{0.5}$, which contains two en molecules in the unit cell. The concentrations, y = 0.296 for powder and 0.274 for a planar crystal (Table 1) show that $TiS_2(en)_{\nu}$ has vacancy-rich intercalate structure. The actual concentrations y turn out to be closer to 1/3, and this concentration is in fact found in a number of metal-intercalated $M_{1/3}TiS_2$ [4]. However, this concentration is incompatible with our $2a_0 \times 2a_0$ in-plane superlattice. The 1/3 concentration of the guest species conforms to a $\sqrt{3}a_0 \times \sqrt{3}a_0$ superlattice. Lattice expansion along the c-axis by 3.917 Å seems suitable for incorporation of en.

Boller and Blaha [16] reported concentrations of x = 0.21-0.39, which are similar to ours, but a different assignment of structural type: 3R (rhombohedral with three layers superlattice).

3.2. Electrical resistivity

The temperature dependence of the electrical resistivity along the *a*-axis, ρ_a , was measured for the planar TiS_{1.385}(en)_{0.274}, and shown in Fig. 2. The $\rho_a(T)$ has a positive temperature dependence in the entire temperature region studied, and is approximated by a polynomial,

$$\rho_a = A_0 + A_1 T + A_2 T^2 \tag{1}$$

with $A_0 = 9.986 \times 10^{-5} \,\Omega \,\mathrm{cm}, \ A_1 = 2.595 \times 10^{-6} \,\Omega$ cm K⁻¹, and $A_2 = 1.806 \times 10^{-8} \,\Omega$ cm K⁻². This quadratic function has been observed in two-dimensional metals based on graphite [22]. Because the Fermi surfaces consisting of cylinders (pockets) are located at the edges of the hexagonal Brillouin zone and are separated from each other, the coefficients A_1 and A_2 represent contributions from intra- and inter-pocket phonon scatterings, respectively, and A_0 represents the impurity scattering [23]. Thompson [12] reported the resistivity for the host TiS₂, and showed that $A_0 = 1.95 \times 10^{-4} \,\Omega \,\mathrm{cm}, \ A_2 = 2.00 \times 10^{-8} \,\Omega \,\mathrm{cm} \,\mathrm{K}^{-2},$ and $A_1 = 0$ approximates the temperature dependence of ρ_a within 10 and 400 K. Results of fitting are summarized in Table 2. Absence of the intra-pocket term proves the semimetallic nature of TiS₂. Growth of the linear term in the intercalated compound shows the enhancement of metallic conduction. On the basis of the rigid band model, enhancement of the metallic nature is understood by an increase in $N(E_{\rm F})$ due to charge transfer from the HOMO of en to the nonbonding titanium 3d band.

3.3. Magnetic susceptibilities and ESR

The static magnetic susceptibility χ_s was measured for pristine TiS₂ and planar TiS_{1.761}(en)_{0.296}, and the results are plotted against temperature in Fig. 3. Except for the steep rise in χ_s at low temperature caused by Curie spins, the most impressive characteristics are the existence of a temperature-independent contribution and especially a significant increase $(8 \times 10^{-5} \text{ emu mol}^{-1} \text{ of Ti})$ in this term by intercalation. This fact suggests an increased Pauli paramagnetism due to charge transfer.

Figure 4(a) shows the temperature dependence of the first derivative ESR line for $\text{TiS}_{1.761}(\text{en})_{0.296}$ powder. Figure 4(b) and (c) shows the temperature dependences of the asymmetry ratio A/B and the peak-to-peak linewidth ΔH_{pp} , respectively. The asymmetric spectra below 200 K and an almost linear increase in ΔH_{pp} with temperature are observed. These behaviors are understood in the context of conduction electron spin resonance. The observed values of A/B (less than 1.5) are out of the estimated range, 2.7 < A/B < 19.0, for the normal skin



Fig. 5. Solid state high resolution NMR spectra of (a) 13 C, (b) 15 N, and (c) 1 H for TiS_{1.761}(en)_{0.296}.

effect [24, 25], and even decrease down to unity at high temperatures. The small A/B ratio is understood by bearing in mind that the observed powder ESR line represents the inhomogeneous superposition of the lines coming from the crystallites oriented at various angles from the static field, and assuming a highly

anisotropic nature of the conduction electrons. A significant decrease in A/B down to unity with increasing temperature stems from the increase in skin depth caused by a decrease in conductivity. The increase in $\Delta H_{\rm pp}$ with increasing temperature reveals the enhancement of spin-orbit relaxation [26].



Fig. 5. Continued.

Pauli susceptibility estimated from the ESR experiment is $\chi_{\text{ESR}} = 2 \times 10^{-6} \text{ emu mol}^{-1}$ of Ti at room temperature, and the electronic density of states at the Fermi energy is thus $n(E_{\text{F}}) = 0.06$ states per eV atom of Ti. Pauli susceptibility χ_{ESR} is significantly smaller than the static susceptibility χ_s , and this fact suggests that orbital paramagnetism contributes significantly to χ_s as observed in alkali-graphite intercalation compounds [27].

3.4. Solid state high resolution NMR

All the elements that constitute en have NMRactive nuclides, and so the structural, electronic, and dynamical properties can be investigated by NMR spectroscopy. Figure 5 shows the solid state high resolution NMR spectra of ¹³C (Fig. 5(a)), ¹⁵N (Fig. 5(b)), and ¹H (Fig. 5(c)) nuclei in powder $TiS_{1.761}$ -(en)_{0.296}. The ¹³C spectrum was a broad singlet appearing at 48 p.p.m., exhibiting paramagnetic shift of only 3p.p.m. from the solution state. The ^{15}N spectrum was also a broad singlet appearing at -327 p.p.m. As compared to the solution spectrum at -363.5 p.p.m., a significant paramagnetic shift as large as 36 p.p.m. was revealed. The remarkable deshielding shift by intercalation for ¹⁵N is understood by the decrease in electron density at the amino group caused by the charge transfer interaction.

One question involves the origin of the broadness

(more than 12 p.p.m.) of the ¹³C and ¹⁵N spectra. The CP/MAS NMR spectrum of ¹³C attached directly to nitrogen exhibits an asymmetric doublet due to residual dipolar interaction with ¹⁴N (I = 1) [28]. However, this broadening mechanism is expected to be diminished for the present compound due to rapid molecular rotation (self-decoupling) which is evidenced by the ¹H spin-lattice relaxation described in the next section. Moreover, the broadness of the ¹⁵N spectrum cannot be explained by this mechanism. The origin of the broad NMR lines is thus attributable to the inhomogeneous broadening caused by the defect-rich structure.

The high resolution ¹H NMR spectrum is shown in Fig. 5(c). An attempt to resolve methylene and amino protons failed, and a broad peak overlapped by both protons appeared at 2.45 p.p.m. The peaks for en in solution are 1.1 and 2.7 p.p.m. An additional peak was found at 7 p.p.m. The possibility of a background signal or pollution by humidity were checked carefully, and it was concluded that this additional signal came from the sample. Probably this peak is attributable to lattice defects where amino protons are strongly hydrogen-bonded to the host sulfur.

Solid state high resolution NMR spectra showed paramagnetic shifts compared to the solution spectra attributable to charge transfer and hydrogen bonding.



Fig. 6. Proton NMR magnetization recovery function of $TiS_{1.761}(en)_{0.296}$ observed at 62 MHz and at three typical temperatures.

Inhomogeneity of the compound was also evidenced by the broadness of the resonances.

3.5. ¹H spin-lattice relaxation

The spin-lattice relaxation rate (T_1^{-1}) of protons was measured at 11 MHz and 62 MHz in the temperature range 1.3-300 K. The magnetization (M_z) recovery was found to be nonexponential. As shown in Fig. 6, the nonexponentiality was more evident at low temperature. In the present analysis of the experimental data, an operational definition of T_1^{-1} is adopted, i.e.

$$M_z(T_1)/M_z(\infty) = 1 - e^{-1} = 0.632$$
 (2)

Figure 7(a) shows the semilogarithmic plot of T_1^{-1} against reciprocal temperature. Two different relaxation mechanisms are evident: a broad maximum of T_1^{-1} at around 10 K, and a steep increase in T_1^{-1} above 100 K. A relaxation component that satisfies the Korringa relation, $(T_1T)^{-1} = \text{constant}$, was not detected. This proves that orbitals belonging to the guest molecule do not mix with the nonbonding conduction band, but contribute only to transferring electrons to the conduction band.

We first analyze the low temperature relaxation. A number of studies have been made of the 'H spinlattice relaxation of amines intercalated into transition metal chalcogenides [29-31]; however, no one has reported a relaxation maximum at such a low temperature as ours. Considering the existence of Curie spins revealed by a magnetic susceptibility



Fig. 7. Temperature dependence of proton spin-lattice relaxation rate of $TiS_{1.761}(en)_{0.296}$ measured at 11 MHz (O) and 62 MHz (\bullet). (a) Whole results. The arrow indicates $\omega_0^{-1/2}$ dependence at low temperature. (b) High temperature area. The solid lines are fitted to the 11 MHz and 62 MHz data according to the axial rotation model with ω_0^{-2} dependence and a common activation energy of 15 kJ mol⁻¹.





experiment, the most probable origin for the low temperature relaxation is nuclear spin diffusion to rapidly relaxing electron spins [32]. The relaxation caused by this mechanism, T_{1C}^{-1} , is

$$T_{1C}^{-1} = 4\pi N_C b_C D_n \tag{3}$$

where D_n is the nuclear spin-diffusion coefficient, N_C is the number density of Curie spins per unit volume, and b_C is the so-called pseudopotential radius which gives an estimate of the scattering radius for single localized spin. The final quantity depends on the electron spin-lattice relaxation time, τ_e , such that

$$b_{\rm C} = \frac{\pi}{4\sqrt{2}\Gamma^2 \left(\frac{5}{4}\right)} \left[\left(\frac{\mu_0}{4\pi}\right)^2 \frac{3\gamma_{\rm n}^2 \gamma_{\rm e}^2}{10D_{\rm n}} \frac{\tau_{\rm e}}{1 + (\omega_0 \tau_{\rm e})^2} \right]^{1/4}$$
(4)

where μ_0 is the vacuum permittivity, γ_n and γ_e are the gyromagnetic ratios of proton and electron, respectively, ω_0 is the nuclear Larmor frequency, and Γ is the gamma function. At low temperature where $\tau_e^{-1} \ll \omega_0$ is satisfied, eqns (3) and (4) predict $T_{1C}^{-1} \propto \omega_0^{-1/2} \tau_e^{-1/4}$, while at high temperature where $\tau_e^{-1} \gg \omega_0$ is satisfied, $T_{1C}^{-1} \propto \tau_e^{1/4}$ is predicted, and T_{1C}^{-1} becomes independent of ω_0 . The maximum in T_{1C}^{-1} corresponds to $\tau_e^{-1} = \omega_0$. In Fig. 7(a) we find a broad maximum for each of the T_1^{-1} (62 MHz) and T_1^{-1} (11 MHz) corresponding to this situation. In Fig. 7(a) an arrow is inserted to indicate the $\omega_0^{-1/2}$ dependence. The $\omega_0^{-1/2}$ dependence at low temperature, the gradual loss of the ω_0 -dependence at elevated temperature, and also the weak temperature dependence of T_1^{-1} support the spin-diffusion mechanism.

To analyze the high temperature relaxation mechanism, the high temperature side of Fig. 7(a) is expanded in Fig. 7(b). The low temperature relaxation mechanism extends up to 200 K, but log $[T_1^{-1}(s^{-1})]$ exhibits nearly a straight line against T^{-1} above 200 K, showing that thermally activated molecular motion is the cause for this relaxation. If axial rotation of spin pairs predominates the spin relaxation, T_{1R}^{-1} (rotation-induced T_1^{-1}) is given by [33, 34]

$$T_{1R}^{-1} = C_R \left[\frac{\tau_R}{1 + (\omega_0 \tau_R)^2} + \frac{4\tau_R}{1 + (2\omega_0 \tau_R)^2} \right]$$
(5)

where

$$C_{\rm R} = \frac{3}{10} I (I+1) \left(\frac{\mu_0}{4\pi}\right)^2 \gamma_{\rm n}^4 \hbar^2 r_{\rm R}^{-6} (\sin^2 2\xi + \sin^4 \xi) \quad (6)$$

under a single correlation time (τ_R) approximation. Here r_R is the inter-proton distance, and ξ denotes the angle between the proton pair vector and the rotation axis. C_R characterizes the motional mode. If the rotational motion is hindered by an activation barrier E_a between the rotational isomeric states, τ_R will be expressed by

$$\tau_{\rm R} = \nu_l^{-1} \exp[E_{\rm a}/RT] \tag{7}$$

where ν_l is the librational frequency at the trapped states. Equations (5)-(7) predict that T_{1R}^{-1} takes its maximum value $(T_{1R}^{-1})_{max} = 1.425 C_R \omega_0^{-1}$ when $\tau_R = 0.616 \omega_0^{-1}$, while in the slow motion regime where $\tau_R \gg \omega_0^{-1}$, $T_{1R}^{-1} \propto \omega_0^{-2} \tau_R^{-1}$ and therefore $\log[T_{1R}^{-1}(s^{-1})]$ is proportional to reciprocal temperature. In Fig. 7(b) two straight lines are drawn corresponding to $T_1^{-1}(11 \text{ MHz})$ and $T_1^{-1}(62 \text{ MHz})$ with the predicted ω_0^{-2} dependence and a common activation energy of $15 \text{ kJ} \text{ mol}^{-1}$, to demonstrate that rotational motion predominates spin relaxation. The fitted value of E_a turns out to be lower than the antigauche potential barrier, $20 \text{ kJ} \text{ mol}^{-1}$, obtained by theoretical calculation for a single molecule [15]. Our expectation of offering a flat potential onto molecular rotation has been successfully achieved. This value of E_a is also impressively low for such an organic molecule in intercalation compounds: it is far smaller than the value of $36.6 \text{ kJ} \text{ mol}^{-1}$ obtained for NH₂ rotation in NH₂CH₃ intercalated in niobium disulfide but similar to $12.5 \text{ kJ} \text{ mol}^{-1}$ obtained for methyl rotation about the C_3 axis of this compound [25]. The en is in a fairly loose environment in the galleries of TiS₂.

We next consider the absolute value of T_1^{-1} . Equations (5) and (6) show that the maximum $T_{1R}^{-1}(11 \text{ MHz})$ is 38 s^{-1} for CH₂ group rotation and 68 s^{-1} for NH₂ group rotation, provided that intergroup dipolar interactions do not contribute to T_1^{-1} but contribute to spin-diffusion only. Figure 7(b) shows that $T_1^{-1}(11 \text{ MHz}) = 73 \text{ s}^{-1}$ at 290 K, which exceeds the above two values and is close to their sum. This means that τ_R is close to the maximum relaxation condition for the 11 MHz frequency (8.9 ns), and also suggests that both the methylene and amine groups are rotating at similar time scales.

Rotational excitation about the central C–C bond would modify the charge transfer interaction and modify the electronic structure of $TiS_x(en)_y$. However, the temperature dependences of metallic conductivity, the ESR lineshape, and the Pauli paramagnetism did not show any significant anomaly. A possible reason for the absence of a significant anomaly in the temperature dependence of electronic properties will be that the specific interaction between the amino group and the host lattice is not very strong, and rotation of the whole molecule takes place without seriously modifying the electronic interaction with the host lattice.

4. SUMMARY

Ethylenediamine was intercalated into titanium disulfide. Charge carrier generation was evidenced by a significant increase in the metallic conductivity and Pauli paramagnetism. Rapid molecular rotation was found from the proton spin-lattice relaxation measurement. However, our attempt at modifying the electronic property by thermally excited molecular motion seems unsuccessful probably because the specific interaction between the amino group and the host lattice is not very strong, and molecular rotation took place in such a way as not to modify significantly the guest-host electronic interaction.

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