

ROOM-TEMPERATURE MOLECULAR FERROMAGNETISM BASED ON NICKEL PHTHALOCYANINE. MAGNETIC RESONANCE, OPTICAL AND XANES SPECTRA

A. S. Manukyan¹, A. A. Mirzakhanyan¹, T. I. Butaeva¹, A. A. Guda², A. V. Soldatov²,
L. A. Bugaev², H. R. Asatryan³, P. G. Baranov³, and E. G. Sharoyan¹

¹*Institute for Physical Research, National Academy of Sciences, Ashtarak 0203, Armenia*

²*Physical Department of Southern Federal University, Rostov-on-Don 344090, Russia*

³*Ioffe Physical-Technical Institute, St.-Petersburg, Russia*

Received 26 October, 2010

Abstract: A method of synthesis of room-temperature ferromagnetic samples of nickel phthalocyanine (NiPc) doped with K and Rb atoms has been developed. These materials are air-stable and have a Curie temperature higher than 300°C. Measurements of optical spectra show that the doping leads to the essential changes in spectra, in particular, to the shift of peaks in the visible range. In the spectra of magnetic resonance of doped samples an intense wide asymmetric line of ferromagnetic resonance and a narrow signal with $g \approx 2$ is observed. In order to reveal the nature of ferromagnetism of the obtained compounds and to determine the nearest local environment of Ni ions, the spectra of X-ray absorption near-edge structure (XANES) were also measured.

1. Introduction

In the field of magnetism of molecular and organic materials the preparation of air-stable room-temperature ferromagnetic compounds remains a challenging problem [1-11].

For a synthesis of highly conducting and magnetic organic-based materials we have developed a technique of doping of solid metal phthalocyanines (MPc, where $\text{Pc}=\text{C}_{32}\text{H}_{16}\text{N}_8$) by donors and acceptors of electrons (alkaline metals and iodine, respectively) [12,13]. A number of phthalocyanine-based charge-transfer compounds have been prepared and studied. The phthalocyanines doped with alkaline metals, A_xMPc (where $x > 1.5$), stand out of this group because of their unusual magnetic properties [13-18]. The most significant feature of A_xMPc magnets is their high value of T_{Curie} which sometimes even exceeds room temperature. Magnetic properties of A_xMPc compounds vary within a broad range. They strongly depend on the degree of doping ($0 < x < 4$), the nature of the central metal ($M = \text{Zn}, \text{Cu}, \text{Ni}, \text{Co}, \text{Fe}, \text{Mn}$), as well as on the type of alkaline metal ($A = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$).

In the eighties we discovered and investigated a room-temperature ferromagnetism in samples of A_xFePc , A_xCoPc , A_xNiPc ($x \gg 1$) [13-18]. In these works we carried out synthesis of MPc polycrystalline samples by the intercalation method. During synthesis the condensation of vapors and formation of a liquid alkaline metal took place on the surface of phthalocyanines with further diffusion into solid sample. Therefore the amount of alkaline metal in A_xMPc samples was large ($x \gg 1$). Apparently, Fe, Co, and Ni nanoparticles, which are formed during synthesis along with MPc anions, cause the observable room-temperature ferromagnetism. To avoid strong collective interactions of A with MPc which can result in decomposition of molecules, we have recently developed a new gas-phase intercalation method of MPc doping at which the formation of a liquid

alkaline metal on the surface of MPc is excluded [19]. Our recent experiments have shown that formation of ferromagnetic samples at intercalation from a gas-phase also takes place. The samples of Na_xNiPc and Rb_xNiPc with $x \geq 1$ are ferromagnetic at room temperature with $T_{\text{Curie}} > T_{\text{Room}}$. In Na_xNiPc and Rb_xNiPc T_{Curie} values are much higher than in that of the well-known [TDAE] C_{60} compound. There are many similarities between A_xMPc and anions of C_{60} [20]. However, there are also essential distinctions, e.g., the distances between C_{60} molecules are about 10\AA , whereas the distances between MPc molecules along the \bar{b} axis are 3.8\AA for α -modification and 4.79\AA for β -modification. The exchange interactions on shorter distances are more strong, therefore the room-temperature ferromagnetism with $J/k > 300\text{K}$ is possible in some molecular organic materials.

In order to reveal the mechanisms which are responsible for establishing the magnetic ordering in molecular organic compounds with such high temperatures T_C , we have investigated magnetic resonance, optical and XANES spectra of ferromagnetic samples based on NiPc.

2. Results and Discussion

Using the modified method of doping of NiPc with alkali metals K and Rb and the corresponding chemical treatment, we have prepared air-stable ferromagnetic samples with a Curie temperature higher than 300°C .

The ESR and FMR spectra were measured with X-band JEOL-JES-PE-3X and EPR-2 spectrometers in the temperature range of 5–300 K. Figure 1 shows the magnetic resonance spectra of $(\text{NiPc})^{n-}$ anions recorded in the magnetic fields 0–5000 Oe. As is seen, there are simultaneously a broad asymmetrical ferromagnetic signal and a narrow paramagnetic signal with $g \approx 2.0$. The temperature dependence of observed spectra is rather complex and requires further investigations.

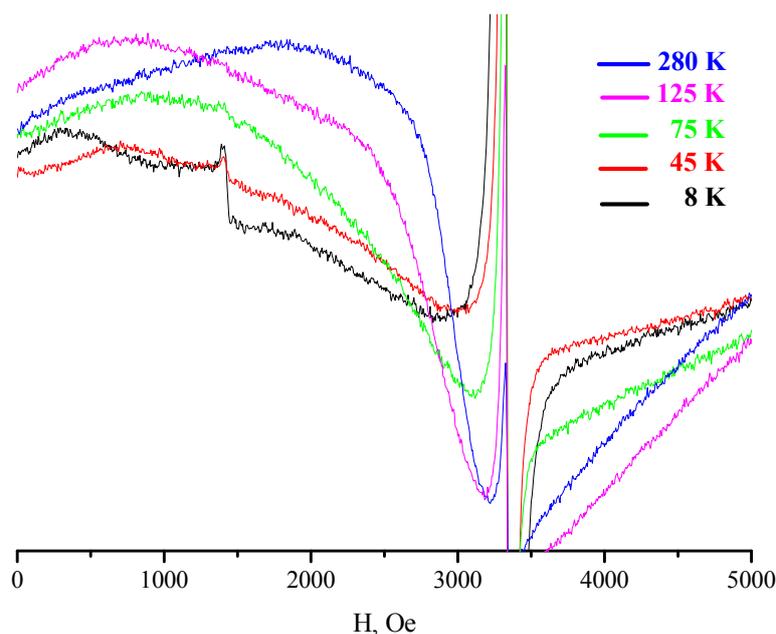


Fig. 1. Spectra of the magnetic resonance of $[\text{NiPc}]^{n-}$ anions, $2 < n < 3$.

Optical spectra of NiPc and its anions $[\text{NiPc}]^{n-}$ ($2 \leq n \leq 3$), obtained after doping, recorded in the region 400–1000 nm are presented in Fig. 2. One can see that the spectrum of anions is shifted with respect to the initial NiPc sample. These spectra confirm that the molecules of NiPc are not destroyed during the doping and subsequent treatment.

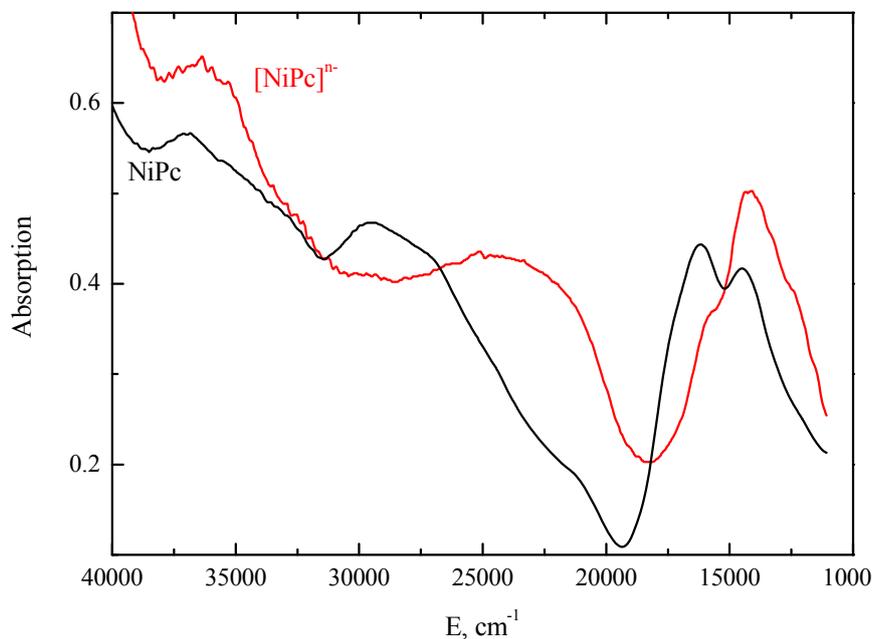


Fig. 2. Optical spectra of NiPc and $[\text{NiPc}]^{n-}$ samples.

In order to determine the nearest local environment of Ni ions, the XANES spectra were measured (Fig. 3). From these spectra it follows that the plots for bulk Ni and pyrolysis products of NiPc (where Ni is in the form of nanoparticles) are similar. On the other hand, the XANES spectra of initial NiPc and NiPc anions are also similar.

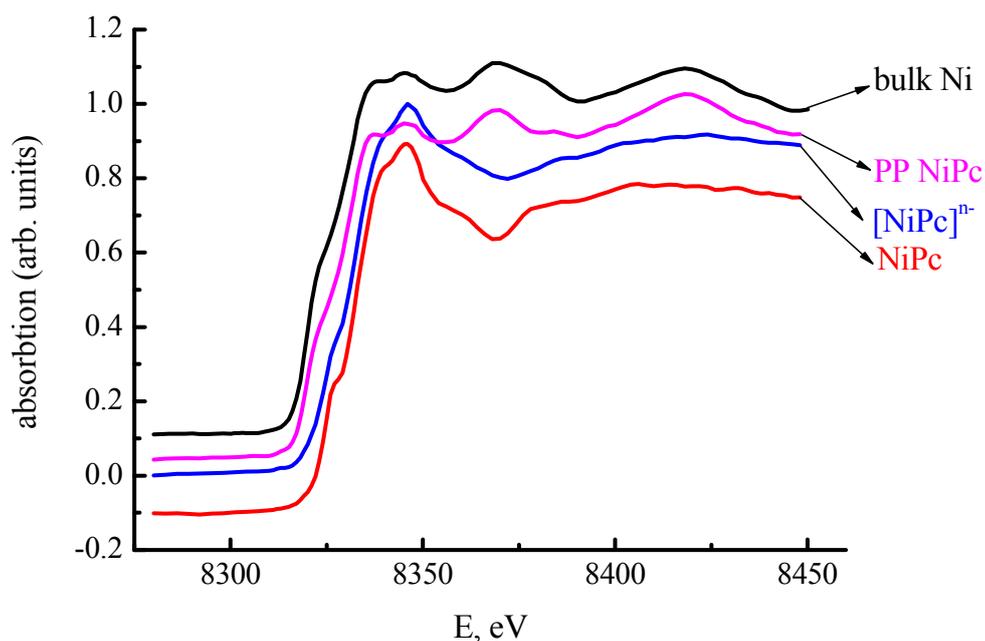


Fig. 3. XANES spectra of bulk Ni, PP NiPc, NiPc and $[\text{NiPc}]^{n-}$ samples.

Thus, on the basis of all obtained experimental data one can conclude that the nature of high-temperature ferromagnetism in doped samples is conditioned by the molecular anions $[\text{NiPc}]^{n-}$, ($2 \leq n \leq 3$).

REFERENCES

1. S.J.Blundell, F.L.Pratt, *J.Phys.: Condens. Matter*, **16**, R771 (2004).
2. K.Itoh, M.Kinoshita, *Molecular Magnetism: New Magnetic Materials*, G & B Science Pub., 2000.
3. D.Arčon, R.Blinc, *Str. and Bond.*, **109**, 231 (2004).
4. E.Coronado, P.Delhaes, D.Gatteschi, J.S.Miller, in: *Molecular Magnetism: From Molecular Assemblies to the Devices*, NATO ASI Series E, Kluwer, Dordrecht, 1996, 381.
5. J.Veciana, in [4], pp. 425-448.
6. M.Kinoshita, P.Turek, M.Tamura, et al. *Chem. Let.*, 1991, p. 1225.
7. P.-M.Allemend, K.C.Khemani, A.Koch, et al. *Science*, **301**, 253 (1991).
8. W.Fujia, K.Awaga, *Chem. Phys. Let.*, **357**, 385 (2002).
9. F.Wudl, J.D.Thompson, *J. Phys. Chem. Solids*, **53**, 1449 (1992).
10. T.Kawamoto, *Solid State Com.*, **101**, 231 (1997).
11. R.Blinc, P.Jeglič, T.Apih, J.Seliger, D.Arčon, A.Omerzu, *Phys. Rev. Let.*, **88**, 086402 (2002).
12. L.S.Grigoryan, M.V.Simonyan, E.G.Sharoyan, *Patent of the USSR*, 1984, №120686.
13. A.R.Harutyunyan, L.S.Grigoryan, E.G.Sharoyan, *Patents of the USSR*, 1987, № 1385583, 1385584, 1385585, 1385586.
14. A.R.Harutyunyan, L.S.Grigoryan, E.G.Sharoyan, *Materials Science*, **14**, 121 (1988).
15. E.G.Sharoyan, V.E.Sharoyan, F.M.Ovsyannikov, *J. Porphyrins Phthalocyanines*, **2**, 237 (1998).
16. E.G.Sharoyan, *First Int. Conf. on Porphyrins and Phthalocyanines*, Dijon, France, 2000, p. 170.
17. E.G.Sharoyan, *Proc. International Seminar ISTC*, Yerevan, Armenia, 2000, pp. 199-202.
18. J.A.Ibers, *J. Porphyrins Phthalocyanines*, **4**, 425 (2000).
19. A.S.Manukyan, P.A.Varderesyan, E.G.Sharoyan, *Proc. Conference on Laser Physics-2007*, Ashtarak, Armenia, 2008, pp.111-113.
20. E.Tosatti, M.Fabrizio, J.Tóbič, G.E.Santoro, *Phys. Rev. Lett.*, **93**, 117002 (2004).