1Ep08 Localization of Conduction-band Electrons in β"-(BEDT-TTF)$_4$ NH$_4$ [Cr (C$_2$O$_4$)$_3$]·DMF Single Crystals

Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

A. A. Baskakov, L. R. Dunin-Barkovskiy, T. Kato, ○R. B. Morgunov, Y. Tanimoto, E. Yagubskiy

Preface. Recently synthesized β"-(BEDT-TTF)$_4$ NH$_4$ [Cr (C$_2$O$_4$)$_3$]·DMF [1] single crystals represent a compound that could be considered as a material for spintronics since crystals of this type possess giant magnetoresistance and, under condition of magnetic ordering in the subsystem of localized spins, could be an analog of heterostructures providing spin polarization of conduction electrons emitted from the magnetic layer to the conducting one [2]. This makes investigation of interactions between conduction electrons and localized magnetic moments in crystals to be attractive. The purpose of the presented work was in design of the conditions for separation of contributions of localized magnetic moments and conduction electrons into magnetic properties of single crystals of the mentioned compound as well as in an attempt of finding and investigation of mutual influence of s- and conduction π-electrons.

Experimental. Single crystals on the base of organic donor molecules of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) and chromium oxalate Cr(C$_2$O$_4$)$_3$ were obtained by electrocrystallization from solution (for details see [1]). According to X-ray structural analysis [1], the single crystals are characterized by the *C*2/*c* symmetry and consist of alternating layers of β"-phase of BEDT-TTF and approximately hexagonal net of (C$_2$O$_4$)$_3$ and Cr^{3+} with dimethylformamide (DMF) molecules. X-band EPR spectrometers Bruker ESP300E and E500 (rectangular H$_{102}$ cavity) with the modulation frequency 100 kHz and the range of static magnetic field sweep B$_0$ = 0–15 kOe were used. The measured EPR signal was proportional to the first derivative of the real part of magnetic susceptibility χ of the specimen. The temperature was varied within the range 1.5–300 K. During the measurements the specimen investigated was placed into a fused quartz ampoule, pumped out and sealed.

Results of experiments. EPR spectrum of the investigated single crystals consists of two lines (figure). One, consisting of three Gaussian shape components, is the EPR response of Cr^{3+} ions. The other line at temperatures close to the room one represents a spectrum of clearly Lorentzian shape if the electrical component **E** of the microwave field is directed normal to the (*ab*) plane of the crystal. In the orientation **E** ⊥ (ab) an asymmetric Dysonian shape line is observed. It is logical to associate its origin with resonance in the subsystem of conduction electrons of BEDT-TTF. So, presence of two magnetic subsystems in the crystal, predicted by X-ray structural analysis [1], becomes apparent in the form of two separated EPR lines. This gives one the possibility of independent investigation of magnetic features of each the subsystem and interaction between them.

Figure. Angular dependence of ESR spectrum of β"-(BEDT-TTF)$_4$ NH$_4$ [Cr (C$_2$O$_4$)$_3$]·DMF single crystal.

Decreasing of the temperature from 300 K down to 1.5 K causes changes in the EPR spectra for the lines of both the magnetic subsystems. The real part of magnetic susceptibility of chromium ions χ^{Cr} is
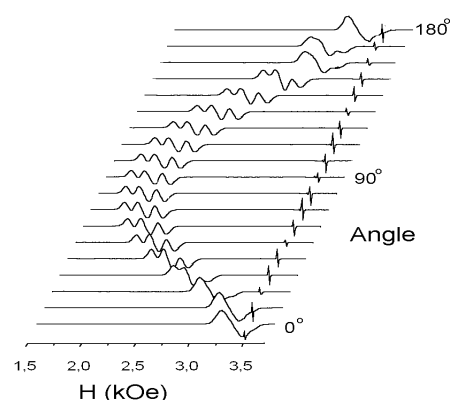
close to the Curie-Weiss law $\chi^{Cr} = C^{Cr}/(T-\Theta^{Cr})$, where $\Theta^{Cr} = -2$ K, however the temperature dependence of the value $\chi^{Cr}T$, proportional to the number of spins in the specimen, allows one to find out deviations from the Curie-Weiss law. At the temperature $T \approx 20$ K an abrupt decrease of the value $\chi^{Cr}T$ is observed.

The temperature dependence of the effective g-factor depends on orientation of $\mathbf{H_0}$ relative to the crystal: if $\mathbf{H_0}$ is normal to the BEDT-TTF layer, at $T \approx 20$ K increase of g^{ET} occurs, whereas under parallel orientation of $\mathbf{H_0}$ relative to the BEDT-TTF layer an abrupt decrease of g^{ET} is observed. In the case when the $\mathbf{H_0}$ vector is directed at the angle of $\sim 20°$ to the (ab) plane, the g^{ET} value does not depend on temperature in all the investigated temperature range.

At temperatures $T > 20$ K the ET spectrum in the orientation $\mathbf{E} \perp (ab)$ has the Lorentzian shape within the accuracy 99%. At $T < 20$ K, when jump-like decrease of the number of Cr^{3+} spins occurs, an abrupt broadening on the wings of the BEDT-TTF spectrum is observed, what does not allow one to approximate it by a Lorentzian line any more. In order to quantitatively characterize this deviation, we used the relation $\delta = Y_{max}'/Y'(3/2\Delta H_{pp}^{ET})$, that is ratio of amplitude of the first derivative of the EPR signal $Y_{max}' = (dY/dH_0)_{max}$ at the width H_{pp}^{ET} to its amplitude $Y'(3/2\Delta H_{pp}^{ET})$ at the width $3/2\Delta H_{pp}^{ET}$. According to [9], this value has to be equal to 0.33 for a purely Lorentzian line and becomes equal to 0.05 for a purely Gaussian one. It was found that $\delta = 0.33$ at $T > 20$ K and it abruptly decreases down to 0.1 as the temperature is decreased from 20 to 3.3 K. Since the described above change of the line shape does not disturb its symmetry, decomposition of the BEDT-TTF spectrum into two lines of Lorentzian and Gaussian shapes was carried out with account of the fact that the effective g-factors of both the components coincide. It was found that at $T < 20$ K relative contribution of the Lotentzian component χ_L decreases and the portion of the magnetic susceptibility corresponding to the Gaussian line χ_G increases. This occurs most effectively for the crystal orientations in which the BEDT-TTF layers are normal to the static magnetic field. Change of the line shape is the mostly pronounced under the orientation of the magnetic field $\mathbf{H_0}$ along the BEDT-TTF layers. As one approaches the mutually perpendicular orientation of $\mathbf{H_0}$ and the BEDT-TTF layers, line distortions caused by the temperature decreasing turn to be weaker.

Conclusion.

1. Separated ESR lines of BEDT-TTF radicals and Cr^{3+} ions were found in spectra of β''-(BEDT-TTF)$_4$ NH$_4$ [Cr (C$_2$O$_4$)$_3$]·DMF single crystals. Comparison of angular dependencies of Cr^{3+} g-factor with anisotropy of ESR spectra in Cr (C$_2$O$_4$)$_3$ revealed influence of BEDT-TTF layers on splitting of Cr^{3+} spin sublevels. Angular variation of line-width and its mean value at the room temperature are in agreement with the BEDT-TTF packing and predictions of the Elliot theory.

2. It was found that decrease of temperature below $T \approx 20$ K leads to abrupt reorganization of ESR spectrum. Transformation of the BEDT-TTF Lorentzian line-shape to the Gaussian one indicates localization of conduction-band electrons. Interdependence between changes of the BEDT-TTF and Cr^{3+} lines showed that temperature variations of Cr^{3+} susceptibility are accompanied by changes in conduction-band electrons behavior.

References

1. T. G. Prokhorova et al., Advanced Functional Materials, **13**, 1 (2003).
2. M. Ziese, M. J. Thornton, "Spin electronics", Berlin: Springer, 2001, p. 500.