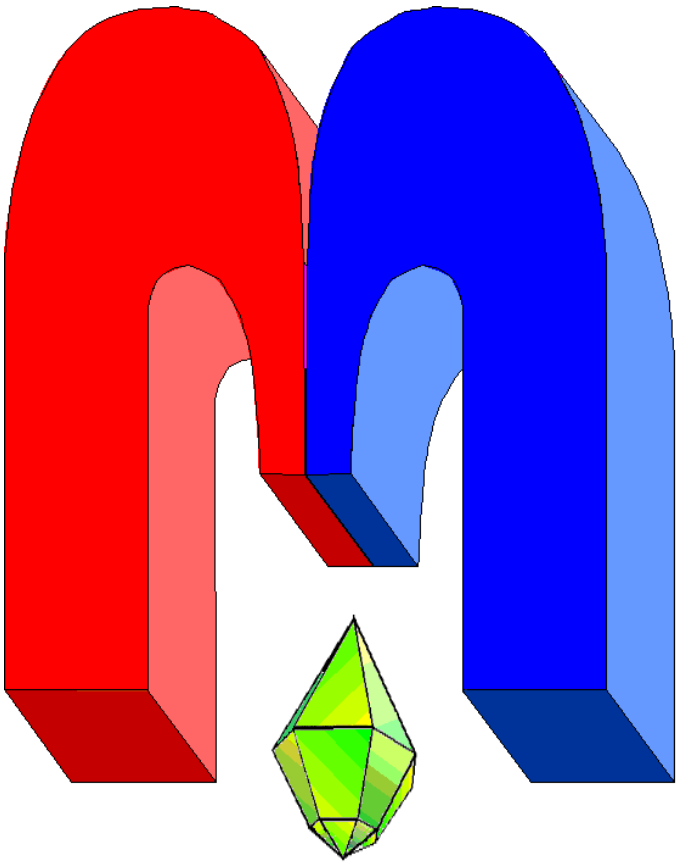
ISSN 2072-5981



Magnetic Resonance in Solids

Electronic Journal

Volume **12,** *No.* **2**
pages **17-21**
2010

http://mrsej.ksu.ru

Established and published by Kazan University
Sponsored by International Society of Magnetic Resonance (ISMAR)
Registered by Russian Federation Committee on Press, August 2, 1996
First Issue was appeared at July 25, 1997

"***Magnetic Resonance in Solids. Electronic Journal***" (**MRS*ej***) is a peer-reviewed, all electronic journal, publishing articles which meet the highest standards of scientific quality in the field of basic research of a magnetic resonance in solids and related phenomena. **MRS*ej*** is free for the authors (no page charges) as well as for the readers (no subscription fee). The language of **MRS*ej*** is English. All exchanges of information will take place via Internet. Articles are submitted in electronic form and the refereeing process uses electronic mail. All accepted articles are immediately published by being made publicly available by Internet (*Editor@ksu.ru*).

* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Spin dynamics and charge order-disorder phase transition detected by EPR in α′-(BEDT-TTF)$_2$IBr$_2$

A.I. Dmitriev*, A.S. Chernenkaya

Institute of Problems of Chemical Physics Russian Academy of Sciences, Semenova, 1, Chernogolovka 142432, Russia

**E-mail*: aid@icp.ac.ru

(Received October 28, 2010; revised December 8, 2010; accepted December 13, 2010)

Stepwise changes in electron paramagnetic resonance (EPR) parameters (integral intensity, linewidth) accompanying localization of charge carriers have been found in the α'-(BEDT-TTF)$_2$IBr$_2$ crystals. In single crystal exchange narrowing of the EPR lines and sharp decrease in static and dynamic magnetic susceptibility caused by antiferromagnetic interaction of localized charge carriers is observed at $T < 50$ K. At $T > 50$ K a difference between static and dynamic magnetic susceptibility is observed in the α'-(BEDT-TTF)$_2$IBr$_2$ crystals which is due to that the frequency of thermally activated charge carrier jumps is higher than the microwave frequency of measuring field of an EPR spectrometer.

PACS: 75.50.Xx, 76.30.-v.

Keywords: charge order, order-disorder, BEDT-TTF

1. Introduction

Organic metals based on bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) molecules are suitable objects for investigation of localization of charge carriers and strong spin-spin and charge correlations in conditions of lower dimensionality [1]. Layered structure of these compounds provides strong anisotropy of electric conductivity along and across the BEDT-TTF layers. Thus, the crystals of BEDT-TTF based compounds can be considered as quasi-two-dimensional systems. It is known that competition between thermal kinetic energy and Coulomb interaction of charge carriers can result in different types of localization which is observed with the temperature decrease down to a certain critical value [2]. In general, localization of charge carriers is evidenced by a sharp or a long-continued (in the temperature scale) decrease in electric conductivity. The localization process is identified using infrared spectroscopy sensitive to vibrational modes of molecules. Thus, infrared spectroscopy allows one to identify charge carriers localization areas.

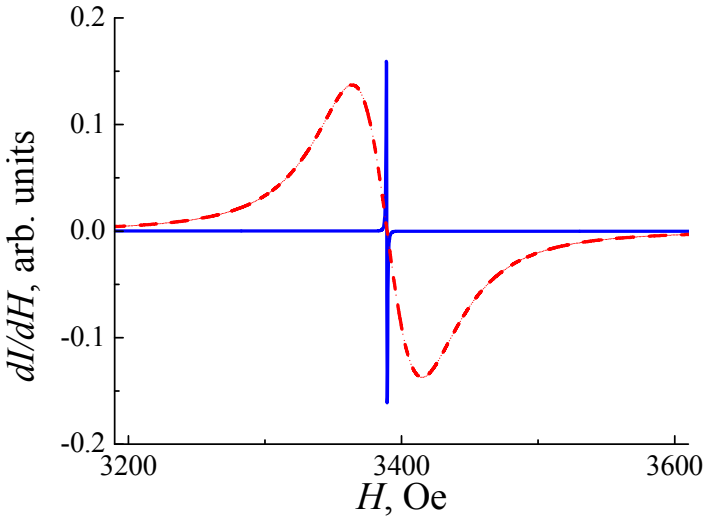


Figure 1. EPR spectra for α'-(BEDT-TTF)$_2$IBr$_2$ at $T = 300$ K (red dashed line) and $T = 4$ K (blue solid line). The angle between static magnetic field of a spectrometer and crystal plane $\theta = 0^0$.

The α'-(BEDT-TTF)$_2$IBr$_2$ radical cation salt was synthesized about 20 years ago by the team of professor E.B. Yagubskii from Institute of Problems of Chemical Physics of Russian Academy of Sciences [3]. Its crystal structure, conductivity and infrared spectra were analyzed in detail [4, 5]. The experimental data allowed one to reliably identify holes localization near 208 K [4, 5] and gradual freezing of thermally activated

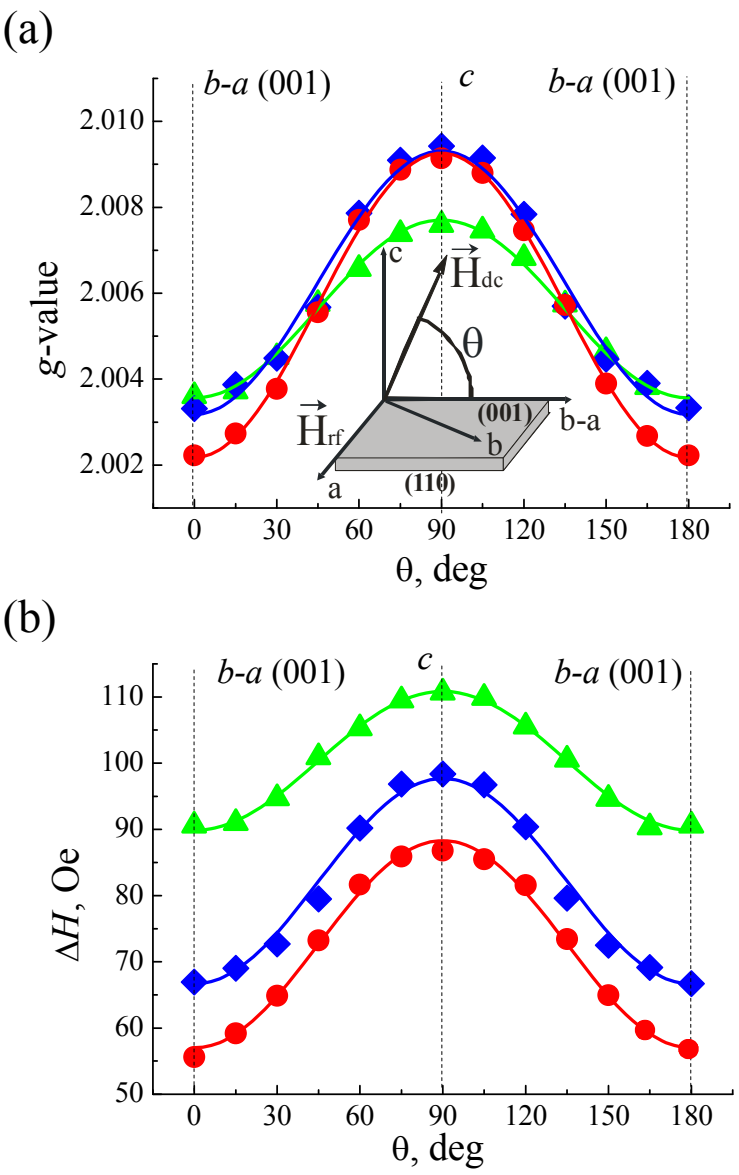


Figure 2. Angular dependences of *g*-factor (a) and Δ*H* (b) below hole localization temperature (at $T = 100$ K (green triangles) and $T = 190$ K (blue squares)) and above hole localization temperature ($T = 220$ K (red circles)) in the α'-(BEDT-TTF)$_2$IBr$_2$ single crystal. Approximation is shown by solid line. The insert shows radio frequency and static magnetic field orientations with respect to the crystal and the direction of its rotation when measuring angular dependence. Angle $\theta = 0^0$ corresponds to static magnetic field lying in *ab* plane of the crystal.

rotation of ethylene groups from 250 K down to 70 K. It was reliably established using X-ray diffraction, reflection spectroscopy and infrared spectroscopy that a sharp transition in a charge carrier subsystem at 208 K is fully electronic one and is not accompanied by the changes in crystal or molecular structure [4, 5]. Therefore, α'-(BEDT-TTF)$_2$IBr$_2$ crystals attract great attention since the given system provides the opportunity not to consider drastic changes in potential energy modulated by crystal lattice. Thus, localization processes can be considered as a result of electron-electron interactions.

Previously, physical properties of α'-(BEDT-TTF)$_2$IBr$_2$ have been studied which evidenced charge interaction. Spin dynamics of holes and its response to localization and other processes in crystals was neither analyzed nor discussed. It should be noted that static magnetic measurements were reported in [4]. It was shown that a sharp decrease in static magnetic susceptibility of the crystals is observed at $T < 50$ K which according to the authors of [4] is evidence of antiferromagnetic interaction of localized holes. In our work, electron paramagnetic resonance (EPR) was studied additionally to measurements of integral magnetic moment of the sample. It was shown that EPR spectroscopy is a powerful tool to be used to find localization of charge carriers from the changes in line shape and other parameters of EPR spectra [6].

2. Experiment

Relatively large α'-(BEDT-TTF)$_2$IBr$_2$ single crystals were used in experiments which appeared as naturally faceted plates of ~ 0.2 × 2 × 5 mm^3. X-ray analysis showed that the samples were free of twins and their crystal structure corresponded to that described in detail in [3, 4].

High-frequency spin dynamics ant its contribution to magnetic susceptibility were studied using a Bruker EMX EPR spectrometer operating at X-band (9.650 GHz) equipped with a rectangular resonator of H_{102} type and 100 kHz modulation frequency. Magnetic field scanning range was 0-16 kOe. Temperature was varied from 6 K to 280 K with 0.1 K accuracy in a ESR900 Oxford Instruments cryostat. As a result of EPR measurements on single crystals, the dependences of the first derivative of imaginary part of microwave absorption on crystal orientation, *dI/dH*, at $T = 295$ K and the temperature dependence of the first derivative of microwave absorption at fixed crystal location were obtained. A comparative analysis of the doubly integrated EPR line and that of a reference sample allowed dynamic magnetic susceptibility χ_{AC} to be determined. It should be noted that samples were cooled down in ESR900 cryostat at constant (room) temperature of a resonator and spectrometer sensitivity which was dependent of *Q*-factor was normalized to a calibration curve. In angular dependence measurements, the sample was oriented in a holder with an optical microscope with absolute accuracy of $\pm 5^0$ and its rotation in a resonator was realized using a ER218PG1 automatic goniometer with relative accuracy of $\pm 0.1^0$.

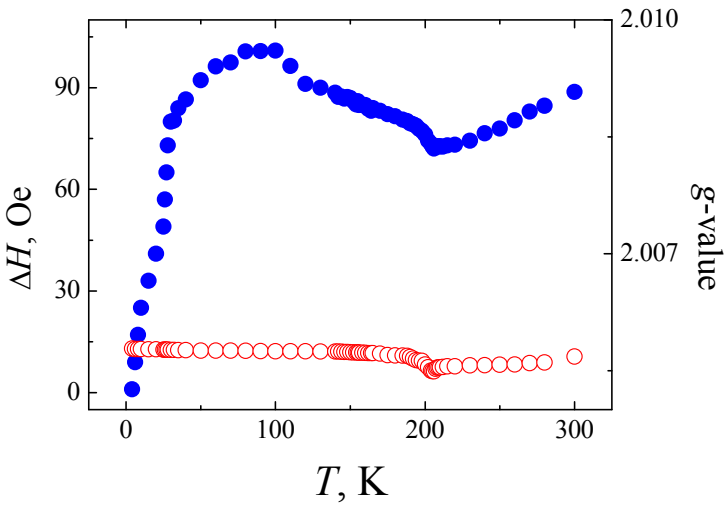


Figure 3. Temperature dependences of linewidth ΔH (solid blue circles) and *g*-factor (open red circles) of the EPR signal from the α'-$(BEDT\text{-}TTF)_2IBr_2$ single crystals. The angle between static magnetic field of the spectrometer and the *ab* plane is $\theta = 0^0$.

The dependence of magnetic moment *M* for single crystal samples on temperature ($T = 2$-300 K) in magnetic field $H = 1000$ Oe was measured using a MPMS 5XL (Quantum Design) SQUID magnetometer.

3. Results and discussions

The EPR spectrum for the α'-$(BEDT\text{-}TTF)_2IBr_2$ single crystal was a single Lorentz line (fig. 1). At $T > 50$ K the linewidth was 70 - 90 Oe (fig. 1) and at low temperatures it strongly narrowed and attained 0.8 Oe at 4 K. Since there are no other paramagnetic particles except charge carriers in the α'-$(BEDT\text{-}TTF)_2IBr_2$, crystals, we ascribed the observed line to holes in this compound.

"Out-of-plane" angular dependencies of *g*-factor and linewidth (fig. 2) were approximated by standard formulas for axial symmetry of crystalline field [7, 8]. Approximation parameters are close to generally observed EPR parameters for the BEDT-TTF molecules [9, 10]. It is seen from fig. 2 that localization of holes at 208 K is not accompanied by changes in symmetry or essential changes in parameters of these equations. In the α'-$(BEDT\text{-}TTF)_2IBr_2$ crystals, the absence of changes in the EPR line shape in the process of holes localization (fig. 2) and insensitivity of the angular dependence of *g*-factor and linewidth to this process in the α'-$(BEDT\text{-}TTF)_2IBr_2$ crystals (fig. 2) can be interpreted as an indicator of ordered state of localization areas with similar local crystal fields. This fact is in good agreement with localization models proposed earlier in [4] according to which one delocalized hole is per two neighboring BEDT-TTF molecules oriented at a certain angle to each other. As a result of localization, a hole belongs to one of these molecules only. Therefore, holes are localized on regular (periodic) molecules of crystal.

On the contrary, EPR linewidth was found to be sensitive enough to both localization of holes at $T = 208$ K (fig. 3) and low-temperature antiferromagnetic correlations which result in sharp decrease in static and dynamic magnetic susceptibility at $T < 50$ K (fig. 3). Drastic changes in linewidth at holes localization in α'-(BEDT-TTF)$_2$IBr$_2$ (fig. 3) can be interpreted using the data obtained in [4] from the analysis of vibrational infrared spectra. It was shown that dynamically averaged symmetry of the crystallographic cell containing inversion occurs in the high-temperature range ($T > 208$ K). At low temperatures ($T < 208$ K) this symmetry is lost because of localization of charge carriers, i.e. crystal field symmetry lowers. Probably this results in a sharp broadening of the EPR line changes in *g*-factor value (corresponding an orbital component) at temperatures below 208 K.

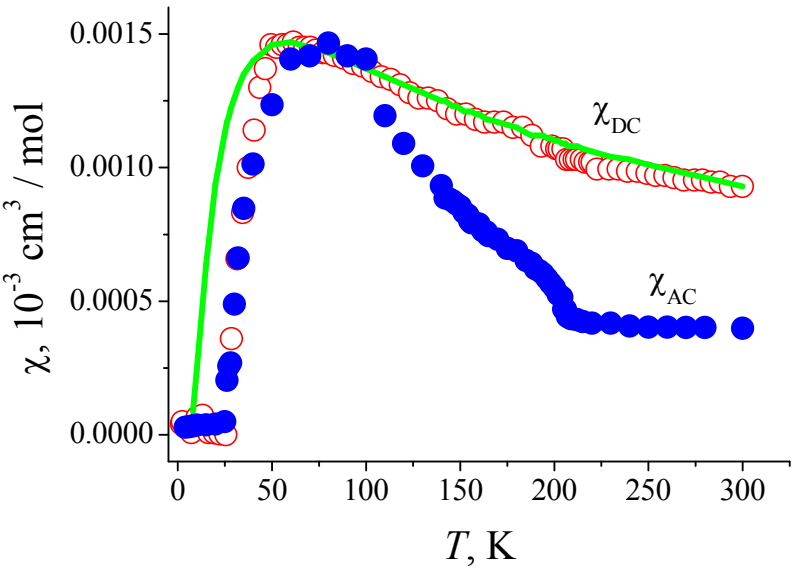


Figure 4. Temperature dependences of static χ_{DC} (open red circles) and dynamic χ_{AC} (solid blue circles) magnetic susceptibility determined from SQUID measurements in static magnetic field of 1 kOe strength and double integration of the spectrum for α'-(BEDT-TTF)$_2$IBr$_2$, respectively. Solid green line indicates approximation of the temperature dependence of static magnetic susceptibility $\chi_{DC}(T)$ by the model of Heisenberg chain.

We suggest that an important feature is the difference of static magnetic susceptibility χ_{DC} from dynamic magnetic susceptibility χ_{AC} at $T > 110$ K (fig. 4). A series of calibration experiments was purposefully performed for a SQUID magnetometer and an EPR spectrometer. The tests showed that the difference cannot be due to variations of sensitivity of the instruments with changing temperature. The difference between χ_{DC} and χ_{AC} at 110 K can be due to frequency-sensitive character of AC measurements in an EPR spectrometer. At $T < 110$ K $\chi_{DC} = \chi_{AC}$ and the dependences are different at higher temperatures. Since spin carriers movement is almost frozen at low temperatures, a sharp decrease in χ_{DC} and χ_{AC} can be due to exchange interaction between charge carriers. Considering crystal symmetry of the arrangement of localization areas, one can use the Heisenberg model for a uniform spin chain $S = 1/2$ undergoing alternating exchange interactions [11]. Such approximation can be chosen since the distance between spins inside a unit cell is shorter than that between spins in the neighboring cells. Exchange interactions are in agreement with an extremely narrow EPR linewidth at low temperatures (fig. 3), if it is assumed that this effect is due to Anderson-Weiss exchange narrowing [12].

Thus, the analysis of spin dynamics of charge carriers in α'-(BEDT-TTF)$_2$IBr$_2$ provides more information as compared with static measurements. Moreover, it provides additional information on kinetics of hopping conductivity and participation of charge carrier spins in the process.

4. Summary

Localization of charge carriers in α'-(BEDT-TTF)$_2$IBr$_2$ is accompanied by drastic changes in parameters of the EPR spectrum: integral intensity, *g*-factor and linewidth. In α'-(BEDT-TTF)$_2$IBr$_2$ charge carriers are localized in regular positions of the unit cell. The increase in symmetry of the EPR spectra at low temperatures indicates certain geometry of exchange-bound spins. In the α'-(BEDT-TTF)$_2$IBr$_2$ crystals, exchange narrowing of the EPR line and harp decrease in static and dynamic magnetic susceptibility stipulated by antiferromagnetic interaction of localized charge carriers is observed at low temperatures ($T < 50$ K). The difference between static χ_{AC} and dynamic χ_{DC} magnetic susceptibility at $T > 50$ K in the α'-(BEDT-TTF)$_2$IBr$_2$ crystals is due to that the frequency of carriers thermally activated hopping between localization areas is higher than the frequency of measuring microwave frequency field of a spectrometer.

Acknowledgments

We are grateful to scientific advisor professor R.B. Morgunov and professors K. Yakushi and K. Yamomoto for samples providing.

References

1. Ishiguro T., Yamaji K. *Organic superconductors*, Springer-Verlag, Berlin, Heidelberg (1989).
2. Watanabe M., Nishikawa M., Nogami Y., Oshima K., Saito G. *J. Kor. Phys. Soc.* **31**, 215 (1997).
3. Yagubskii E.B., Shchegolev I.F., Shibaeva R.P., Fedutin D.N., Rozenberg L.P., Sogomonyan E.M., Lobkovskaya R.M., Laukhin V.N., Ignat'ev A.A., Zvarykina A.V., Buravov L.I. *JETP Letters* **42**, 206 (1985).
4. Yue Y., Nakano C., Yamamoto K., Uruichi M., Wojciechowski R., Inokuchi M., Yakushi K., Kawamoto A. *J. of Phys. Soc. Jpn.* **78**, 044701 (2009).
5. Yue Y., Nakano C., Yamamoto K. Uruichi M., Yakushi K., Kawamoto A. *J. Phys.: Conf. Ser.* **132**, 012007 (2008).
6. Morgunov R.B., Shibaeva R.P., Yagybskii E.B., Kato T., Tanimoto Y. *JETP* **102**, 121 (2006).
7. Morgunov R., Dmitriev A., Chernenkaya A., Yamamoto K., Yakushi K., Tanimoto Y. *Physica B* **405**, S138 (2010).
8. Morgunov R., Dmitriev A., Chernenkaya A., Yakushi K., Yamamoto K. *JETP* **111**, 970 (2010).
9. SuganoT., SaitoG., KinoshitaM. *Phys. Rev. B* **35**, 6554 (1987).
10. Parkin S.S.P., Miljak M., Cooper J.R. *Phys. Rev. B* **34**, 1485 (1986).
11. Johnston D.C., Kremer R.K., Troyer M. Wang X., Klümper A., Bud'ko S.L., Panchula A.F., Canfield P.C. *Phys. Rev. B* **61**, 9558 (2000).
12. Anderson P.W., Weiss P.R. *Rev. Mod. Phys.* **25**, 269 (1953).