

Pressure Effects on an Organic Radical Ferromagnet γ -BBDTA•GaCl₄

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Introduction

A radical cation salt, BBDTA(= benzo[1,2-d:4,5-d']bis[1,3,2]dithiazole)•GaCl₄, has three polymorphs, labeled α , β and γ . The γ -phase with orthogonal three-dimensional network shows the ferromagnetic ordering at 7.0 K, in contrast to diamagnetic properties of the α - and β -phases with one-dimensional stacking [1]. The very high T_C of 7.0 K in this salt originates from compact intermolecular linkages through S••S or S••N interatomic contacts, and largely exceeds the previous record, 1.5 K [2], in the organic radical system. The further increase of T_C might be realized by making these contacts shorter. In this study, the pressure effects on the organic ferromagnet, the γ -phase BBDTA•GaCl₄, have been investigated through the ac magnetic susceptibility measurements and structural analysis experiments in the pressure region up to 17.8 kbar.

Experiment

The thiazyl organic crystal, BBDTA•GaCl₄, was prepared according to the procedure elsewhere [1]. The γ -phase crystallizes in the monoclinic system $C2/c$ with $a = 11.260(5)$ Å, $b = 10.851(6)$ Å, $c = 13.209(7)$ Å, $\beta = 114.853(2)^\circ$ and $V = 1464.44(13)$ Å³. On the other hand, the diamagnetic α - and β -phases crystallize in the triclinic system. Measurements of the ac magnetic susceptibilities were performed with the ac field of amplitude 2 Oe (peak-to-peak) and frequency 100 Hz in the region up to 16.2 kbar using a piston cylinder type of pressure cell. The SR powder structural analysis experiments at room temperature were carried out in the pressure region up to 17.8 kbar using a diamond anvil cell at the beamline 1B.

Results and Discussion

First we have observed that the magnitude of ac susceptibility is remarkably suppressed with increasing pressure, and decreases down to about a half of the initial by little pressure of 0.10 kbar [3]. At around $P = 2.0$ kbar, there remains only the magnetic signal for the 3.5 % of the initial, and the amount is finally suppressed down to 0.07 % of the initial at $P = 16.2$ kbar.

However, in spite of the suppression of the ac susceptibility, the transition temperature T_C itself is enhanced by pressure. The T_C increases with linear fashion against pressure in the considered pressure region. The amount of the gradient, dT_C / dP , is estimated to be $+ 5.1 \times 10^{-1}$ K/kbar. The normalized gradient with the value of $T_C(P = 0)$, is $+ 7.3 \times 10^{-2}$ /kbar, which is larger than those of a few ferromagnets. Finally, the T_C of the γ -phase

BBDTA•GaCl₄ arrives at 14.5 K at $P = 16.2$ kbar, and nearly approaches 16 K for TDAE-C₆₀ [4].

Figure 1 shows the diffraction pattern of the γ -phase of BBDTA•GaCl₄ in the pressure region up to 17.8 kbar, with that of the β -phase for the reference. The data for $P \leq 2.9$ kbar represents that the diffraction peaks of the γ -phase, labeled with the $C2/c$ system, shift toward higher angles with increasing pressure. However, for $P \geq 6.6$ kbar, a steady graze makes us find two pronounced anomalies related to a triclinic system at around $2\theta = 8.5$ - 9.5 degree, which can be seen clearly in the α and β -phases. Thus, we have come to interpret the results of ac susceptibility as the influence of two factors, (1) the structural transformation from the ferromagnetic γ -phase to the nonmagnetic α - and/or β -phases and (2) the increase of ferromagnetic interaction in the surviving γ -phase.

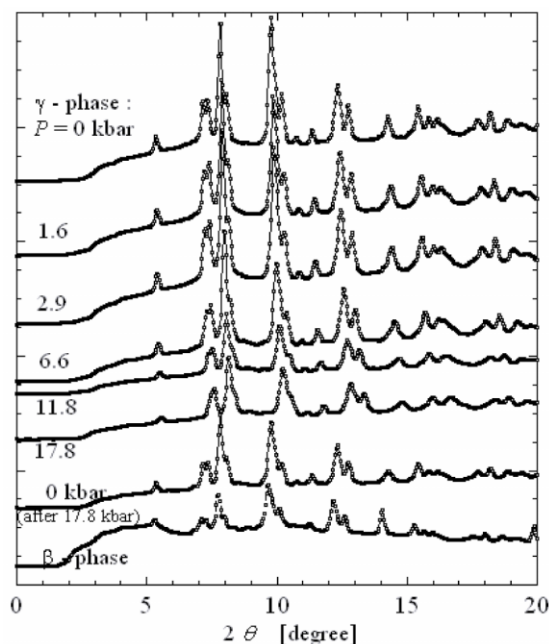


Fig.1. Powder diffraction pattern of the γ -phase BBDTA•GaCl₄ in the pressure region up to 17.8 kbar..

References

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