

Chapter 2

Experimental

Abstract Charge-order or charge-glass states are in principal characterized by charge configuration on lattices, offering the opportunity to probe their dynamics by charge-sensitive measurements. It is an experimental advantage for studying glassiness in charge, which is distinctive from the case of the atomic or molecular systems. In this chapter, four different methods we performed are described; (i) resistivity measurements, (ii) resistance fluctuation spectroscopy (so-called noise measurements), (iii) X-ray diffuse scattering measurements, and (iv) NMR measurements.

Keywords Resistivity measurements • Resistance fluctuation spectroscopy • X-ray diffuse scattering measurements • NMR measurements

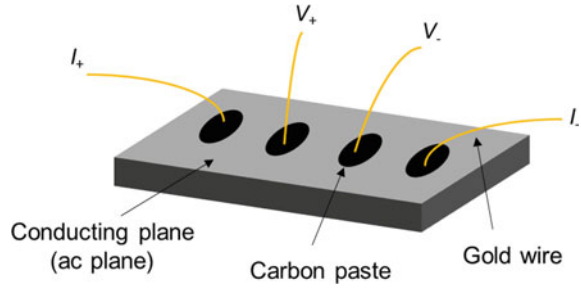
2.1 Sample Preparation

All single crystals of θ -RbZn, θ -CsZn and θ -TiCo were synthesized by the electrochemical method, as described in the literature [1]. The supporting electrolyte for θ -RbZn, θ -CsZn and θ -TiCo, is the mixture of MSCN ($M = \text{Rb, Cs, Ti}$), $M'(\text{SCN})_2$ ($M' = \text{Zn, Co}$), 18-crown-6 ether in 1,1,2-trichloroethane, and 10% vol. of ethanol. The θ -RbZn and θ -CsZn were prepared by Dr. Miyagawa. The θ -TiCo was synthesized by Prof. Mori and Dr. Ueda at the University of Tokyo. The θ -RbZn and θ -CsZn single crystals have long and thin shape with the typical size of $0.1 \text{ mm} \times 0.2 \text{ mm} \times 1 \text{ mm}$. The θ -TiCo, on the other hand, has a block-like shape with the typical size of $0.2 \text{ mm} \times 0.5 \text{ mm} \times 0.5 \text{ mm}$.

2.2 Resistivity Measurements

The in-plane conductance of the series of materials was measured by using the conventional four-probe dc method. The gold wires of 15 or $25 \text{ } \mu\text{m}$ ϕ were attached

Fig. 2.1 Schematic picture of electronic terminals

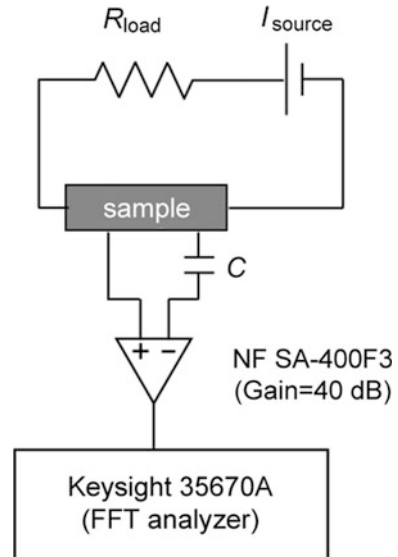


to the crystals with carbon paste, as shown in Fig. 2.1. The measurements were performed under different levels of applied currents, and we took the data in the ohmic regime as those free from the Joule heating.

2.3 Resistance Noise Measurements

In this thesis, we performed the resistance fluctuation spectroscopy, namely, resistance noise measurements, for two different materials θ -CsZn and θ -RbZn. The noise spectra were measured by the four-terminal dc method [2, 3]. A schematic diagram of the noise measurements is shown in Fig. 2.2. The voltage drop under a dc current along the c -axis generated by a low-noise voltage source was amplified by a low-noise preamplifier (NF SA-400F3). Then generated voltage data in the time domains were fed into a FFT analyzer (Keysight 35670A) to obtain the noise

Fig. 2.2 Schematic circuit diagram for four-probe resistance fluctuation spectroscopy



power spectrum density (PSD), S_R . The capacitor, C , is used as a high pass filter, which prevents the dc voltage offset from entering the FFT analyzer. Note that the resistance generally fluctuates in the time domains. Noise measurements capture the fluctuations in resistance as a form of voltage fluctuations by inducing a stable current.

Observed PSD inevitably includes three components as follows; (i) intrinsic fluctuations in sample resistance, (ii) background noise, and (iii) extrinsic noise, which mainly comes from the voltage source and/or contact noise at the sample, etc. Note that in our study, the non-essential noise of (iii) was successfully eliminated by using a large-load resistor, R_{load} , as confirmed below. Consequently, the observed PSD can be described in the following equation;

$$S_V(f, I) = G^2 [I^2 S_{\text{sample}}(f) + S_V^0(f)], \quad (2.1)$$

where G is the gain of the preamplifier. $S_V^0(f)$ is a floor noise, i.e. the background noise, $S_V(f, I = 0)$. It is $S_{\text{sample}}(f)$ that originates from intrinsic fluctuations in sample resistance [the term (i)]. In general, the sensitivity of the dc technique is governed by the background noise $S_V^0(f)$, which is dependent on the thermal noise and the preamplifier's noise figure (NF) defined as

$$\text{NF} = 10 \text{ dB} \times \left[\frac{S_V^0(f)}{S_{\text{nyquist}}} \right], \quad (2.2)$$

where S_{nyquist} is the theoretical value of the thermal noise expected by the Nyquist rule, $S_{\text{nyquist}} = 4k_B T R$, in which k_B is Boltzmann's constant and T is the temperature measured [4]. Figure 2.3 shows the noise figure of the preamplifier (NF SA-400F3) we used, which gives a measure of the amount of noise added by the preamplifier above the thermal noise. By setting the measurements parameter closer to the “eye” of the noise figure, the preamplifier noise becomes lowered. The typical value of sample resistance we measured is in the order of 1–100 Ω , thus the impedance matching is almost achieved in our measurements.

Figure 2.4a displays the observed PSDs of θ -CsZn at 155 K taken at different bias currents I . We confirmed that the background thermal noise [black line in (a)] is frequency-independent (so-called “white noise”) and nearly equal to the expected value expected by Eq. (2.2) (See the dashed horizontal line in Fig. 2.4a). It proves that extrinsic effects of (iii) were successfully eliminated. Then, the intrinsic resistance noise can be deduced by subtracting the value of thermal noise from that of S_V for $I \neq 0$, resulting in the $1/f$ -type PSDs as shown in Fig. 2.4b. Since one expects that the noise level of the voltage is proportional to the square of the applied current, $S_V \propto V^2 \propto I^2$, a necessary condition for checking if the measured noise indeed is solely due to resistance fluctuations of the sample is a scaling behavior above. The data in Fig. 2.5 is found to be scaled very well by the square of current. Also, as expected and required, the observed scaling is independent of the ratio

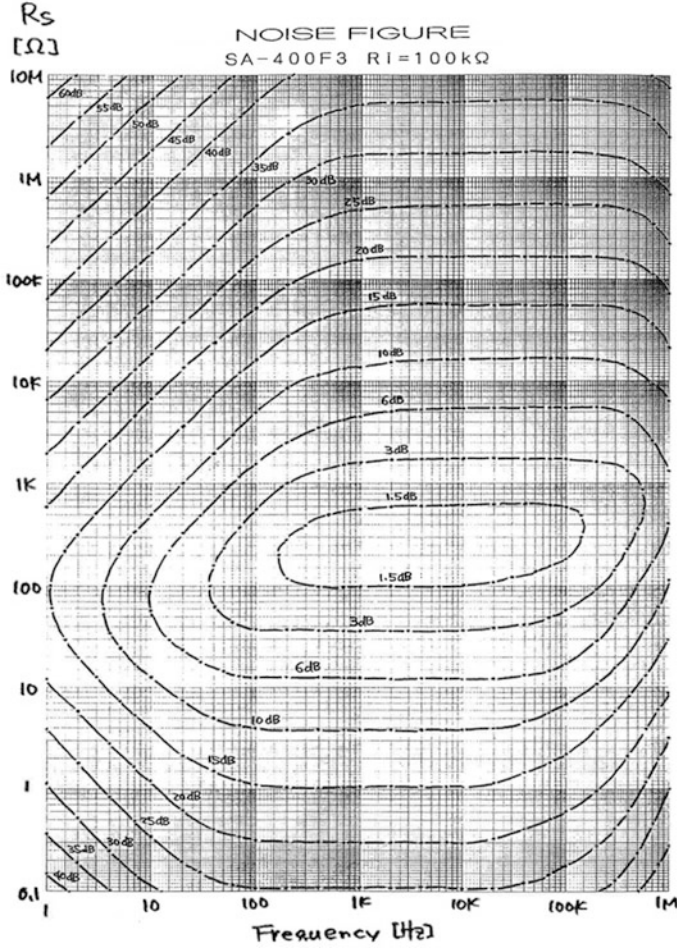


Fig. 2.3 Noise figure contour of NF SA-400F3 preamplifier

R_{load}/R , where R is the sample resistance (see Fig. 2.2). All these tests confirmed that the measured $1/f$ noise originates from the sample and is related to the resistance fluctuations in it.

2.4 X-Ray Diffuse Scattering Measurements

We also measured the X-ray diffraction of θ -CsZn, θ -RbZn, and θ -TiCo single crystal, using a Rigaku DSC imaging plate diffractometer and Si(111) monochromatized synchrotron radiation X-rays ($E = 18$ keV, $\lambda = 0.689$ Å) at the BL-8A and

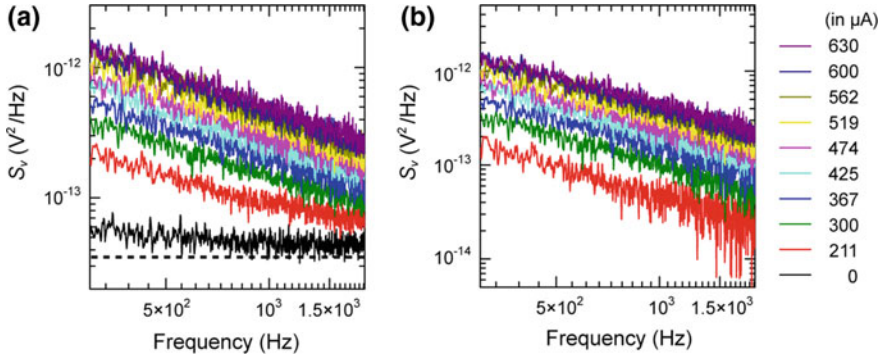
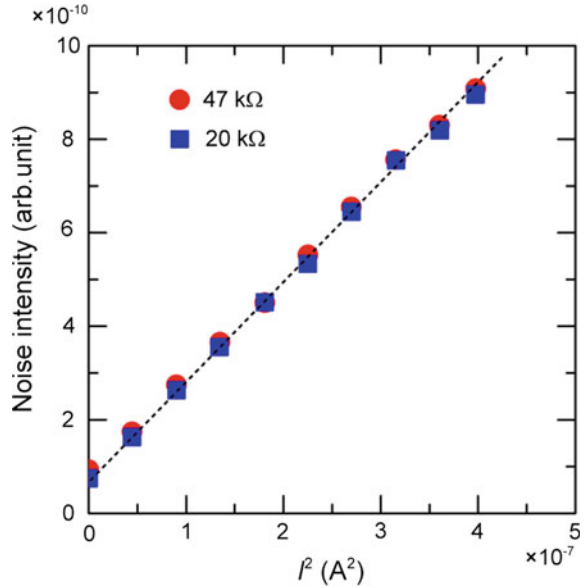


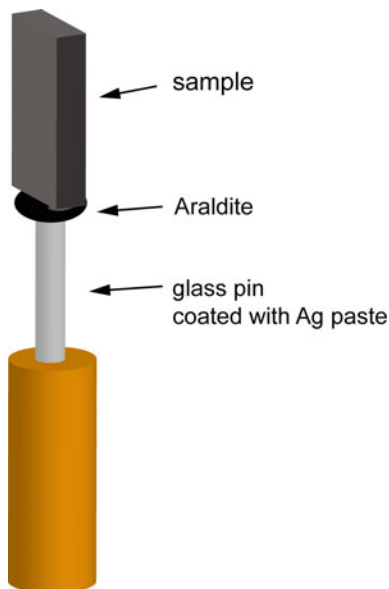
Fig. 2.4 Voltage noise PSD, $S_V(\text{V}^2/\text{Hz})$, for different bias currents I . **a** The observed raw data, and **b** deduced PSDs by subtracting the value of thermal noise from the value of S_V for $I \neq 0$ are shown, respectively. The data in **(b)** correspond to the intrinsic resistance noise

Fig. 2.5 Scaling behavior of S_V (integrated from 300 to 1900 Hz) against the square of bias currents, I . Red and blue plots represent the intensities of the spectra obtained for a different the load resistance



8B beamline of the Photon Factory (PF) at the High Energy Accelerator Research Organization (KEK). Since almost all the θ -TiCo are polycrystalline, we broke down them into smaller pieces with the size of $0.1 \text{ mm} \times 0.1 \text{ mm} \times 0.1 \text{ mm}$, being able to obtain clear oscillation photographs for single crystal. Each sample was mounted by Araldite on the tip of a glass pin, which is coated with Ag paste so as to conduct the heat efficiently (Fig. 2.6). Helium gas was sprayed on the samples to regulate the temperature, which makes it possible to cool them down with maximum rate of approximately 150 K/min.

Fig. 2.6 Schematic figure for mounted sample for X-ray scattering



We analyzed the set of oscillation photographs of conducting planes, focusing on the diffuse scatterings not on the Bragg reflections. The position and the line profile of the observed diffuse scatterings provide the information about the wave vector and the correlation length, ξ , of the short-ranged CO domains, respectively. The ξ can be defined as the inverse of FWHM from the line profile, where FWHM denotes the height of the full-width at half-maximum of the Lorentzian fit to the data.

2.5 NMR Measurements

First, the block diagram of the homodyne-type NMR spectrometer used in this work is shown in Fig. 2.7. Our experiments were performed under an external field (6 T). The spin echo signals after the $(\pi/2)_x - \tau - (\pi)_x$ pulse sequence with $\tau = 10 \mu\text{s}$ were converted into NMR spectra through the Fast Fourier transformation. The typical duration time of the $\pi/2$ pulse was $1.0 \mu\text{s}$, which covers the NMR spectra within approximately $\pm 80 \text{ kHz}$ from the observation frequency. In each spectrum, the line position of TMS (tetramethylsilane) is used as the origin of the NMR shift.

For the ^{13}C -NMR measurements, two central carbon atoms in the BEDT-TTF molecules were selectively enriched by ^{13}C isotopes (Fig. 2.8). As mentioned in the previous chapter, the crystal structure of θ -(BEDT-TTF) $_2\text{X}$ at room temperature is orthorhombic (with space group $I222$); thus, all BEDT-TTF molecules are crystallographically equivalent. As for the NMR spectra, however, each BEDT-TTF

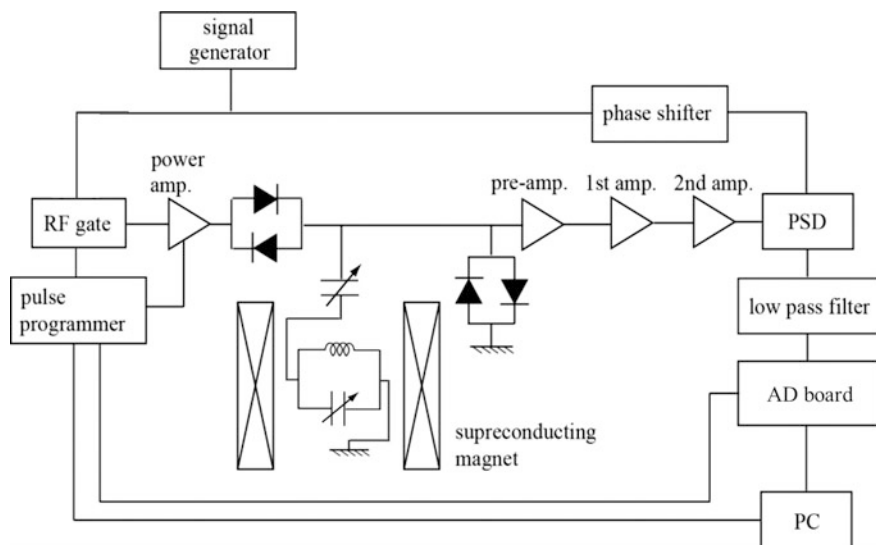
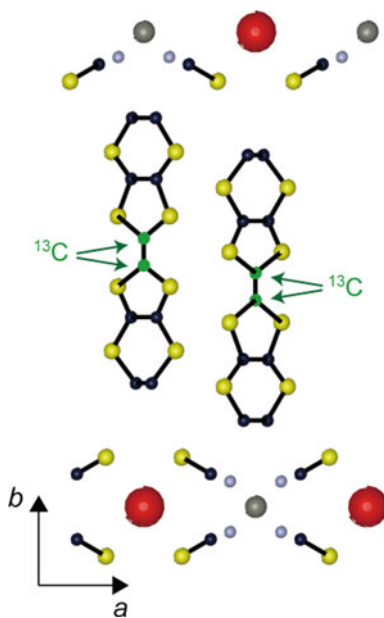


Fig. 2.7 Schematic diagram of the homodyne-type NMR spectrometer

Fig. 2.8 ^{13}C -substituted BEDT-TTF molecule. Arrows indicate the position of the carbon atoms enriched by ^{13}C isotopes



molecule with two ^{13}C nuclear spins gives a spectrum of multiple peaks up to 8 for the following reasons (i)–(iii). (i) The two adjacent ^{13}C nuclei are non-equivalent in the molecule and thus give separate resonance lines. (ii) The nuclear dipole interaction between the adjacent ^{13}C nuclei causes each resonance line split into a

doublet. The splitting width, d , depends on the angle, ϕ , between the directions of the applied magnetic field H and the $^{13}\text{C} = ^{13}\text{C}$ vector (Fig. 2.9a), and is given by

$$d = \left(\frac{3}{2r^3} \right) \gamma_n^2 \hbar (1 - 3 \cos^2 \phi), \quad (2.3)$$

where $\gamma_n/2\pi = 10.7054$ MHz/T is the gyromagnetic ratio of the ^{13}C nucleus, $\hbar$ is the Planck constant divided by 2π , and r is the distance between the adjacent ^{13}C nuclei. (iii) BEDT-TTF molecules form a zig-zag configuration in the conducting layer, as shown in Fig. 2.9b. Therefore, the α and β molecules denoted in Fig. 2.9b are not equivalent with respect to the field directions, except for the particular ones described below, and exhibit separate spectra. Consequently, the number of resonance lines is a maximum total of $2 \times 2 \times 2 = 8$.

In our experiments, we applied the magnetic field in a particular direction to eliminate the splitting sources of (ii) and (iii). If the field direction is within the ab plane, then the α and β molecules are equivalent against the field direction and thus exhibit identical lines; namely, the third effect is eliminated. Furthermore, if the field is directed in the ab plane to form the “Magic angle” against the $^{13}\text{C} = ^{13}\text{C}$ vector, ϕ , that satisfies the condition of $d = \left(\frac{3}{2r^3} \right) \gamma_n^2 \hbar (1 - 3 \cos^2 \phi) = 0$, then the nuclear dipole coupling effect on spectra between the ^{13}C nuclei vanishes, leading to simply two lines positioned at the NMR shifts of the two ^{13}C nuclei. In the experiments, we first adjusted the magnetic field in a direction parallel to the b -axis and then rotated the field direction in the ab plane to realize the magic angle.

Figure 2.10 shows NMR spectra for θ -RbZn that were acquired under the field direction. At 295 K, the spectrum is comprised of two lines, which correspond to the two adjacent ^{13}C nuclei in a BEDT-TTF molecule (Fig. 2.10a). It confirms that

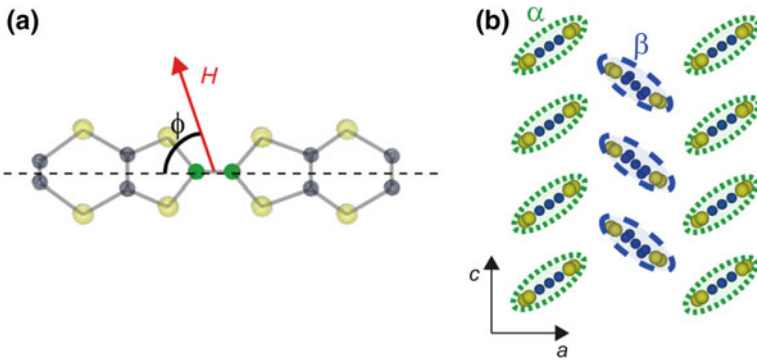


Fig. 2.9 **a** Definition of the angle, ϕ , between the applied magnetic field H and the line connecting adjacent ^{13}C nuclei. **b** Top view of the schematic arrangement of BEDT-TTF molecules in the conducting ac plane. Two molecules, α and β , (highlighted by green dotted line and blue dashed line, respectively) are nonequivalent with respect to arbitrary field direction except for the parallel field configurations to the ab or bc planes

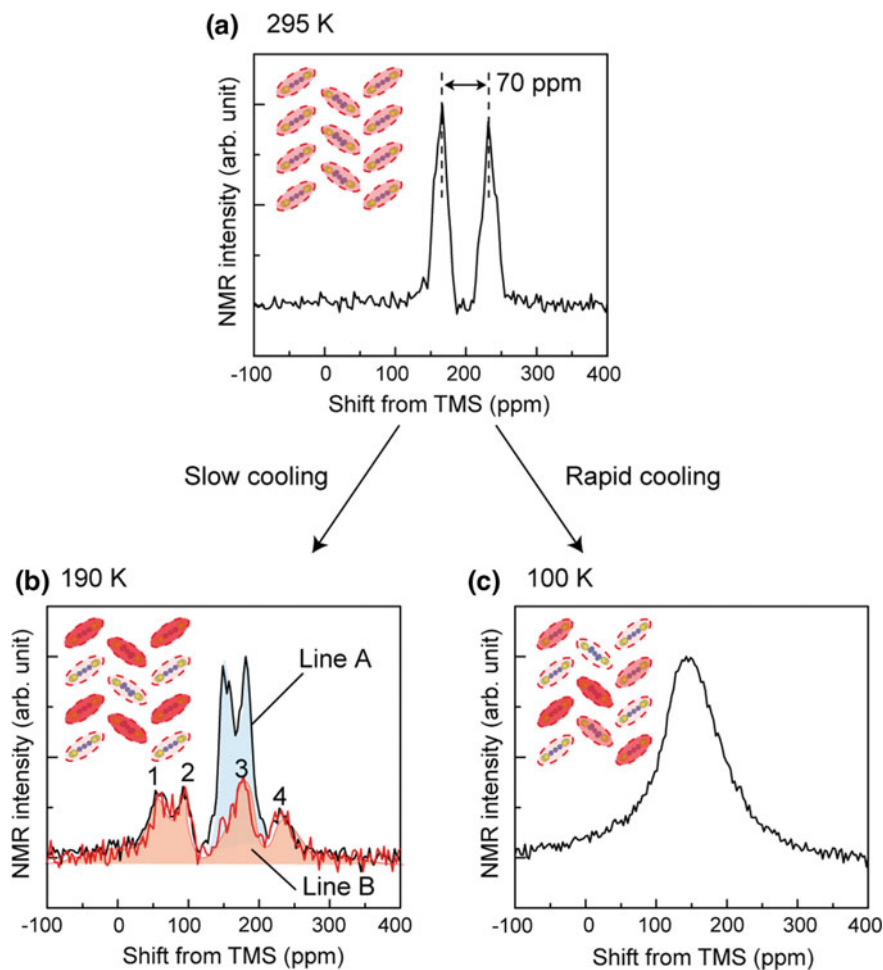
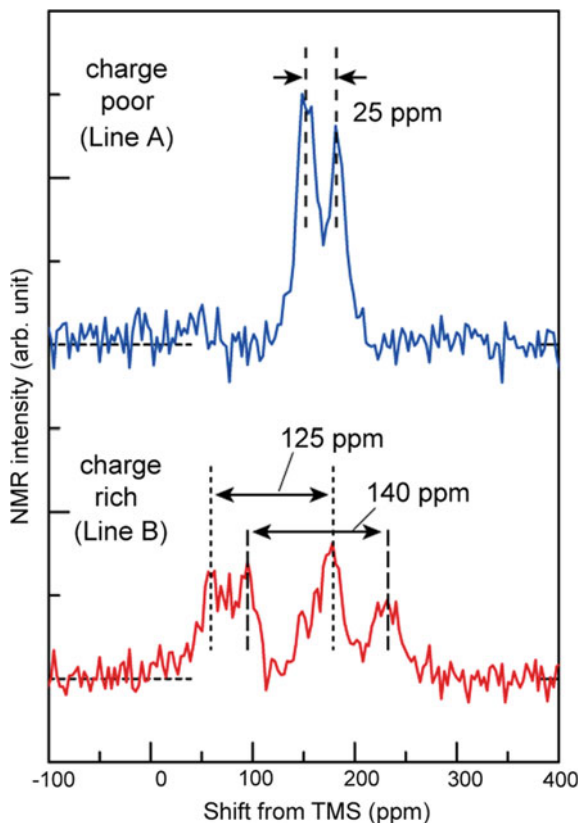


Fig. 2.10 ^{13}C -NMR spectrum for the $\theta\text{-RbZn}$ at several temperatures. **a** The spectrum in the metallic state at room temperature. The two peaks originate from the nonequivalent adjacent ^{13}C nuclei in the center of the molecule. **b** The spectrum in the CO state at 190 K when the sample was slowly cooled (at a rate of approximately 0.1 K/min) through T_{CO} . Spectra A and B are acquired in 1.5 s and 10 ms after the saturation of nuclear magnetization, respectively. **c** NMR spectrum after rapidly cooled (at a rate of 4 K/min) to 100 K

the applied field is precisely set in the desired angle described above, and the electronic state at room temperature is homogeneous.

When $\theta\text{-RbZn}$ is slowly cooled through T_{CO} , the spectrum changes its shape into a complicated structure that is characteristic of the CO state (Fig. 2.10b). The reconstructed spectrum below T_{CO} consists of two components: a doublet (line A, shaded in blue in Fig. 2.10b) and a broad line having four peaks (line B, shaded in red in Fig. 2.10b). Line B is observable at the time of 10 ms after the saturation of

Fig. 2.11 Decomposed ^{13}C -NMR spectrum for the θ -RbZn at 190 K into charge-rich and charge-poor components



nuclear magnetization, whereas line A becomes appreciable only on the order of second or later after the saturation, indicating that the relaxation time of line A is far longer than that of line B. The relaxation time is inversely proportional to the square of the charge-density in the paramagnetic state; thus, the charge disproportionates in the CO state, in agreement with the previous result. Figure 2.11 shows line A, which is obtained by subtracting the 10-m sec spectrum from the 1.5-sec spectrum in Fig. 2.10b, as well as line B. Line A, originating from the charge poor molecule, is a doublet of a shift difference of $\delta_{\text{poor}} = 25$ ppm, whereas line B has a four peaked structure, although the separation of the left two lines is not so clear. The shift difference between the adjacent ^{13}C sites in a molecule is proportional to the local spin susceptibility on the molecule. Referring to the charge disproportionation ratio estimated at 295 K and the reported spin susceptibility, 6.1×10^{-4} emu/mol at 295 K and 7.1×10^{-4} emu/mol at 190 K [1], the shift differences in the poor and rich molecules are expected to be $\delta_{\text{poor}} = (7.1/6.1) \times (0.14/0.50) \times 70 = 23$ ppm and $\delta_{\text{rich}} = (7.1/6.1) \times (0.86/0.50) \times 70 = 140$ ppm. The profile of line A is consistent with this expectation. As for line B, its interpretation of the structure is not straightforward. Considering the expectation of $\delta_{\text{rich}} = 140$ ppm, it is likely that

two nonequivalent charge-rich molecules with the shift differences of 140 and 125 ppm appears below T_{CO} , as indicated in Fig. 2.11. According to the X-ray study, all the charge-rich molecules are equivalent in crystallography [5]; as a result, the observed non-equivalence is attributable to the configuration of the molecule against the field direction. The X-ray study also revealed that the dihedral angle between the neighboring charge-rich molecules increases by 10° upon undergoing the charge ordering transition, i.e., the rotation of the molecules by 5° about the molecular long axis. In the present experiments, the possible error in fixing the field to the desired direction is estimated to be $\pm 3^\circ$; this error may explain the subtle structure of each line at 295 K. It is likely that the small misalignment of magnetic field above T_{CO} is enlarged by the molecular rotation below T_{CO} , giving rise to the nonequivalence between α and β molecules in Fig. 2.9b. If the applied field is rotated, e.g., by 3° in the ac -plane from magic angle, then the Knight shifts in molecules α and β are expected to differ by 35–40 ppm, referring to the known anisotropic hyperfine field. This quantitatively explains the emergence of the two pairs of lines (1–3 and 2–4), which originate from the charge-rich α molecules and the charge-rich β molecules.

Alternatively, when θ -RbZn is cooled rapidly across T_{CO} , the spectrum exhibits a broad and structureless feature (Fig. 2.10c), indicating a continuous distribution in charge density.

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