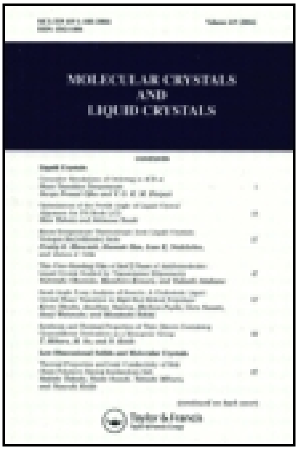

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

charge disproportionation and its ordering pattern in θ and α types of BEDT-TTF salts studied by raman and infrared spectroscopies

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Version of record first published: 18 Oct 2010

To cite this article: Kaoru Yamamoto, Kyuya Yakushi, Makoto Inokuchi, Minoru Kinoshita & Gunzi Saito (2003): charge disproportionation and its ordering pattern in θ and α types of BEDT-TTF salts studied by raman and infrared spectroscopies, Molecular Crystals and Liquid Crystals, 380:1, 221-226

To link to this article: http://dx.doi.org/10.1080/713738722

Mol. Cryst. Liq. Cryst., Vol. 380, pp. 221-226

1058-725X/02 \$12.00 + .00
DOI:10.1080/10587250290101612

CHARGE DISPROPORTIONATION AND ITS ORDERING PATTERN IN θ AND α TYPES OF BEDT-TTF SALTS STUDIED BY RAMAN AND INFRARED SPECTROSCOPIES

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Raman and infrared conductivity spectra are investigated to reveal two-dimensional patterns of stripe charge-ordering in θ*-(BEDT-TTF)*$_2$*RbZn(SCN)*$_4$ *and* α'*-(BEDT-TTF)*$_2$*IBr*$_2$*. Either compounds exhibit similar multiple peak pattern around the C=C stretching region in both Raman and infrared spectra owing to the electron-molecular vibration coupling and charge disproportionation. We discuss the spatial symmetry of the charge-ordering stripes from the group theoretical arguments on the selection rule of these peaks.*

Keywords: charge ordering; α-modification; θ-modification; BEDT-TTF; Raman; vibrational spectroscopy

This study is supported by Grant-in-Aid for Scientific Research on Priority Areas (B) of Molecular Conductors and Magnets (Area No. 730/No. 11224212), the similar grant for Encouragement of Young Scientists (No. 12740392) from the Ministry of Education, Science, Sports and Culture of Japan, and the Joint Studies Program (1999 ~ 2000) of the Institute for Molecular Science.

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INTRODUCTION

Stripe charge ordering has drawn growing attention as an uncultivated area for the study of high T_c materials. Recently, a closely related phenomenon has been suggested to emerge in several organic charge transfer salts with two-dimensional electronic system [1]. Bis(ethylenedithio)tetrathiafulvalene (ET) based salts with α and θ donor arrangements are the typical instances relevant to the phenomenon. As is shown in Figure 1, both types of compounds are based on a similar molecular arrangement, so-called herringbone motif, except whether the presence of dimerization (α) or not (θ). Their band structure with a circular 2D Fermi surface appears to be favor of metallic, but it has been known that most of compounds behave as insulator in low temperature. In the present study, we investigated the molecular vibration spectra to study charge distribution in such an anomalous insulating phase found in θ-$(ET)_2RbZn(SCN)_4$ (RbZn) and α'- $(ET)_2$ IBr_2 (IBr_2).

It has been reported that RbZn salt shows a first-order MI transition between 150 and 190 K possibly accompanied by charge disproportionation [2,3]. By X-ray diffraction, it was confirmed that the first order transition causes a slight dimerization of donor molecules. Such lattice modulation may remind the Peierls distortion. However, Mori et al. have pointed out that the nesting required for the transition mechanism is incompatible with the two dimensional circular Fermi surface of the salt [4]. On the other hand, IBr_2 salt shows anomaly in the conductivity around 200 K, though it is already a semiconductor at room temperature [5]. We found a drastic change of the Raman spectrum pattern at the temperature and have suggested that the conductivity anomaly can be related to the charge ordering [6].

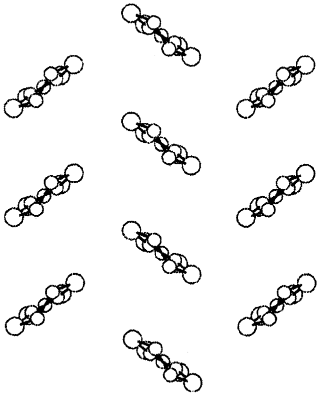

FIGURE 1 Molecular arrangement in the donor layer of θ and α salts.

In the present study, we investigate the C=C related modes of the two substances by Raman and infrared spectroscopies to reveal the symmetry of stripes in the charge ordering state. The two substances give very similar feature in the Raman spectra, indicating emergence of charge disproportionation in both compounds, but the group theoretical analysis suggests that the charges are arranged in stripes with a different orientations.

RESULTS AND DISCUSSION

Figure 2 shows the polarized Raman spectrum of RbZn in the insulating phase. The spectrum shows a large number of peaks within the characteristic frequency for C=C stretching. We have completed the assignment of the multiple peaks by isotope shift measurements [7]. According to the assignment, the multiple peaks have been attributed to two a_g C=C normal modes of ET molecule, which are usually called as v_2 and v_3. Between the two modes, v_3 gives larger electron-molecular vibration (EMV) coupling effect. Because the vibronic effect stems from an interaction between molecular vibration and an intermolecular charge transfer, the spectral features will strongly reflect the symmetry of charge distribution in addition to the unit cell symmetry. Here, focusing on the v_3 related vibronic modes, we discuss the spatial pattern of the ordered charge.

Remark that the multiple Raman peaks show two different polarization dependences; peaks $\mathbf{b_1}$ and $\mathbf{b_2}$ appear only in the (b,b) polarization, on the

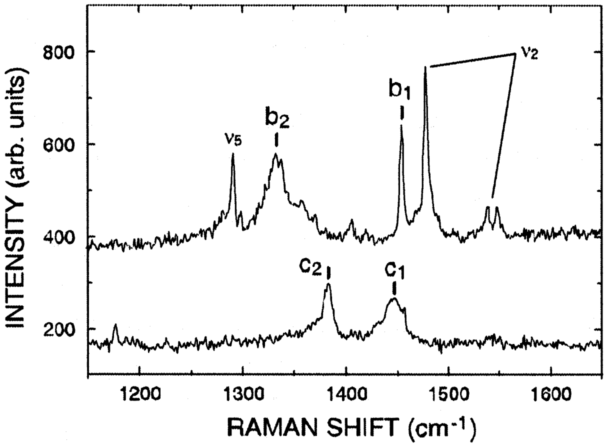

FIGURE 2 Polarized Raman spectra of θ-$(ET)_2RbZn(SCN)_4$ measured at 50 K. Upper and lower curves show the (b,b) and (b,c) polarizations, respectively.

other hand, peaks $\mathbf{c_1}$ and $\mathbf{c_2}$ exist in the (b,c) polarization. This polarization dependence turned out to be satisfactorily understood in terms of the lattice symmetry determined by the X-ray study. The structural analysis showed that the insulating phase belongs to monoclinic system with space group $C2$. Four ET molecules included in the unit cell can be classified into a couple of crystallographically equivalent pairs. As distinguished by α and β in Figure 3 (a), the crystallographically equivalent molecules are arranged perpendicularly to the molecular columns. Each normal mode should be split to give a couple of two combination modes with the A and B symmetries (irreducible representations) in the factor group C_2.

The group theory predicts that the A modes are Raman active in the (b,b) polarization, but inactive in the (b,c) polarization, whereas the B symmetry modes behave oppositely. Hence, by attributing the peaks $\mathbf{b_1}$ and $\mathbf{b_2}$ to the A and peaks $\mathbf{c_1}$ and $\mathbf{c_2}$ to B modes, we can explain the polarization dependence of the Raman signals. This means the charge ordering forms the stripe pattern perpendicular to the molecular columns.

The unit cell of IBr_2 salt also includes two pairs of inequivalent ETs. In contrast to RbZn salt, however, crystallographically equivalent molecules combined by inversion center are stacked in the same columns, as is shown in Figure 3 (b) [8]. Figure 4 shows the Raman (a) and infrared conductivity spectra (b) of the salt. The two spectra exhibits complicated multiple peaks, indicating the charge disproportionation similar to the case of RbZn. Without the help of isotope shift measurements, it would be hard to give the complete assignment for the multiple peaks. Nevertheless, one can find a clue to the selection rule of the multiple peaks; the Raman spectrum

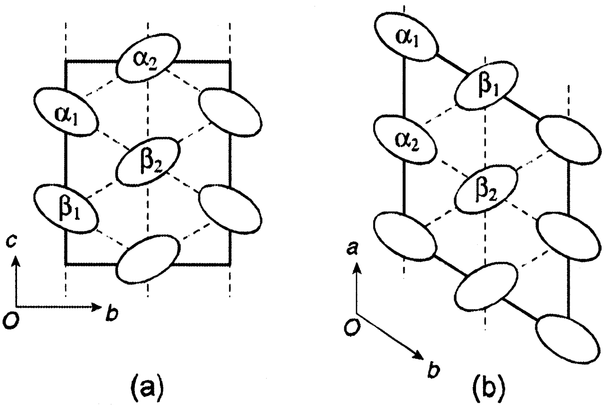

FIGURE 3 Molecular arrangement in the unit cells of (a) RbZn and (b) IBr_2 salts.

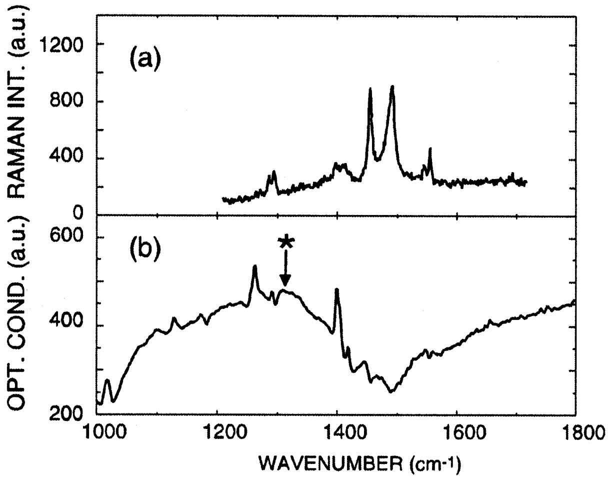

FIGURE 4 (a) Raman and (b) infrared spectra of α'-$(ET)_2IBr_2$ salt measured at 50 K and 60 K, respectively. The asterisk indicates an EMV mode of v_3.

doesn't show any signal corresponding to the rather broad band around 1300 cm^{-1} found in the conductivity spectrum (marked by an asterisk in Figure 4 (b)). This band is attributed to an EMV mode of ν_3 because of its shape and frequency. It is usually difficult to experimentally prove absence of signals. However, missing of the infrared active peak in the Raman spectrum suggests that the exclusion rule based on a inversion symmetry still works in the charge ordering phase. Remaining inversion symmetry requires that the charge ordering runs along the arrangement of the crystallographically equivalent molecules to form the stripes parallel to the molecular columns, in contrast to the perpendicular pattern found in RbZn salt.

CONCLUSION

We have studied the vibrational spectra of RbZn and IBr_2 salts to investigate the symmetry of charge ordering found in low temperature. Both compounds show multiple peaks around the C=C stretching region due to the charge disproportionation and EMV coupling. By the group theoretical interpretation of the multiple peaks, we confirmed that the ordering of the charge stripes in RbZn salt is perpendicular to the molecular columns. On the other hand, it was suggested that IBr_2 salt forms the charge stripes oriented in parallel to the columns.

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