

Temperature induced de-polymerization in TDAE-C₆₀[☆]

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Abstract

The phase change due to the polymerization of the ferromagnetic tetrakis-dimethylamino-ethylene (TDAE)-C₆₀ has been reconfirmed by applying pressures in situ up to $P_c = 7$ kbar in an ESR cavity. This transition is irreversible and the phase above P_c is stable even after releasing pressure. The pressure-dependent g -factor indicates the revival of the TDAE⁺ spins. Moreover, the ferromagnetism disappears simultaneously at P_c . The de-polymerization of the polymerized (pressure-released) crystal has been confirmed for the first time by the high-temperature ESR study. This transition is also irreversible and the polymer phase is stable up to 470 K. The de-polymerized phase is considered to be the original ferromagnetic one.

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Keywords: TDAE-C₆₀; Ferromagnetic; Polymer; De-polymerization; High-pressure ESR

1. Introduction

The mechanism of the ferromagnetic interaction in TDAE-C₆₀ has been discussed so long, where TDAE is tetrakis-dimethylamino-ethylene, but is still the subject of discussion. Recently, Kawamoto proposed that the antiferro-type orbital ordering of Jahn-Teller distorted C₆₀ leads to the ferromagnetic interaction between C₆₀ [1]. Actually, we have shown the structural phase transition around 180 K in the ferromagnetic crystal [2]. This orbital ordering model also proposed the pressure dependence of the ferromagnetic transition temperature (T_c) [3]. Mizoguchi et al. found that T_c is depressed by applying pressure and that the polymer phase is stabilized under pressure [4]. In this report, we restudy the polymerization induced by pressure by using the high-pressure ESR technique in detail and demonstrate the de-polymerization by the high-temperature ESR study.

2. Experiments

Single crystals have been prepared by the diffusion method. The details of sample preparation are given in [2]. The high-pressure ESR system consists of two sub-assemblies: (1) the

double-stacked dielectric resonator (DR), and (2) the miniature sapphire anvil pressure cell (SAC). We can apply pressures in situ in an ESR cavity. The resonance frequency of DR cavity is ~ 9.4 GHz. The maximum pressure obtained is ~ 9 kbar by using the brass-made gasket. The typical sizes of the samples used were $0.3 \text{ mm} \times 0.3 \text{ mm} \times 0.3 \text{ mm}$. A hydrostatic pressure was mediated by commercial Daphne oil. One small ruby crystal was put into a gasket hole together with the single crystal TDAE-C₆₀ in order to calibrate the hydrostatic pressure. We put the Mn/MgO powder sample into the high-pressure cavity in order to calibrate both g -factors and ESR intensities under pressure. After releasing the pressure, the crystal was measured in a high-temperature ESR cavity at ambient pressure in order to observe the de-polymerization induced by temperature.

3. Results and discussion

Fig. 1 shows the pressure dependences of the peak-to-peak linewidth (ΔH_{pp}) and the g -factor at room temperature. The irreversible phase transition is clearly observed in both quantities at $P_c = 7$ kbar and the phase above P_c is stable even after releasing pressure. The pressure dependence of ΔH_{pp} is qualitatively consistent with the low-frequency ESR results [4]. The g -factor linearly depends on the pressure even below P_c and is obtained to be ~ 2.0025 above P_c . As the g -factor above P_c is comparable with the mean value between TDAE⁺ (2.0036) and C₆₀⁻ (2.000), the spins

[☆] Yamada Conference LVI, The Fourth International Symposium on Crystalline Organic Metals, Superconductors and Ferromagnets.

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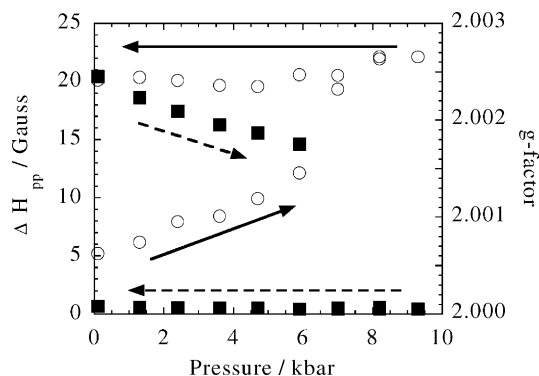


Fig. 1. Pressure dependences of ΔH_{pp} (closed-squares) and g -factor (open-circles).

should be equivalently distributed on both TDAE and C_{60} molecules. Thus, the spins of $TDAE^+$ revive in the polymer phase [4]. The pressure dependence of the g -factor below P_c suggests the possibility that the numbers of the spins on individual molecules change with the pressure because the effective g -factor should be related to the fraction of the spin susceptibility. The ESR intensity of the polymerized crystal follows the simple Curie law down to 5 K, indicating the localized electrons. The parabolic depression of T_c with increasing pressure is also reproduced in our measurements, but T_c disappears simultaneously at P_c . Though this is slightly in contrast to the phase diagram obtained by the low-frequency ESR [4], it is natural that the ferromagnetism disappears with the formation of the polymer. In the ferromagnetic phase, we can simply consider the ferromagnetic interaction between C_{60} because of the spin-cancellation on TDAE molecules. On the contrary, $TDAE^+$ spins revive gradually under the pressure in the present case. The well-narrowed Lorentzian-type line shape testifies the existence of exchange interaction between $TDAE^+$ and C_{60}^- . Thus, the interchain interaction has to contain the path connecting both molecules. Though the orbital ordering model treated only the spins on C_{60} molecules [3], we should consider the contributions of both spins to explain the parabolic pressure dependence of T_c .

Fig. 2 shows the temperature dependences of ΔH_{pp} and g -factor for the polymerized (pressure-released) sample at ambient pressure. The polymer phase is stable up to $T_p = 470$ K. Above this temperature, both ΔH_{pp} and g -factor are recovered to their values of the ferromagnetic phase. The de-polymerization is also the irreversible transition. The lower g -factor of the de-polymerized sample indicates the spin-cancellation of TDAE molecules as observed in the ferromagnetic crystal. The de-polymerization of TDAE- C_{60} occurs at a higher temperature than the one-dimensional polymer AC_{60} ($A = K, Rb, Cs$) ($T_p \sim 300$ K) [5], but rather comparable to the two-dimensional polymer Na_4C_{60} ($T_p \sim 500$ K) [6]. The polymer-nonpolymer phase transitions of these salts are reversible

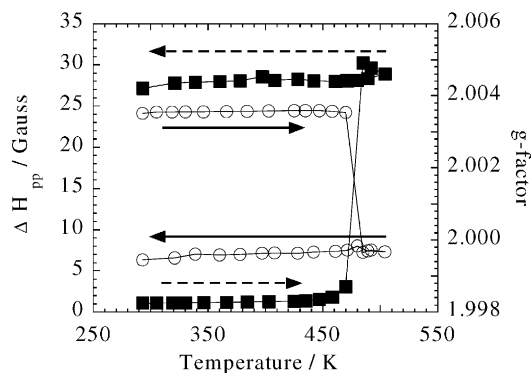


Fig. 2. Temperature dependences of ΔH_{pp} (closed-squares) and g -factor (open-circles).

with the temperature hystereses. The phase above P_c is proposed to be a one-dimensional polymer with (2 + 2)-cycloaddition [4]. Then, these differences in T_p and the irreversibility cannot be explained by the different bonding between C_{60} . Further structural study of the polymer phase is now in progress.

At low temperatures, the de-polymerized crystals show the same temperature dependences of ESR parameters as those of the ferromagnetic crystals. Especially, below 15 K, the g -factor shifts remarkably. The shift of g -factor is due to the demagnetization field, which is proportional to the ferromagnetic spontaneous magnetization. It indicates that the de-polymerized crystal undergoes the ferromagnetic phase transition around 15 K.

4. Conclusion

We have reconfirmed the phase change due to the polymerization of the ferromagnetic TDAE- C_{60} at $P_c = 7$ kbar and have shown the de-polymerization of the pressure-released crystal at 470 K for the first time. These phase transitions are irreversible. $TDAE^+$ spins revive in the polymer phase and the ferromagnetism disappears simultaneously with the formation of the polymer.

References

- [1] T. Kawamoto, Solid State Commun. 101 (1997) 231.
- [2] T. Kambe, Y. Nogami, K. Oshima, Phys. Rev. B61 (2000) R862.
- [3] T. Kawamoto, M. Tokumoto, H. Sakamoto, K. Mizoguchi, J. Phys. Soc. Jpn. 70 (2001) 1892.
- [4] K. Mizoguchi, M. Machino, H. Sakamoto, T. Kawamoto, M. Tokumoto, A. Omerzu, D. Mihailovic, Phys. Rev. B63 (2001) 140417.
- [5] D. Arcon, K. Prassides, S. Margadonna, A.L. Maniero, L.C. Brunel, K. Tanigaki, Phys. Rev. B60 (1999) 3856, and references are there in.
- [6] G. Oszlanyi, G. Baumgartner, G. Faigel, L. Granasy, L. Forro, Phys. Rev. B58 (1998) 5.