Spin-glass behaviour of nanocrystalline diamond intercalated with potassium

M E Kozlov†‡‖, H Uwe†, M Tokumoto‡ and K Yakushi§

† Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305, Japan
‡ Electrotechnical Laboratory, Tsukuba, Ibaraki 305, Japan
§ Institute for Molecular Science, Okazaki, Japan

Abstract. The magnetic susceptibility and field dependence of the magnetization of pristine and potassium-intercalated nanocrystalline diamond were studied using a SQUID magnetometer. The host material was found to possess paramagnetic properties along with a small irreversible magnetization recorded for zero-field-cooled and field-cooled cycles of susceptibility measurements. Upon intercalation the irreversibility increases, and the magnetization of the material reveals a distinct ferromagnetic loop at 5 K. This is essentially different from the results for potassium intercalation in graphite or C_{60} fullerene, and shows that sp^3 bonding promotes magnetic ordering in carbon. The measurements present the first experimental evidence of an intercalation-induced spin-glass state in a nanocrystalline diamond system.

1. Introduction

The magnetic properties of carbon are rather controversial. Diamagnetic in all of its crystalline forms—diamond, graphite, and Buckminster fullerene, the material was reported to become ferromagnetic in its amorphous pyrolytic modification. The carbonaceous substances [1–4] obtained by pyrolysis of various organic species reveal marked ferromagnetism at room and higher temperatures. The unusual magnetic properties of the material were ascribed to a large density of unpaired electrons localized on various defects in its incomplete graphite-like structure. A soft itinerant ferromagnetism was observed at low temperature in several compounds prepared from C_{60} fullerene [5–8]. Complexes of C_{60} with the strong organic donor tetrakis(dimethylamino)ethylene (TDAE-C_{60}) and halogens are probably the most famous representatives of the family.

The facts can be related to the existence of a magnetic carbon form. However, the structural data on the material are quite contradictory, and its synthesis is not always reproducible. According to [1, 4], for instance, a three-dimensional network constituent of both sp^2- and sp^3-coordinated carbon atoms is important for the formation of magnetic domains in carbon matrices. It was pointed out also that the incorporation into the carbon skeleton of other atomic activators—metals in particular—increases the yield of the magnetic phase. In order to check these points directly, we performed magnetic measurements on a fine diamond powder, and examined the influence of its intercalation with potassium. The latter technique is widely used for the modification of transport and other properties of graphite [9] and C_{60} fullerene [10], the substances formed by

‖ On leave from the Institute of Semiconductors, Kiev, Ukraine.

sp^2-coordinated carbon. The host material studied by us contained diamond clusters of nanocrystalline size with small inclusions of non-diamond carbon. It was found that diamond nanoparticles possess paramagnetic properties which upon intercalation develop into weak but distinct ferromagnetism at 5 K. This is completely different from the results for potassium intercalation in graphite and C_{60} fullerene—both substances exhibit superconductivity at low temperature [9–11]. Our measurements show that sp^3 bonding promotes magnetic ordering in carbon, and give the first experimental evidence of an intercalation-induced spin-glass state in a nanocrystalline diamond system.
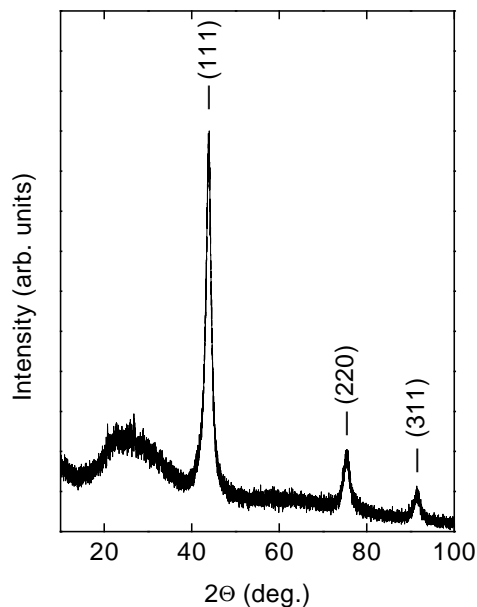

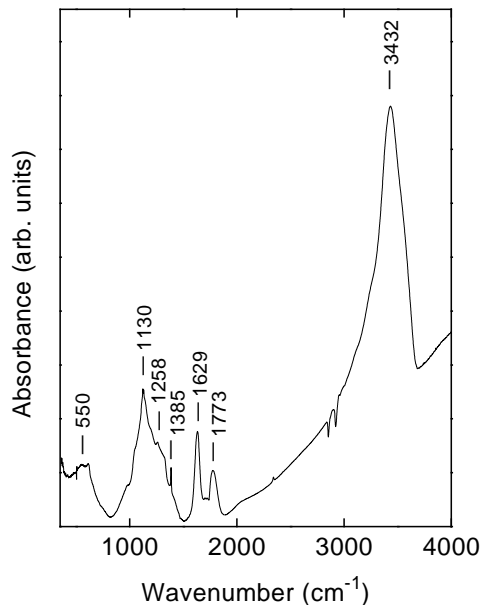**Figure 1.** The x-ray diffraction pattern of nanocrystalline diamond powder. Diamond peaks are marked.

Figure 2. The infrared absorption spectrum of nanocrystalline diamond powder recorded for a pellet with KBr.

2. Experimental procedure

Nanocrystalline diamond was obtained by an explosive method; see [12] for details. According to its specification, the grey insulating powder contained diamond grains about 4 nm in diameter, and had approximately 2% of non-diamond carbon incorporated into the grains. In order to characterize this uncommon substance, we report its x-ray powder diffraction pattern (figure 1) and infrared absorption spectrum (figure 2). The former was taken with a Rigaku RINT 1000 diffractometer (Cu Kα radiation) and the latter was recorded using a Jasco FTIR VM7 spectrometer for a pellet with KBr. Raman and EELS data on the material were reported earlier [12, 13]. Three sharp peaks in the x-ray pattern (figure 1) have *d*-values of 2.06, 1.26, and 1.08 Å, and are in excellent agreement with the (111), (220), and (311) reflections of cubic diamond. Strong broadening of the peaks caused by the fine size of the crystallites is consistent with the analysis [12]. A very broad structureless peculiarity near 25° (*d* = 3.56 Å) originates from the admixture of non-diamond carbon, though the relative amount of the fraction is difficult to estimate. The infrared spectrum of the material (figure 2) exhibits several defect-activated absorptions at 550, 1130, 1258, and

1385 cm^{-1} that are typical for diamond; see the discussion in reference [14] for details. Strong bands at 1629, 1773, and 3432 cm^{-1} in the spectrum are due to olefinic C=C, C=O, and C–H bonds, respectively. They provide evidence of the presence of oxygen and hydrogen, which probably saturate the carbon bonds in the surface layer of nanoparticles. Similar bands are normally observed in spectra of amorphous hydrogenated carbon prepared by different methods [15, 16].

Intercalation of the material was carried out by a standard two-zone vapour transport technique [9], though special precautions were taken to exclude any contamination with magnetic impurities. All of the chemicals used for the intercalation, including potassium and its oxide, were carefully checked with a SQUID magnetometer. Also, the following procedure was employed for the preparation of the specimens. 10–20 mg of diamond powder was put in a thin-walled quartz ESR tube and separated from its open end by a neck. Subsequently, a few mg of potassium was placed above the neck, and the tube was pumped to a vacuum of 10^{-5} Torr. While maintaining vacuum, the end with the diamond powder in it was heated to 300 °C for three hours in order to remove the oxygen and other gases adsorbed on the surface of the grains. After cooling to room temperature, the end of the tube near the potassium was slightly heated until the metal melted and went through the neck into the sample space. Then the tube was sealed in such a way that the distance between the diamond powder and the drop of pure potassium attached to its wall was about 15 cm. At this stage, the magnetization of the diamond powder (here on referred to as pristine material) was measured with a SQUID magnetometer as described below. Intercalation of the specimens was carried out in a horizontal furnace with a small temperature gradient for 3–6 h. The temperatures near the diamond and potassium ends were normally set to 300 °C and 290 °C, respectively, although some other temperature regimes were also employed. These conditions are usual for the preparation of stage-1 graphite–potassium compounds [9]. Directly after the intercalation, the magnetization of the diamond powder was measured with the SQUID again. We believe that such treatment completely excluded any contamination with magnetic impurities, and that the changes in the magnetic properties of the diamond powder were induced by the intercalation.

The magnetization of the material was recorded with a Quantum Design MPMS-5 SQUID magnetometer. Both zero-field-cooled (M_{ZFC}) and field-cooled (M_{FC}) measurements of the magnetic moment (M–T curves) were performed. The prepared specimens were first cooled down to 5 K under zero field, then a field of 100 Oe was applied and M_{ZFC}-values were recorded while the temperature was increased to 300 K. Subsequently, M_{FC}-data were taken under a field of 100 Oe while the specimens were cooled to 5 K. For the measurements of the field dependencies of the magnetization (M–H curves) we first cooled the specimens to 5 K under zero field, then applied a field of 1500 Oe and changed it in the following way: 1500 Oe $\rightarrow$ -1500 Oe $\rightarrow$ 1500 Oe. No correction was made for the diamagnetic contribution from the quartz tube, although the tube was screened to ensure the absence of ferromagnetic impurities.

3. Results and discussion

Figure 3 shows the temperature dependencies of the d.c. magnetic susceptibility of the host diamond powder and the material intercalated with potassium. The data obtained from the zero-field-cooled and the subsequent field-cooled measurements are marked with right-pointing and left-pointing arrows, respectively. Unlike that of bulk diamond crystal, the susceptibility of the pristine material is positive (paramagnetic) over the whole temperature range investigated (5–300 K). This fact can be attributed to the substantial number of
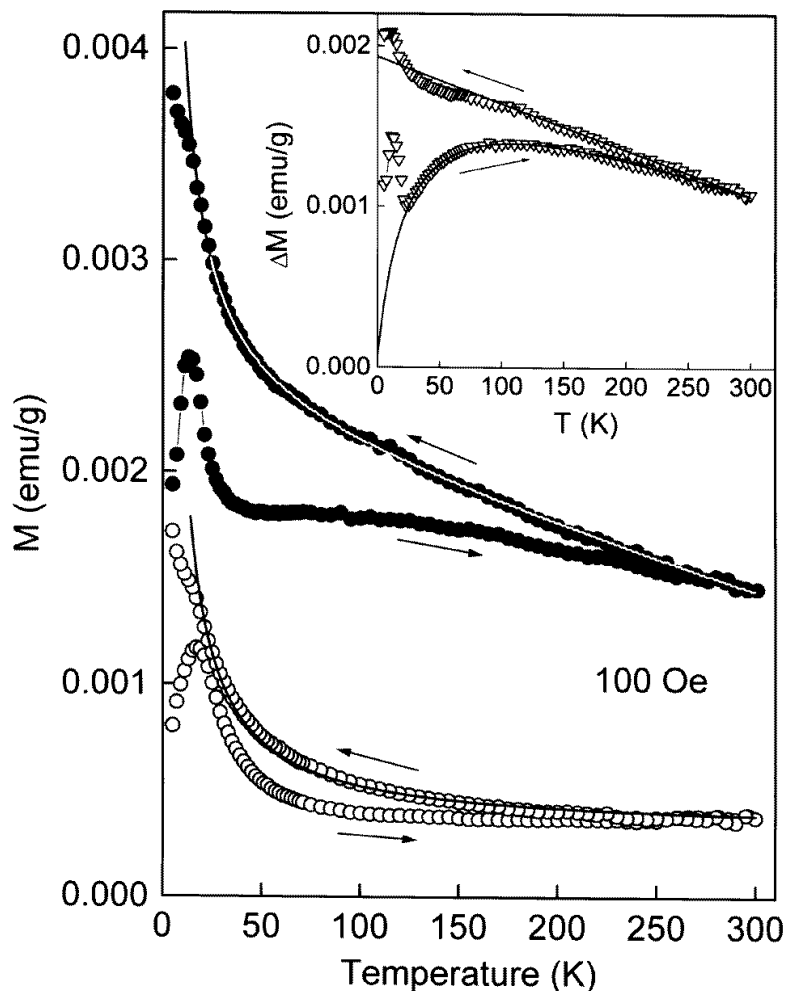
Figure 3. The temperature dependencies of the magnetization (*M–T* curves) for nanocrystalline diamond powder before (○) and after (●) intercalation with potassium, recorded under a field of 100 Oe. Right-pointing and left-pointing arrows indicate respectively zero-field-cooled (M_{ZFC}) and subsequent field-cooled (M_{FC}) measurements. Fits of M_{FC} to the Curie-like expressions $M_{FC}(T) = (3.2 + 206/T) \times 10^{-4}$ emu g^{-1} for the pristine substance and $M_{FC} = (22.5 - 0.029T + 199/T) \times 10^{-4}$ emu g^{-1} for the intercalated substance are shown with solid lines. The temperature dependence of the difference in magnetization ΔM caused by the intercalation (∇) is shown in the inset. The upper and lower branches of the $\Delta M–T$ curve were approximated with the smooth functions $\Delta M_{FC} = (19.3 - 0.029T) \times 10^{-4}$ emu g^{-1} and $\Delta M_{ZFC} = (20.9 - 0.029T - 512/(T + 25.3)) \times 10^{-4}$ emu g^{-1}, respectively (solid lines; see the text for details).

unpaired electrons localized at structural defects in diamond grains, and the extended surface layer of nanoparticles with multiple non-saturated (dangling) bonds. The magnetic susceptibility of the substance increases upon intercalation. This trend is consistent with the appearance of a marked paramagnetic contribution in graphite intercalated with potassium and other alkali metals [9]. The magnitude of the contribution was reported to depend

on the concentration of the intercalate, and was explained by Pauli paramagnetism arising from the injected free carriers [9]. The difference in susceptibility between the stage-1 compound C_8K and graphite [9] is very similar to that recorded by us for intercalated and pristine diamond powder ($\sim 10^{-5}$ emu g^{-1} Oe^{-1} at 300 K). This shows that some potassium penetrated into the diamond grains.
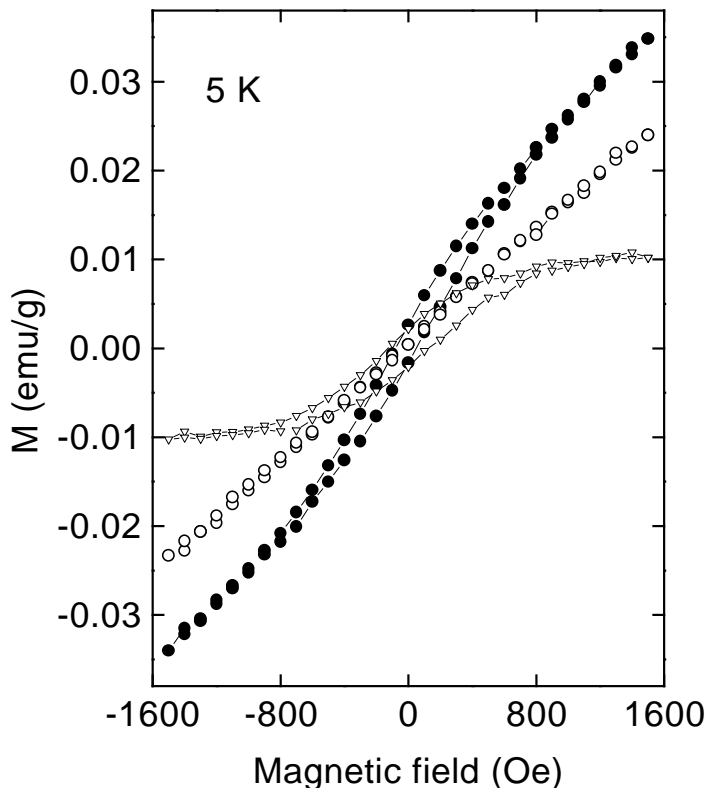

Figure 4. The field dependencies of the magnetization (*M–H* curves) of nanocrystalline diamond powder before ($\bigcirc$) and after ($\bullet$) intercalation with potassium, recorded at 5 K. Also shown is the difference in magnetization caused by the intercalation (∇).

The field dependencies of the magnetic moment of diamond powder before and after the intercalation are shown in figure 4. The two sets of measurements were carried on the same specimen, at 5 K. The behaviour of the magnetization of the host material is typical for a paramagnetic substance. Within the accuracy of our experiment it does not exhibit any sign of remanence or saturation in the field range investigated (open circles). The shape of the *M–H* curve dramatically changes upon intercalation of the diamond: a characteristic hysteresis loop shows up on the inclined paramagnetic background (solid circles). The ferromagnetic contribution (triangles) becomes apparent after subtraction of the *M–H* data recorded for the host material. Analysis of the dependency shows that the saturation magnetization M_s, remanence M_r, and coercivity H_c of the intercalated specimen are equal to 0.01 emu g^{-1} (less than $0.000\,02\mu_B$ per carbon atom), 0.002 emu g^{-1}, and 125 Oe, respectively. Although the observed coercivity H_c is comparable with that for pyrolytic carbon, M_s is two to three orders of magnitude smaller than the values reported in [1–4].

The ferromagnetic contribution should reveal itself in the temperature dependencies of the magnetization of the material (figure 3). The low-temperature region in the dependencies has an unusual shape, which makes their analysis quite complicated. Figure 3 shows that M_{ZFC} for pristine and intercalated diamond exhibits a pronounced peak with maxima near 17 K and 13 K, respectively. A very weak peculiarity is also observed in the vicinity of 90 K. In contrast to this, M_{FC} monotonically increases with the decrease of temperature, and for pristine material can be described as the sum of constant and Curie-like contributions: $M_{FC}(T) = (3.2 + 206/T) \times 10^{-4}$ emu g^{-1}. The latter curve is shown in figure 3 as a solid line. In the same manner as described above, we can subtract the M–T data for the host material from the magnetization of the intercalated substance, and separate out in this way the ferromagnetic contribution caused by the intercalation from the paramagnetic one characteristic of diamond grains. The difference ΔM shown in the inset in figure 3 consists of two branches corresponding to M_{FC}- and M_{ZFC}-measurements. The upper branch (ΔM_{FC}) is almost linear with temperature, and can be approximated with the expression $\Delta M_{FC} = (19.3 - 0.029T) \times 10^{-4}$ emu g^{-1}. The lower branch (ΔM_{ZFC}) basically decreases with decreasing T down to 23 K, where an uncommon peculiarity shows up. The latter evidently arises from the host material. In order to exclude the peculiarity from consideration, we can extrapolate ΔM_{ZFC} to $T = 0$ by means of a fitting of experimental data in the range 23–300 K with a smooth function, like for instance $\Delta M_{ZFC} = (20.9 - 0.029T - 512/(T + 25.3)) \times 10^{-4}$ emu g^{-1} (see the inset in figure 3). After fitting, the ΔM–T curves strongly resemble those of a typical frozen spin-glass system [17]. The freezing temperature seems to be quite high, probably 250–300 K. The linearity of ΔM_{FC} originates from almost the same paramagnetic Curie-like contributions in both the pristine and the potassium-intercalated substances. In the latter case, the fitting of M_{FC}–T with the expression $M_{FC} = (22.5 - 0.029T + 199/T) \times 10^{-4}$ emu g^{-1} gives excellent agreement with the experiment (figure 3, main plot). A small deviation is observed only in the low-temperature region $T < 11$ K. The difference between the Curie constants for pristine and intercalated materials is less than 2%.

We can compare M_{FC} and M_{ZFC} at 5 K (figure 3) with values corresponding to the upper branch and middle point of the hysteresis loops at 100 Oe (figure 4). The data should be consistent. For the intercalated material the former two magnitudes are 30–40% smaller than the latter, but the difference $M_{FC} - M_{ZFC}$ is practically the same as the magnitude deduced from M–H measurements. The slight dissimilarity of the two sets of data may be related to the peculiarity near 13 K, which is very sharp in the temperature dependence of the magnetization. The agreement becomes worse for $\Delta M_{FC} - \Delta M_{ZFC}$, but it can be improved with the fitting as shown in the inset in figure 3. Finally, for the pristine substance, the M_{FC}-value coincides with the susceptibility obtained from M–H cycling, but the difference $M_{FC} - M_{ZFC}$ does not reveal itself in M–H measurements at all. Within the experimental uncertainty, the M–H curve of the pristine material has no detectable hysteresis. The paramagnetic properties of nanocrystalline diamond are not surprising, but the evident discrepancy between this fact and the low-temperature M–T data requires some comment.

The deviation of M_{ZFC} from M_{FC} in the host material is quite substantial below 17 K, and decreases at higher temperature (figure 3). This indicates the existence of an irreversible magnetization, and can be related to some sort of magnetic ordering in the system. The difference $M_{FC} - M_{ZFC}$ increases upon intercalation—the changes can occur not only below 17 K, but also at any temperature in the range investigated. The apparent increase in irreversibility should be associated with the carbon system, and shows that the magnetic correlations in the intercalated substance are stronger. This fact is obvious from the low-

temperature M–H measurements as well. On the other hand, the irreversibility at 5 K for the pristine material does not reveal itself in M–H cycling, and may therefore be of different nature. It may originate from some peculiar paramagnetic centres. Quite similar behaviour of the magnetic susceptibility was reported for the fullerene-based C_{60} iodine compound [8]. Specimens of this compound exhibited marked irreversibility below 60 K in M–T measurements and no explicit M–H hysteresis at any temperature down to 5 K. The behaviour was suggested to be characteristic of superparamagnetism. We should mention also that, even in the case of a frozen spin-glass state with a strong interaction between the magnetic moments of domains, the description of a broad hysteresis loop requires a combination of several parameters [17]. The existence of a small irreversibility in measurements of M_{FC}/M_{ZFC} is far from sufficient for the characterization of the system in terms of a strong magnetic ordering. The nature of the 17 K peculiarity in M_{ZFC} for the host material has still to be understood. Fortunately, however, its influence on the low-temperature magnetic properties of the substance diminishes upon intercalation. For intercalated material, the agreement between the M–T and M–H data is reasonably good, and allows one to draw definite conclusions concerning the spin-glass behaviour.

The observation of a ferromagnetic fraction at 5 K in intercalated diamond was reproducible, but the amount of magnetic phase varied with treatment conditions. Strong variations were also detected in the temperature dependencies of the saturation magnetization. In several specimens, traces of ferromagnetism were found even at room temperature. However, because of large paramagnetic contribution from the host material, unambiguous determination of the saturation magnetization at high temperature was difficult. This point, and the possibility of increasing the yield of the magnetic fraction in the compound, require additional study.

It is known that the intercalation process provides a mechanism for the injection of carriers into the matrix formed by the host material. The intercalation of graphite with alkali metals results in a large increase in conductivity that involves mainly the graphite layers adjacent to the intercalate layer [9]. The first-stage graphite compound with nominal composition C_8K was found to be superconducting at temperatures below 1 K. A significant increase of the free-carrier concentration upon intercalation with alkali metals, and the occurrence of superconductivity at 18–30 K were reported for fullerene-based K_3C_{60} and Rb_3C_{60} compounds [10, 11]. One might suggest that a similar charge transfer from the intercalant to the carbon matrix takes place in the diamond powder investigated. It would probably involve the surface layer of grains, or regions containing some amount of non-diamond carbon, where the diffusion rate of potassium is the highest. In contrast to the case for graphite and C_{60}, the intercalation of the substantially paramagnetic sp^3-rich system results in an apparent strengthening of the magnetic correlations. One can speculate that the injected carriers become trapped by various imperfections in the diamond lattice and raise the density of paramagnetic centres. They should also influence the exchange interaction between unpaired electrons localized at the multiple defects in the grains. This probably stabilizes the magnetic ordering in the paramagnetic matrix, and is responsible for the weak ferromagnetism in the material at 5 K. The effect of intercalation superimposes on the peculiar magnetic properties of host material, producing rather complicated behaviour of the magnetic susceptibility at low temperature. Although a substantial part of the compound remains paramagnetic, we can conclude that the outcome of the intercalation of potassium into a diamond-like substance essentially differs from the case for graphite and fullerenes. Our data unambiguously show that sp^3 bonding promotes magnetic ordering in carbon, and the intercalation induces a spin-glass state in the nanocrystalline diamond system.

Acknowledgments

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