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MAGNETIC PROPERTIES OF COLOURED VARIETIES OF SPODUMENE

Abstract. The high-field magnetization and magnetic susceptibility of two coloured varieties of spodumene from Pamir, i.e. kunzite and hiddenite, containing small amounts of transision metal ions have been studied for the first time. The magnetization has been measured for several temperatures between 1.5 and 300 K at fields up to 14 T and susceptibility has been determined as a function of temperature in the range 1.5–300 K. It appears that, for both varieties, the total magnetization and susceptibility consist of the paramagnetic contribution resulting from the temperature-dependent Brillouin-type behaviour of magnetic ions and temperature-independent diamagnetic contribution of the spodumene matrix. Based on the results obtained, we have determined the diamagnetic susceptibility of the spodumene matrix (-2.3×10^{-7} emu/g) and the molar concentration of Mn^{2+} ions in kunzite (0.23%).

Key-words: spodumene, kunzite, hiddenite, magnetization, magnetic susceptibility, magnetic ion concentration.

INTRODUCTION

Spodumene $LiAl[Si_2O_6]$ is a mineral which occurs in several varieties with their colour depending on kind and quantity of chromatic elements contained in the host matrix. The unit cell of spodumene is monoclinic, space group C^6_{2h} (C2/c), with two inequivalent metal cation sites M1 and M2 occupied by Al and Li ions, respectively, and these sites may be substitutionally occupied by the ions of the transision metal elements, such as Mn, Fe, Cr and the others (Holuj 1968; Jurczyk et al. 1997; Manoogian et al. 1965; Walker et al. 1997).

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The colour of natural spodumene crystals can vary from pale mauve-pink for the kunzite variety to a deep green for the hiddenite variety. At room temperature, most spodumenes exhibit strong orange luminescence under electron-beam or laser excitation due to the Mn^{2+} ions and, when lowering temperature, an additional luminescence emerges which is ascribed to the Cr^{3+} ions (Walker et al. 1997), however, the amounts of these and other magnetic ions in the spodumene matrix remain unknown.

One of the methods of determination of small or trace amounts of elements is the X-ray fluorescence (XRF) technique which can also be applied to powdered samples, including spodumenes (Jurczyk et al. 1997). According to that work, kunzite contains small amount of Mn, while hiddenite, apart from this, contains a similar amount of Fe; as for Cr, this element has not been found as being below the detection limit.

In view of the results of luminescence measurements and XRF method, we have undertaken, to our knowledge for the first time, the studies of the magnetic properties of natural spodumenes, in order to characterize these minerals in a greater detail by a completely different, but complementary and nondestructive method.

EXPERIMENTAL

We have studied the magnetic properties of two coloured varieties of spodumene, i.e. kunzite and hiddenite from Pamir. The chemical composition of powdered samples prepared from these minerals was determined by XRF method (Jurczyk et al. 1997). It was found that the sample of kunzite contains 0.04 wt.% of Mn, while sample of hiddenite, apart from 0.02—0.03 wt.% of Mn, contains the similar amount of Fe; the presence of other elements, such as Cr, V and Co, has been found to be below the detection limit, i.e. 10 ppm approximatively.

The magnetization measurements have been performed at several temperatures between 1.5 and 300 K in dc magnetic fields up to 14 T by the sample extraction method. The magnetization data at a given temperature yield also the magnetic susceptibility which has been derived from the linear part of magnetization. Apart from this, we have carried out the standard susceptibility measurements at low fields ($H \leq 0.2$ T) with an electronic balance by the Faraday method and in the temperature range 77—300 K. It appears that, even in the case of very low measured signals, both methods give, within the experimental error, the same susceptibility values at the same temperatures which is very important from the point of view of reliability of the final results.

RESULTS AND DISSCUSION

The results of the magnetic susceptibility and magnetization measurements performed for samples of kunzite and hiddenite are shown in Figs. 1—4.

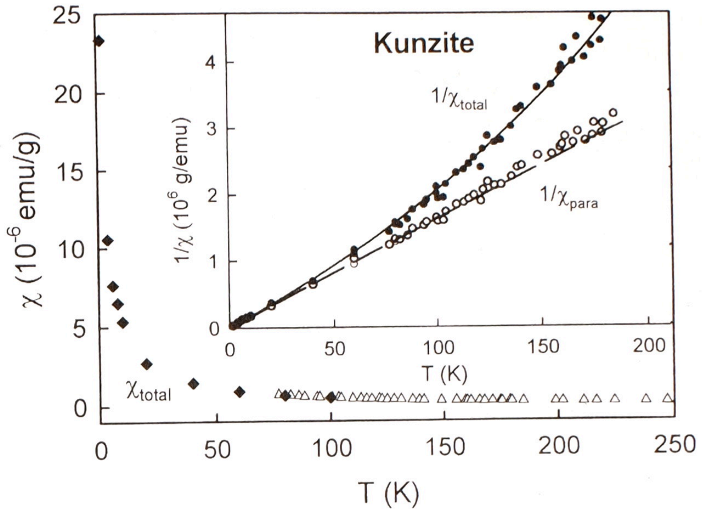

Fig. 1. Temperature dependence of the total magnetic susceptibility of kunzite. Experimental data obtained by the sample extraction method and by the Faraday balance are marked by diamonds and triangles, respectively. The inset shows the inverse total susceptibility (full circles) together with the fitting curve [Eqs. (4) and (5); solid line] and the inverse paramagnetic susceptibility (open circles) together with the dashed line representing the Curie law [Eq. (5)]

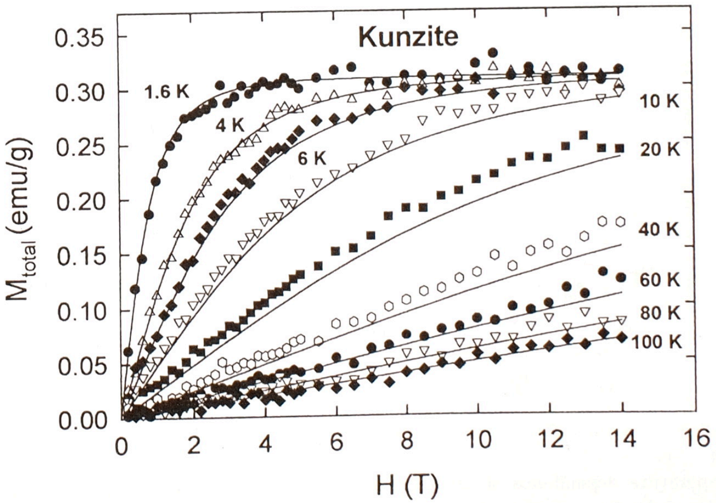

Fig. 2. Total magnetization of kunzite as a function of magnetic field at different temperatures. Solid lines represent the sum [Eq. (1)] of the paramagnetic term containing the Brillouin function [Eq. (2)] with $M_{sat} = 0.31$ emu/g and the diamagnetic term with $\chi_{dia} = -1.5 \times 10^{-7}$ emu/g

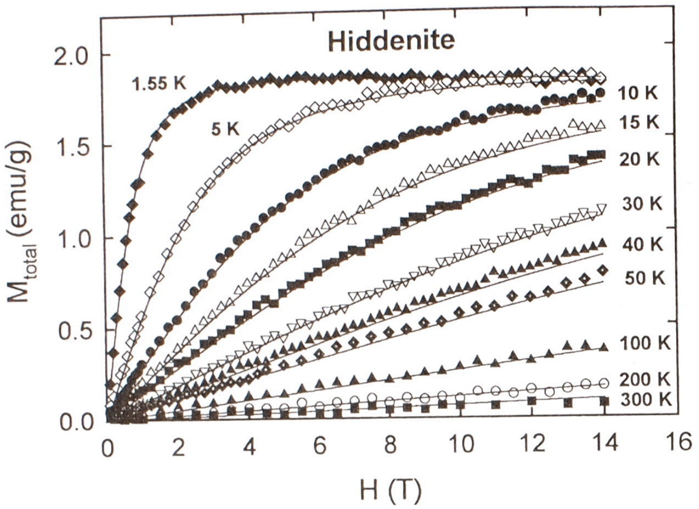

Fig. 3. Total magnetization of hiddenite as a function of magnetic field at different temperatures. Solid lines represent the sum [Eq. (1)] of the paramagnetic term containing the Brillouin function [Eq. (2)] with M_{sat} = 1.85 emu/g and the diamagnetic term with $\chi_{dia} = -2.3 \times 10^{-7}$ emu/g

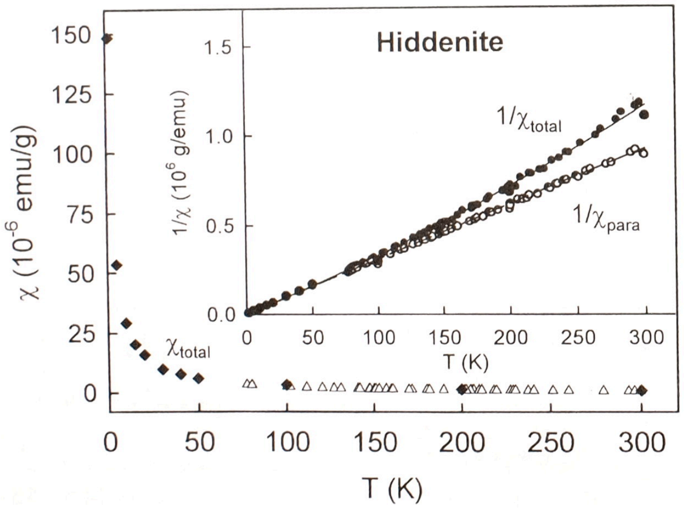

Fig. 4. Temperature dependence of the total magnetic susceptibility of hiddenite. Experimental data obtained by the sample extraction method and by the Faraday balance are marked by diamonds and triangles, respectively. The inset shows the inverse total susceptibility (full circles) together with the fitting curve [Eqs. (4) and (5); solid line] and the inverse paramagnetic susceptibility (open circles) together with the dashed line representing the Curie law [Eq. (5)]

Generally, the magnetic response of the kunzite sample is much weaker than that of hiddenite. This fact influences our approach to analysis of the experimental data obtained for both minerals. For kunzite, we will analyze first the susceptibility data shown in Fig. 1 and then we will describe the magnetization data which exhibit a considerable scatter, including those measured above 5 T at 1.6 K (Fig. 2). In the case of hiddenite, the low temperature and high-field magnetization data exhibit a considerable less scatter (Fig. 3), so we will analyze first such data gathered at 1.55 K, followed by description of other magnetization results and susceptibility (Fig. 4).

In order to proceed further, first we recall the basic formulae describing magnetic behaviour of paramagnetic materials. As it is known (see e.g. Morrish 1970), the measured total magnetization as a function of magnetic field H of a diamagnetic material containing magnetic ions consists of two terms:

$$M_{total} = M_{para} + \chi_{dia} \cdot H \tag{1}$$

i.e. the temperature dependent positive contribution of magnetic ions M_{para} and the temperature independent negative diamagnetic contribution of the host matrix $M_{dia} = \chi_{dia} \cdot H$, where χ_{dia} is the diamagnetic susceptibility. Since the concentration of magnetic ions in both minerals studied is expected to be very small, these ions may be treated as isolated allowing us to describe the paramagnetic contribution to magnetization as

$$M_{para} = M_{sat} B_J(y) \tag{2}$$

where M_{sat} is the saturation value of magnetization and $B_J(y)$ is the Brillouin function given by:

$$B_J(y) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J} y\right) - \frac{1}{2J} \coth \frac{y}{2J} \tag{3}$$

with

$$y = \frac{q\mu_B JH}{k_B T}$$

In these expressions, g is the Landé factor, μ_B is the Bohr magneton, J is the total angular momentum of the magnetic ion and k_B is the Boltzmann constant.

In the limit of extremely high magnetic field, the Brillouin function tends to unity, giving $M_{para}(H \to \infty) = M_{sat} = g\mu_B J$ per magnetic ion. Practically, as it follows from Eqs. (1) and (2), at low temperatures and sufficiently high magnetic fields, M_{total} should begin to decrease because of the increasing negative diamagnetic term which is indeed observed when looking at the experimental data at $T \cong 1.6$ K for both spodumenes studied and especially for hiddenite.

Similarly as in the case of magnetization, the measured total susceptibility χ_{total} is a sum of paramagnetic and diamagnetic contributions:

$$\chi_{total} = \chi_{para} + \chi_{dia} \tag{4}$$

The paramagnetic contribution to susceptibility is easily obtained from Eq. (3) in the limit of low magnetic field, leading to the Curie law in the form:

$$\chi_{total} - \chi_{dia} = \chi_{para} = \frac{C}{T} \tag{5}$$

where C is the Curie constant.

The results of the susceptibility measurements as a function of temperature for kunzite are presented in Fig. 1. It can be observed that the total measured susceptibilty of kunzite decreases quickly with increasing temperature and approaches zero at higher temperatures, indicating that the diamagnetic contribution becomes comparable with the paramagnetic contribution. The inset in Fig. 1 shows the inverse susceptibility limited to 200 K in order to avoid a large scatter of data at higher temperatures. It can be seen that the inverse total susceptibility of kunzite exhibits an upturn in the considered temperature range, indicating once again an increasing role of the diamagnetic contribution with increasing temperature.

Based on Eqs. (4) and (5), we have determined the values of $C = 6.0 \times$ $\times 10^{-5}$ K emu/g and $\chi_{dia} = -1.5 \times 10^{-7}$ emu/g by the least-squares fit to the experimental data as shown in the inset of Fig. 1 by the solid line. After subtraction of the proper value of χ_{dia} from χ_{total}, one gets the net inverse paramagnetic susceptibility $1/\chi_{para}$ vs. T which indeed follows the straight line (dashed line in Fig. 1) as expected from the Curie law (Morrish 1970).

As follows from the EPR (Holuj 1968) and luminescence (Walker et al. 1997) measurements, the dominant chromatic ion in kunzite is Mn^{2+}. An isolated Mn^{2+} ion in the ground state represents the simplest spin-only case with its total momentum equal to the spin momentum, i.e. $J = S = 5/2$ and $g = 2$. Using these values along with χ_{dia} obtained from the suceptibility data, we have fitted the magnetization data of kunzite gathered at 1.6 K, basing on Eqs. (1—3). This gives us the value of $M_{sat} = 0.31$ emu/g which has been subsequently used to calculate the magnetization at higher temperatures as shown by the solid curves in Fig. 2.

For isolated Mn^{2+} ions, we can determine their molar concentration x either from the value of M_{sat} or from the Curie constant C which (in emu/g) are equal to:

$$M_{sat} = \frac{xN_A}{\mu} g\mu_B S \tag{6}$$

and

$$C = \frac{xN_A(g\mu_B)^2}{3k_B\mu} S(S+1) \tag{7}$$

where N_A is the Avogadro number and μ is the molar mass of a given material. Using these formulae for kunzite, one gets from M_{sat} and C the molar concentration $x = 0.21\%$ and $x = 0.25\%$, respectively, which are in satisfactory agreement to each other, bearing in mind small measured signals, possible presence of trace amounts of other magnetic ions and uncertainty of fitting procedures. The averaged value $x = 0.23\%$ can be converted to the weight percentage $x_{wt} = x\mu_{Mn}/\mu$, where μ_{Mn} is the atomic mass of Mn, as shown in Table 1.

Table 1

Contents of transition elements in spodumenes from Pamir determined by XRF method (Jurczyk et al. 1997) and by magnetic measurements (in wt.%)

Variety of spodumene	Element	XRF method (Jurczyk et al. 1997)	Magnetic measurements (this work)
Kunzite	Mn	0.04	0.068
Hiddenite	Mn Fe	0.02—0.03 0.02—0.03	0.38 (sum of both)

The Mn^{2+} ions are also present in hiddenite (Walker et al. 1997) and therefore we may first try to describe the magnetization data for this mineral also with $g = 2$ and $S = 5/2$, starting with the magnetization at 1.55 K (Fig. 3) which, at $H \approx 5$ T, begins to decrease linearly with field because of the diamagnetism of the spodumene matrix. Fitting Eqs. (1—3) to the experimental data at 1.55 K, we have determined the values of $\chi_{dia} = -2.3 \times 10^{-7}$ emu/g and $M_{sat} = 1.85$ emu/g for hiddenite which have been then used to calculate the field dependence of magnetization (represented by the solid lines in Fig. 3) at higher temperatures.

In the next step, we have fitted the Curie law to the susceptibility data obtained for hiddenite (Fig. 4) with χ_{dia} determined from magnetization. This way, we have formally determined the Curie constant $C = 3.2 \times 10^{-4}$ K emu/g for the investigated sample of hiddenite.

As it can be seen from Figs. 1—4, the calculated curves describe quite well the experimental data for both minerals, indicating the temperature dependent Brillouin-type paramagnetic character of the dominant ions embedded in the spodumene matrix. This is obvious in the case of kunzite containing, as we have already mentioned, the Mn^{2+} ions as the dominant ones. The fact that we do not observe a clear decrease of the total magnetization of kunzite at $H \geq 5$ T and at 1.6 K (Fig. 2), as expected for Mn^{2+} ions, may be connected with the presence of Cr^{3+} ions (Walker et al. 1997), giving an additional and non-saturating magnetization contribution. This contribution may also be responsible for the difference between the values of χ_{dia} determined for both varieties of spodumene. In view of this and taking into account the clear linear decrease of the total magnetization observed for hiddenite at $H \geq 5$ T and at 1.55 K, we can admit the value of $\chi_{dia} = -2.3 \times 10^{-7}$ emu/g, determined for this mineral, as the diamagnetic susceptibility of the spodumene matrix.

The obtained averaged value $x_{wt} = 0.068$ wt.% of Mn in the investigated sample of kunzite is comparable with 0.04 wt.% of Mn found in a powdered sample of the same mineral by XRF method (Jurczyk et al. 1997), keeping in mind its complexity and a possible inhomogeneity of the Mn distribution.

As far as hiddenite is concerned, XRF analysis (Jurczyk et al. 1997) reports the presence of similar amounts of Mn and Fe (see Table 1) and the Brillouin-type behaviour of magnetization and susceptibility indicates that, apart from Mn^{2+} ions, this mineral contains much greater amount of Fe^{3+} ions, characterized by the same values of $g = 2$ and $S = 5/2$. Another possibility, the presence of Fe^{2+} ions, is much less probable, since such ions exhibit, at low temperatures, the temperature-independent van Vleck-type paramagnetism which should influence the experimental results below 10 K (Twardowski 1990). The values of $x = 1.23\%$ and $x = 1.36\%$ formally obtained for hiddenite from M_{sat} [Eq. (6)] and C [Eq. (7)], respectively, give us therefore the sum of Mn and Fe ion concentrations which, on the average, corresponds to $x_{wt} = 0.38$ wt.% and appear to be about 7 times greater than the same sum found by XRF method (Jurczyk et al. 1997) as shown in Table 1, suggesting a big inhomogeneity of this kind of spodumene which, additionally, may contain inclusions of iron hydroxide (FeOOH) with Fe^{3+} ions.

CONCLUSIONS

Studies of the magnetic properties of two coloured varieties of spodumene, i.e. kunzite and hiddenite from Pamir, have shown that both minerals behave like paramagnetic materials and their total magnetic susceptibility and magnetization is a sum of the positive temperature-dependent Brillouin-type contribution of magnetic ions and negative temperature-independent diamagnetic contribution of the spodumene matrix. The analysis of the experimental data has allowed us to determine the diamagnetic susceptibility of spodumene $\chi_{dia} = -2.3 \times 10^{-7}$ emu/g and the amount of Mn^{2+} ions in kunzite $x_{wt} = 0.068$ wt.%. As for hiddenite, our results, in connection with the XRF data (Jurczyk et al. 1997), indicate that, apart from Mn^{2+} ions, this mineral contains also much greater amount of Fe^{3+} ions, the part of which may originate from the inclusions of iron hydroxide in this kind of spodumene.

Finally, our investigations show that the magnetic measurements can be treated as an efficient and nondestructive method to characterize minerals containing various magnetic ions.

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WŁASNOŚCI MAGNETYCZNE KOLOROWYCH ODMIAN SPODUMENU

Streszczenie

Zbadano po raz pierwszy namagnesowanie w wysokich polach i podatność magnetyczną dwóch kolorowych odmian spodumenu, tj. kunzytu i hiddenitu pochodzących z Pamiru i zawierających niewielkie ilości jonów metali przejściowych. Namagnesowanie zmierzono w kilku temperaturach między 1,5 a 300 K w polach do 14 T, a podatność wyznaczono w funkcji temperatury w przedziale 1,5—300 K. Okazuje się, że dla obu odmian całkowite namagnesowanie i podatność składają się z części paramagnetycznej, wynikającej z zależnego od temperatury zachowania się jonów magnetycznych ze spinem $S = 5/2$ i czynnikiem Landégo $g = 2$, a opisanej funkcją Brillouina, oraz z niezależnej od temperatury części diamagnetycznej pochodzącej od matrycy spodumenu. Na

podstawie uzyskanych wyników określono podatność diamagnetyczną spodumenu (–2,3 × 10^{-7} emu/g) oraz koncentrację molową jonów Mn^{2+} w kunzycie (0,23%). Koncentracja ta odpowiada 0,068% wag. zawartości Mn w kunzycie, co jest porównywalne z wynikiem otrzymanym rentgenowską analizą fluorescencyjną (0,04% wag.), jeżeli uwzględnić złożoność tej metody oraz możliwą niejednorodność rozkładu jonów Mn w badanym minerale. W przypadku hiddenitu, uzyskane wyniki, w połączeniu z wynikami badań fluorescencyjnej analizy rentgenowskiej, wskazują na to, że zawiera on, oprócz jonów Mn^{2+}, o wiele więcej jonów Fe^{3+}, z których część może pochodzić z wtrąceń FeOOH w tego rodzaju spodumenie i świadczy o dużej niejednorodności badanego minerału. Reasumując, nasze badania wykazują, że pomiary magnetyczne można traktować jako efektywną i nieniszczącą metodę służącą do charakteryzowania minerałów zawierających różne jony magnetyczne.