ZESZYTY NAUKOWE POLITECHNIKI ŚLĄSKIEJ 1999
Seria: MATEMATYKA-FIZYKA z. 87 Nr kol. 1443

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MAGNETIC MEASUREMENTS AS A TOOL TO CHARACTERIZE PARAMAGNETIC MATERIALS

Summary. Methods of analysis of measurements of the temperature dependence of the magnetic susceptibility and the low-temperature magnetization are presented for materials containing small amounts of randomly distributed magnetic ions. The usefulness of the presented methods is illustrated by the analysis of experimental results obtained by us and by other authors for a number of paramagnetic materials, including natural crystals and dilute magnetic semiconductors containing small amounts of transition metal ions.

POMIARY MAGNETYCZNE JAKO NARZĘDZIE DO CHARAKTERYZOWANIA MATERIAŁÓW PARAMAGNETYCZNYCH

Streszczenie. W pracy przedstawiono metody analizy pomiarów namagnesowania i podatności magnetycznej pozwalające na charakteryzowanie materiałów paramagnetycznych, tj. momentu jonów magnetycznych i ich koncentracji oraz podatności matrycy diamagnetycznej. Użyteczność opisanych metod jest zilustrowana przykładami analizy wyników doświadczalnych uzyskanych dla dwóch paramagnetyków zawierających jony metali przejściowych.

1. Introduction

When studying various paramagnetic materials, the main properties of the magnetic centres embedded in the diamagnetic matrix, such as their total angular momentum J, the Landé factor g and concentration x, are of upmost importance. The knowledge of J and g is mostly achieved by the electron paramagnetic- (EPR) and the electron spin (ESR) resonance measurements, while x is being estimated by various physical and chemical methods, whose precision drastically decreases with decreasing x. In view of this, the measurements of high-field-magnetization and the temperature dependence of susceptibility are very useful, both being dependent on different combinations of J, g and x.

In this work, we demonstrate the basic description of magnetic methods and their usefulness in characterizing various paramagnetic materials. In particular, we present a new, efficient, and simple method of the analysis of the low-temperature magnetization as providing complete information on the magnetic centres of low concentration.

2. Description of magnetization and magnetic susceptibility

At sufficiently low temperatures, the magnetization of noninteracting centres in a wide range of magnetic fields H can be often expressed by a sum of a temperature (T)-dependent Brillouin-type- (M_B) and a temperature-independent van Vleck-type contributions (M_V) which correspond to the ground- and excited states of the centre, respectively [1,2]. Taking also into account the diamagnetic contribution of the matrix (M_d), the total magnetization (M_{tot}) of such a paramagnet is then written as

$$M_{tot} = M_B + M_V + M_d = M_s B_J(y) + \chi_V \cdot H + \chi_d \cdot H \,, \tag{1}$$

where $M_S = N_m g_J \mu_B J$ (with N_m being the number of magnetic centres per mol and μ_B the Bohr magneton), $B_J(y)$ is the Brillouin function with $y = g_J \mu_B J H / k_B T$ (with k_B being the Boltzmann constant), χ_V is the van Vleck susceptibility and χ_d is the (negative) diamagnetic susceptibility of the matrix.

For $y \ll 1$, i.e. in the limit of low magnetic field, $B_J(y) \to (J+1)y/3J$, leading to the low-field magnetization M_l (without the diamagnetic contribution) in the form

$$M_l = \frac{N_m (g\mu_B)^2}{3k_B T} J(J+1) \cdot H + \chi_V \cdot H \tag{2}$$

For the opposite case, i.e. in the limit of high magnetic field, $B_J(y) \to 1$, giving the high-field magnetization M_h as

$$M_h = M_s + \chi_V \cdot H = N_m g \mu_B J + \chi_V \cdot H \,. \tag{3}$$

Eqs. (2) and (3) represent straight lines as a function of magnetic field which intercept at the field

$$H_{eq} = \frac{3k_B T}{g\mu_B (J+1)}. \tag{4}$$

The key significance of Eq. (4) lies in that H_{eq} does not depend on x and gives directly the product $g(J+1)$ (in which J is a multiple of 1/2), allowing one to determine or to verify the main features of a given magnetic centre. It should be also stressed that linear, van Vleck-type- and/or diamagnetic contributions, do not change the position of H_{eq} which, for a given magnetic centre, depends only on temperature and can be practically determined from the intercept of extrapolated linear parts of low- and high-field magnetization. Knowing g and J, one can easily determine the concentration of noninteracting magnetic centres from the value of M_S.

Similarly, as in the case of magnetization, the total magnetic susceptibility is a sum of paramagnetic (χ_p)- and diamagnetic contributions

$$\chi_{tot} = \chi_p + \chi_d = \chi_B + \chi_V + \chi_d, \tag{5}$$

where χ_B is the Brillouin-type paramagnetic contribution which is easily obtained from M_B in the limit of low magnetic field, leading to the Curie law of the form $\chi_B = C/T$ with $C = N_m p^2/3k_B T$ being the Curie constant, where $p = g\sqrt{J(J+1)}\mu_B$ is the effective magnetic moment. If we neglect the van Vleck contribution (which is constant at low temperatures but at higher temperatures it behaves similarly to the Brillouin-type contribution [1,2]), we get

$$\chi_{tot} = \frac{C}{T} + \chi_d. \tag{6}$$

The above expression describes a straight line as a function of the inverse of temperature, with the slope being equal to the Curie constant and the intercept yielding the diamagnetic susceptibility.

3. Application to selected paramagnetic materials

The usefulness of the presented method is illustrated below by the analysis of experimental results obtained by us and by other authors for two selected paramagnetic materials containing small amounts of transition metal ions.

Fig. 1 shows our suceptibility data [3] obtained for three different samples of a natural crystal, known as 'kunzite', i.e. $LiAlSi_2O_6$ containing Mn ions. It can be seen that the measured total magnetic susceptibility drawn as a function of the inverse of temperature may be approximated by straight lines as given by Eq. (6). As can be observed in Fig. 1, these lines, fitted to the experimental data for all samples studied, intercept the y-axis close to each other, yielding, on the average, the diamagnetic susceptibility of the spodumene matrix $\chi_d = 3.5\times10^{-7}$ emu/g. On the other hand, the slope of the the straight lines gives the Curie constant equal to 9.16-, 6.86- and 4.82×10^{-5} K emu/g for sample K1, K2 and K3, respectively.

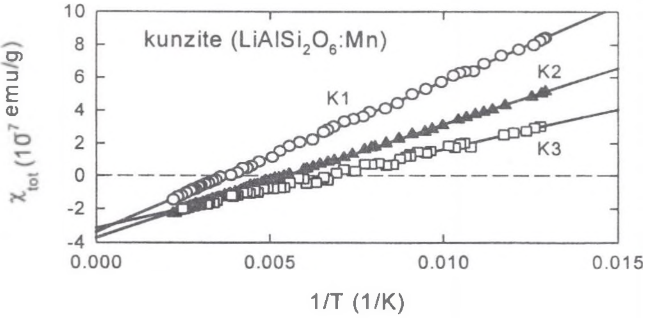

Fig. 1. Total magnetic susceptibility of three samples of kunzite ($LiAlSi_2O_6$:Mn) with various Mn concentration as a function of the inverse of temperature [3]. Solid straight lines represent the least-squares fitting to the experimental data

Rys. 1. Całkowita podatność magnetyczna trzech próbek kunzytu ($LiAlSi_2O_6$:Mn) z różnymi koncentracjami Mn w funkcji odwrotności temperatury [3]. Ciągłe linie proste przedstawiają dopasowanie do wyników doświadczalnych metodą najmniejszych kwadratów

Fig. 2 shows our magnetization data gathered at about 1.6 K at fields up to 14.5 T [3] for the same three kunzites as in Fig. 1. As can be seen in Fig. 2, for $H > 5$ T, the total measured magnetization decreases due to the diamagnetic contribution. Applying our method, one can see that the extrapolated linear parts of low- and high-field magnetization of sample K1, treated as an example, intercept at fields close to $H_{eq} = 1.04$ T (the vertical dashed line in Fig. 2), following from the value of the product $g(J + 1) = 7$ and corresponding to the spin-only Mn^{2+} ion for which $J = S = 5/2$ and $g = 2$, where S is the total spin momentum.

Having verified that in kunzites studied we are dealing with Mn^{2+} ions and taking $\chi_d = -3.5\times10^{-7}$ emu/g, as found from the data of Fig. 1, we have fitted the total magnetization to Eq. (1) (without the van Vleck term), as shown by solid lines in Fig. 2. The paramagnetic

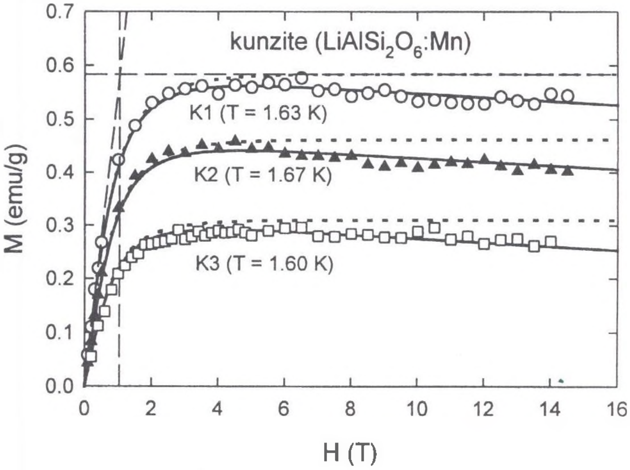

Fig. 2. Low-temperature total magnetization of three samples of kunzite ($LiAlSi_2O_6$:Mn) with various Mn concentrations [3]. The solid curves represent the sum of the paramagnetic Brillouin contribution (denoted by dotted curves) and diamagnetic contribution. The dashed lines represent extrapolated parts of low- anf high-field paramagnetic magnetization of sample K1, and intercept (at 1.63 K) near H_{eq}=1.04 T (the vertical dashed line), corresponding to the noninteracting Mn^{2+} ions with $S = 5/2$ and $g = 2$

Rys. 2. Niskotemperaturowe całkowite namagnesowanie trzech próbek kunzytu ($LiAlSi_2O_6$:Mn) z różnymi koncentracjami Mn [3]. Krzywe ciągłe przedstawiają sumę wkładu paramagnetycznego typu Brillouina (oznaczonego krzywymi kropkowanymi) i wkładu diamagnetycznego. Linie przerywane reprezentują ekstrapolowane części nisko- i wysokopolowego namagnesowania próbki K1, które przecinają się (w 1.63 K) w pobliżu H_{eq}=1.04 (pionowa linia przerywana), co odpowiada nieoddziałującym jonom Mn^{2+} z $S = 5/2$ i $g = 2$

Brillouin-type magnetization is represented in Fig. 2 by dotted lines. Subsequently, we can determine the molar concentration of Mn^{2+} ions x_M ($N_m = x_M N_A$, where N_A is the Avogadro number) from the values of saturation magnetization M_S found from the fitting procedure.Thus, the values of M_S equal to 0.584, 0462 and 0.310 emu/g yield x_M = 0.389, 0.308 and 0.207% for samples K1, K2 and K3, respectively. These values appear to be very close to those found from the values of the Curie constant (x_C) which for Mn^{2+} ions give x_C = 0.389, 0.291 and 0.205% for samples K1, K2 and K3, respectively.

Some representative high-field magnetization results obtained for $Cd_{1-x}Co_xTe$ [4], which exhibits both the Brillouin- and van Vleck paramagnetism, are shown in Fig. 3. It can be seen that the extrapolated linear parts of low- and high-field magnetization intercept at the field very close to H_{eq} = 1.5 T (the vertical dashed line), corresponding to the ground state of Co^{2+} isolated ion with $S = 3/2$ and $g = 2.30$ in CdTe [5]. This allows us to determine the Co concentration in this sample as x_M = 0.25%, being much lower than that found by atomic absorption (0.383%) [4].

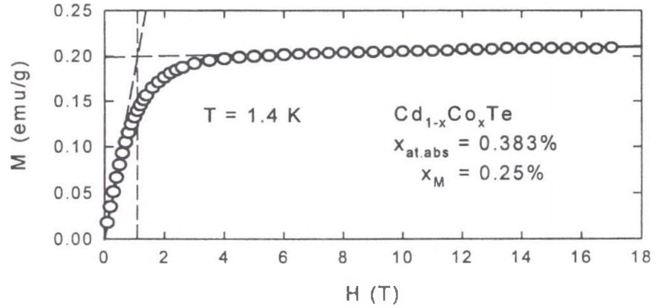

Fig. 3. Paramagnetic magnetization of sample of $Cd_{1-x}Co_xTe$ (with $x_{at.abs}$ = 0.383% as determined by atomic absorption) at 1.4 K Experimental data are taken from [4] and the solid curve represents the sum of the Brillouin- and van Vleck-type contributions. The dashed lines represent extrapolated parts of low- and high-field magnetization, and intercept near H_{eq}=1.08 T (the vertical dashed line), corresponding to the $S = 3/2$ noninteracting Co^{2+} ions with $g = 2.30$ in CdTe matrix [5]

Rys. 3. Namagnesowanie paramagnetyczne próbki $Cd_{1-x}Co_xTe$ (z $x_{at.abs}$ = 0.383% określonym z absorpcji atomowej) w 1.4 K. Wyniki doświadczalne wzięto z [4], a krzywe ciągłe przedstawiają sumę wkładu typu Brillouina i wkładu typu van Vlecka. Linie przerywane reprezentują ekstrapolowane części nisko- i wysokopolowego namagnesowania i przecinają się w pobliżu H_{eq}=1.08 T (pionowa linia przerywana), co odpowiada nie oddziałującym jonom Co^{2+} z $S = 3/2$ i g = 2.30 dla matrycy z CdTe [5]

4. Conclusions

We have demonstrated that the magnetic field, corresponding to the intercept of extrapolated linear parts of low- and high-field magnetization, does not depend on concentration of magnetic centres embedded in a diamagnetic matrix, allowing one to determine their magnetic moment and, as a consequence, also their concentration. We have also shown usefulness of the temperature dependence of the total magnetic susceptibility allowing for determination of diamagnetism of the matrix as well as the Curie constant dependent on the magnetic ion moment and concentration. Thus, the careful measurements of magnetization and magnetic susceptibility and their subsequent analysis can be treated as an efficient, simple and nondestructive method to characterize various paramagnetic materials containing magnetic centres of low concentration.

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Streszczenie

Praca przedstawia metody analizy pomiarów temperaturowej zależności podatności magnetycznej oraz niskotemperaturowego namagnesowania dla materiałów zawierających małą ilość statystycznie rozłożonych jonów magnetycznych. Pokazano, że w przypadku niskotemperaturowego namagnesowania pole magnetyczne, odpowiadające przecięciu się ekstrapolo-

wanych liniowych części nisko- i wysokopolowego namagnesowania, nie zależy od koncentracji jonów magnetycznych, dostarczając przy tym zasadniczych informacji o ich momencie magnetycznym, co z kolei pozwala na precyzyjne wyznaczenie koncentracji jonów. Przypomniano również, że w przypadku jonów izolowanych i wykazujących zachowanie typu Brillouina mierzona podatność całkowita w funkcji odwrotności temperatury jest linią prostą, której przecięcie z osią y daje diamagnetyczny wkład matrycy, a nachylenie zależy od momentu magnetycznego i koncentracji jonów magnetycznych zawartych w matrycy diamagnetycznej. Użyteczność prezentowanych metod zilustrowano poprzez analizę wyników doświadczalnych, uzyskanych przez nas dla kryształów naturalnych kunzytu ($LiAlSi_2O_6$:Mn) oraz przez innych autorów dla półprzewodnika półmagnetycznego $Cd_{1-x}Co_xTe$.