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Metal–insulator and magnetic transitions in heavily irradiated NaCl–KBF_4

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Abstract

We have performed electron spin resonance (ESR), nuclear magnetic resonance (NMR) and static magnetic susceptibility measurements on heavily irradiated NaCl–KBF_4 single crystals in the temperature range $4.2 < T < 350$ K. In these samples, up to about 10% of the NaCl molecules are transformed into extremely small metallic Na particles and Cl_2 precipitates. At high temperatures a one-line ESR signal, i.e. common mode due to strong exchange interaction between conduction electrons and F-aggregate centres, is observed. We propose that the smooth decrease of the ESR spin susceptibility with decreasing temperature, which can be as large as 50%, is due to a metal–insulator transition, taking place at about 40 K. In the same temperature range, the linewidth increases by 18 ± 2 G with decreasing temperature. This anomalous broadening is explained by a reduction of the exchange narrowing at low temperatures. NMR spin–lattice relaxation on ^{23}Na shows a Korringa-type behaviour down to 10 K, which suggests that the conducting phase in heavily irradiated NaCl–KBF_4 behaves as a three-dimensional metal. SQUID experiments have revealed antiferromagnetic ordering at 40 K and a ferromagnetic phase below 20 K. The nature of the observed effects is discussed.

1. Introduction

Exposure of simple (pure, doped or natural) NaCl-type crystals to high doses of irradiation with high-energy electrons at large dose rates leads to appreciable structural changes and, ultimately, it will produce a highly defective state, which shows a metal–insulator transition. Among the various heavily irradiated alkali halide crystals special attention is attracted by NaCl–X samples (X = KCl or KBF_4), because they reveal a metallic phase with unusual dielectric

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and magnetic properties [1–4]. The magnetic resonance and spin susceptibility properties of the above-mentioned heavily irradiated materials are similar to those observed in alkali fullerides AC_{60} (A = K, Rb, and Cs; see, for example [5–7]). At low temperatures, heavily irradiated NaCl–KCl (0.1 mol%) undergoes a metal–insulator transition, which is accompanied by broadening and disappearance of the ^{23}Na nuclear magnetic resonance (NMR) signal and the conduction-electron spin resonance (CESR) line. These observations show that a quasi-one-dimensional metallic phase appears in heavily irradiated NaCl–KCl, and that charge-density wave instabilities might lead to an insulating ground state below 40 K [3, 4].

The nature of the electronic ground state of heavily irradiated NaCl–KBF_4 (with 0.03 mol% KBF_4) at low temperature is less clear. X-band electron spin resonance (ESR) and dielectric measurements confirm high-temperature metallic behaviour similar to that of NaCl–KCl, and the presence of a 'maximum' of the ESR susceptibility at about 160 K suggests weak anti-ferromagnetic (AF) spin ordering at low temperatures [1, 2]. One of the factors [3] aligning electron spins at low temperature may be exchange interaction between F-centres, which are the main defects in heavily irradiated NaCl–X. At high irradiation dose (∼150 Grad), when the new Na phase has already formed and conduction-electron concentration has the largest value, this exchange interaction reaches its maximum (the exchange integral $J \sim 10^{-4}$–10^{-5} eV). These assumptions [2, 3] are intriguing and stimulate further studies.

In this paper, we present a combined study of the electronic and magnetic properties of heavily irradiated NaCl–KBF_4. The most important result is the observation of a magnetic phase transition for the system of 'localized' electrons, which become more and more delocalized with increasing temperature until they finally behave as conduction electrons. We propose that in these heavily irradiated salts a metal–insulator transition occurs. In fact, it is assumed that the electrons associated with lattice defects (F-aggregate centres) give rise to the dominant contribution to the ESR signal at low temperatures, that points to the dielectric side of the transition. At high temperatures, when the electrons behave more or less like conduction electrons, the width of the ESR line is reduced significantly (by ∼18 G) due to a strong dynamic coupling between the two electron types, and as a result metallic behaviour is observed above 160 K.

2. Experiment

The NaCl–KBF_4 (0.03 mol%) samples, used in the present study, were irradiated at controlled irradiation temperatures in the range 325–400 K (the melting point of sodium, $T_m \sim 370$ K) by means of a van de Graaff electron accelerator with an electron energy of 1.35 MeV. The penetration depth is a factor of three to four larger than the thickness of the samples, which is typically 0.7 mm, which implies that the homogeneity of the samples is quite good. The absorbed dose in the samples, which has been calculated by standard methods, reached a value of ∼150 Grad at a dose rate of 250 Mrad h^{-1}. Details of our irradiation facility have been described in [8]. The irradiation temperature was ∼50 °C (sample A) and ∼135 ± 5 °C (sample B). The quantity of Na metal in the heavily irradiated samples was determined by means of latent heat effect measurements using a Perkin Elmer DSC-7 instrument (see also [9]). In accordance with these experiments, we estimate the amount of colloidal Na as 7.2% in sample A, and 9.0% in sample B, which means that 7.2–9.0% of the Na^+ ions are transformed into Na atoms due to the irradiation. The ESR data were obtained with a Bruker BER-418S X-band spectrometer (9.2 GHz), using samples with dimensions of about $3 \times 3 \times 0.8$ mm^3. The spin susceptibility (χ) was determined by the double integration of the ESR signal. The very narrow CESR signal of Li particles in neutron-irradiated LiF crystal was used to determine

the precise value of the g-factor and the signal of a $BaMnF_4$ crystal has been employed as a calibration signal for the intensity to allow measurements of the absolute electron concentration. The NMR experiments at 21 MHz were performed in the temperature interval 10–300 K with a Bruker CXP-100 spectrometer. The values of static magnetic susceptibility (χ_0) have been measured with a highly sensitive, homemade RF-SQUID magnetometer at temperatures between 4.2 and 120 K.

3. Results

Figures 1–3 show a general view of the ESR and NMR results in NaCl–KBF_4 crystals (A and B samples are examples; here, for convenience in describing the data, the characteristic temperature ranges are separated from one another by the dashed lines). At temperatures $T > 160$ K the behaviour of measured parameters and their values were typical for metallic sodium [3, 4]: the Lorentzian ESR lineshape, the almost temperature-insensitive spin susceptibility χ (figure 1(a)), the g-value of 2.0014 ± 0.0002 (figure 2) and an increasing ESR linewidth δH by ∼5 G at $T_m = 370$ K, which is close to the melting point of sodium. The ESR lineshapes at 294 and 9.4 K are shown in figure 1(c). Two NMR lines from ^{23}Na nuclei were measured: a wide line, corresponding to the nuclei of the ionic lattice of NaCl (and therefore of no interest), and a narrow line, arising at a higher frequency as a result of the presence of mobile electrons. This line is characterized by the standard temperature behaviour for the nuclei of metallic sodium (the intensity is inversely proportional to the temperature), a small linewidth ∼0.6 kHz (figure 3(b)), and temperature-independent isotropic Knight shift $K = 0.11\%$. These data confirm the formation of a metallic phase in the samples. The ESR linewidth δH(300 K) in samples A and B is equal to 23 and 17 G, respectively (figure 1(b)); it is approximately three times greater than the electron–phonon linewidth in bulk sodium (∼6 G). The presence of defects (F-aggregate centres) and their interaction with conduction electrons, under conditions of the so-called bottleneck regime, allows one to explain the nature of the ESR line in heavily irradiated NaCl–KBF_4 (see the next section). Note that the difference in linewidth of the samples is caused by the difference in irradiation temperature—the higher the temperature, the narrower and more intensive a line.

With decreasing temperature the spin susceptibility χ behaves unusually—it decreases and approaches the value $\sim\chi$(300 K)/2 (susceptibility decreasing for samples A and B by 40 and 55%, respectively, can be seen from figure 1(a)). As in the case of NaCl–KCl, this can be connected with significant reduction or full disappearance of the conduction-electron spin susceptibility χ_e due to electron localization in the region from 160 to 40 K. Based on such an assumption, conduction-electron concentrations were determined, which were 1.2×10^{19} and 3×10^{19} spins cm^{-3} for samples A and B, respectively. Full electron concentration was obtained at room temperature. In the same temperature range (160 → 40 K), the linewidth δH increases by 18 ± 2 G with decreasing temperature. A dramatic negative ESR lineshift (to lower fields) is observed below ∼40 K (figure 2). Note that the ESR line in NaCl–K shifts towards higher fields, to the position for F-aggregate centres [3].

NMR data reveal the Korringa-type behaviour of nuclear spin–lattice relaxation rate $T_1^{-1}(T)$ down to 10 K (figure 3(a)). Such behaviour and linewidth temperature evolution (figure 3(b)) are typical for metallic three-dimensional sodium.

The SQUID data are most unexpected results of the present study. Figure 4 represents the temperature dependence of the static susceptibility χ_0 (for sample B). A reasonably pronounced peak at about 40 K and an enhancement of the $\chi_0 \sim 1/T$ below 20 K are observed. The behaviour of the magnetization M_0 for the same sample as a function of the magnetic field H at 4.2 K is shown in figure 5.

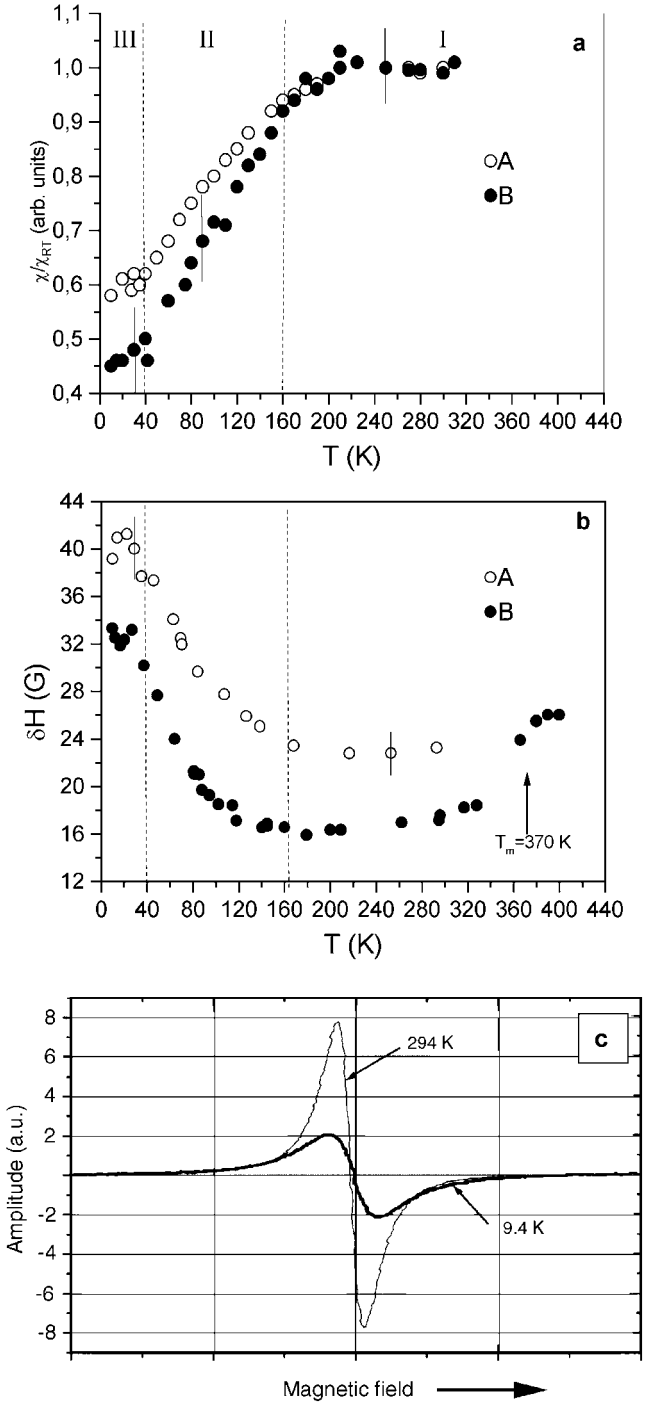

Figure 1. Temperature dependence of the spin susceptibility (a) and the ESR linewidth (b) in heavily irradiated NaCl–KBF_4. (c) Experimental spectra recorded at 294 and 9.4 K. Except for the temperature, the conditions during the measurements were the same.

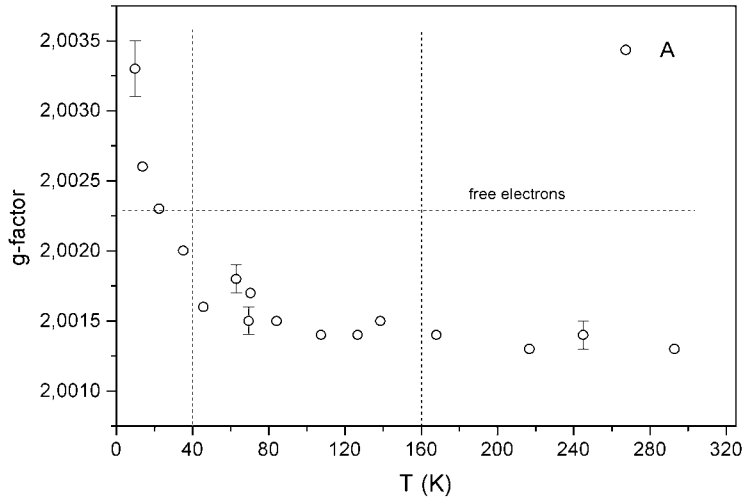

Figure 2. Temperature dependence of the g-value for sample A.

Magnetic resonance and SQUID results of NaCl–KBF_4 crystals allow one to make the following preliminary conclusions.

(1) There are metallic phase and conduction electrons in these samples above 160 K.
(2) Strong conduction-electron localization occurs in the temperature range 160 $\rightarrow$ 40 K, and as a result the metal–insulator transition arises near 40 K. Below 40 K, lattice defects contribute to the total ESR signal.
(3) Comparison of $\chi_0(T)$ and $M_0(H)$ dependences with respective data of magnetic insulators (see, for example, [7, 10, 11]) shows that a new magnetic low-temperature state develops in NaCl–KBF_4.

4. Discussion

Similar to heavily irradiated NaCl–KCl [3] at high temperature we observed a single overall ESR line with a Lorentzian lineshape for conduction electrons (e) and F-aggregate centres (s), which is due to a strong exchange interaction between them. In the present case, the linewidth is determined by the exchange rates $1/T_{\rm se}$ and $1/T_{\rm es}$ between the two species s and e, whereas the lattice relaxation appears to be slow (bottleneck regime [10, 11]). Typical values for heavily irradiated samples are $1/T_{\rm se}$ and $1/T_{\rm es} \sim 10^9$–10^{11} s^{-1}, $1/T_{eL} \approx 10^8$ s^{-1} and $1/T_{sL} \approx 5 \times 10^8$ s^{-1} [3], where T_{eL} and T_{sL} are the spin–lattice relaxation times of the e and s electrons, determined using the 'electron–phonon' linewidth $\delta H = 6$ G for Na and $\delta H \sim 35$ G for F-aggregate centres [3, 4]. As long as the susceptibilities χ_e and χ_s are approximately equal, which is the case in these samples (figure 1(a)), $1/T_{\rm se}$ and $1/T_{\rm es}$ are also approximately the same. This implies that the bottleneck condition ($1/T_{\rm se}$ and $1/T_{es}$) $>$ ($1/T_{eL}$ and $1/T_{sL}$) is fulfilled at temperatures above 160 K. Note that anisotropy effects (of the g-value and the linewidth) are not observed under the condition of dynamic ESR-line narrowing. Thus, expected linewidth is $\sim$20 G as actually observed in experiment at high temperature (figure 1(b)).

The discussion of the observed broadening at low temperatures is particularly interesting. A similar broadening effect of the ESR line has been observed in metals with magnetic

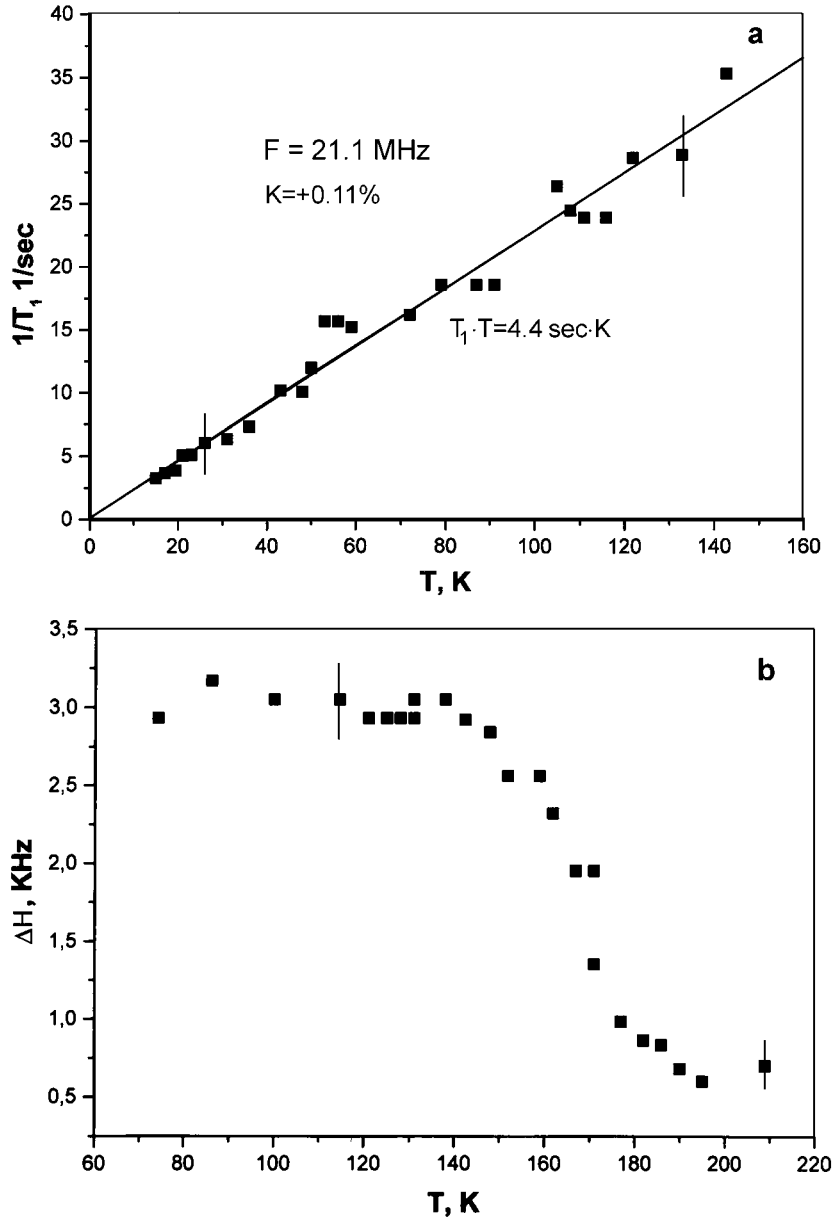

Figure 3. Temperature dependence of nuclear spin-relaxation rate T_1^{-1} (a) and NMR linewidth ΔH (b) for sample B.

impurities, which is frequently connected with either the onset of magnetic ordering of the impurities, or with a reduction of the dynamic exchange narrowing of the dipole linewidth [10–12]. Because until now no peculiarities of $\chi(T)$ (Curie behaviour, etc) have been observed in our samples, we analyse our results in terms of the latter effect. The s spins can relax via the conduction electrons and the corresponding exchange rate can be described

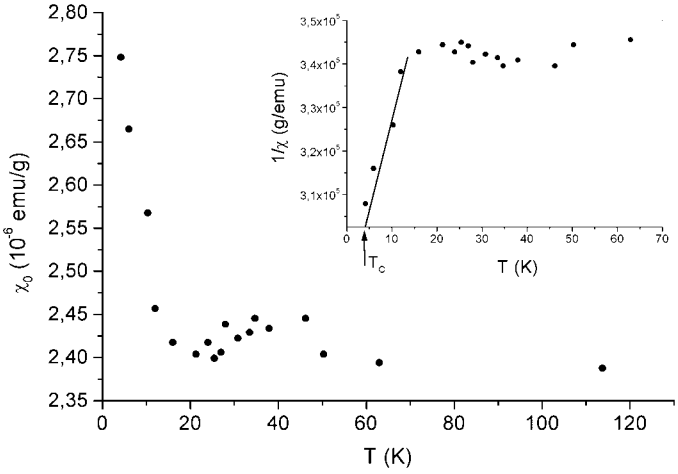

Figure 4. Temperature dependence of the static magnetic susceptibility $\chi_0(T)$ and $1/\chi_0(T)$ (inset) at 736.5 G, obtained from SQUID measurements.

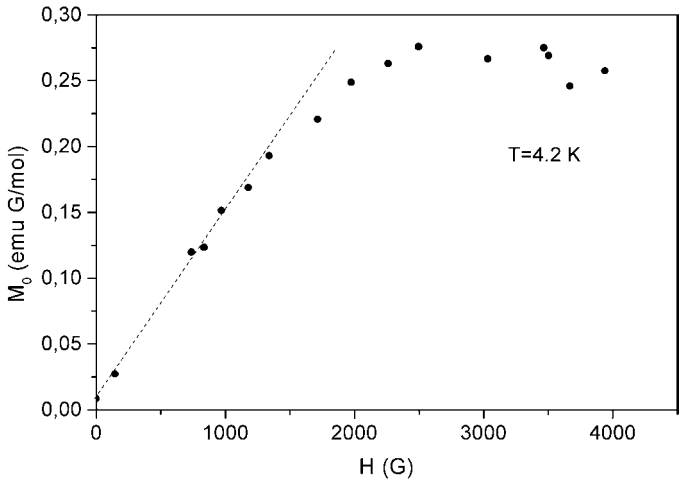

Figure 5. SQUID measurements of the magnetization $M_0(H)$ at 4.2 K.

by the following Korringa-type expression [13, 14]:

$$\frac{1}{T_{\rm se}} = \frac{\pi}{\hbar\mu_B^2}(\chi_{\rm e}J)^2kT, \tag{1}$$

where

$$\chi_{\rm e} = \frac{(g_e\mu_B)^2}{2}\rho(E_F),$$

$\rho(E_F)$ is the density of states at the Fermi level E_F and J is the exchange energy associated with the interactions between the s and e electrons. Line broadening can be caused by interaction with s spins, and $T_{\rm se}$ plays the role of the correlation time [6, 12]. In this way, the extent of the broadening is controlled by the Korringa mechanism, i.e. $T_{\rm se}^{-1} \propto T$. The line width of the conduction ESR signal can be written as $\delta H \approx (\langle\delta\omega\rangle^2/\hbar)T_{\rm se}$ (here $\langle\delta\omega\rangle^2$ is the second

moment of the exchange interaction between s and e spins). Using equation (1), we obtain the expression for linewidth

$$\delta H \cong \frac{\langle \delta\omega \rangle^2 \mu_B^4}{\pi(\chi_e J)^2 kT}. \tag{2}$$

The behaviour of the linewidth for our samples can be described with the following parameters: $\rho = 33.3\ \mathrm{eV}^{-1}$ (this value has been obtained from the free-electron approximation), $J = 5 \times 10^{-5}$ eV, $\omega = 10^{10}\ \mathrm{s}^{-1}$. According to the model, at temperature below 40 K the average g-factor shifts to g_s. In the case of NaCl–KCl the ESR line really shifts towards higher fields, i.e. to the peak position of the F-aggregate centres [3]. In contrast with this behaviour, samples A and B (NaCl–KBF_4) show a negative lineshift (towards lower fields) with decreasing temperatures. Figure 2 demonstrates this behaviour in sample A. The possible reason for this effect is the presence of internal magnetic fields below 40 K. Static magnetic susceptibility measurements were conducted to find proof for this proposition. Thus, the strong dynamic coupling between the s electrons (associated with the F-aggregate centres) and the conduction electrons is broken when the temperature is decreased, due to increasing values of T_{se} [12], and, consequently, the linewidth increases in all samples (by an amount of $\sim$18 G). One can conclude that the ESR results demonstrate the existence of predominantly F-aggregate centres below 40 K, where δH and χ_s are independent of the temperature [15]. Consequently, the low-temperature electronic state in heavily damaged NaCl–KBF_4 can be considered as a dielectric state, i.e. the existence of a metal–insulator transition is assumed to take place. We emphasize that for the description of the ESR properties observed for heavily irradiated NaCl-type structures, a sophisticated electron bottleneck model is required, which must account for the exchange coupling of F-centres in the aggregates.

The analysis of the SQUID data showed that it is quite probable that there is AF ordering at 40 K, which withdraws spins from ESR conditions. By a further decrease of the temperature another, ferromagnetic phase, will develop. The observation of a non-zero value of M_0 at zero field values and the observed saturation (figure 5) support the interpretation in terms of a ferromagnetic phase transition. Our observations favour the interpretation of the results with an ordering of spins rather than impurities in the crystal lattice, because this effect was not observed in similar samples with lower irradiation dose ($\Rightarrow$105 Grad). The spin concentration determined in sample B from both magnetic phases is $\sim 1 \times 10^{20}$ spins g^{-1}. This value is somewhat higher than one measured by ESR, 3×10^{19} spins g^{-1} (with the proposition that the localized conduction electrons form the ordered magnetic phase at low temperatures). Correct account of the F-aggregate centre contribution to χ_0 increases this value up to 6×10^{19} spins g^{-1}, improving the accordance.

Strong exchange coupling between F-aggregate centres might be one of the internal interactions determining the spin ordering and is the subject of well built theoretical treatment.

Reviewing the ESR and SQUID results, one can draw the following conclusion. At temperature in the range $T > 160$ K, a metallic phase exists in heavily irradiated NaCl samples (array I in figure 1(a)). At $40 < T < 160$ K paramagnetic behaviour is observed (array II), and below 40 K the electronic system in heavily irradiated NaCl–KBF_4 transforms into a magnetic insulator state (array III).

Acknowledgments

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