Magnetization and magnetic susceptibility of jadeite

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Abstract: We have studied the high-field magnetization (up to 14.5 T) and magnetic susceptibility in the temperature range $1.7 - 420$ K of two samples of jadeite ($NaAlSi_2O_6$), white and green, containing transition metal ions and originating from Burma (now Myanmar). It appears that the high-temperature susceptibility data obey the Curie-Weiss law indicating the onset of the antiferromagnetic interaction between the magnetic ions. This interaction is also seen in the high-field magnetization data which are well described by the phenomenological cluster model. As a result of our analysis, we have identified the Fe^{3+} ions as the dominant ones in the studied jadeites and we have determined the molar concentration of these ions (0.8% in white- and 2.5% in green jadeite) as well as the diamagnetic susceptibility of the jadeite matrix (-3.8×10^{-7} emu/g).

Key-words: jadeite, magnetization, magnetic susceptibility, magnetic ion concentration.

Introduction

Jadeite ($NaAlSi_2O_6$) is a mineral which belongs to the clinopyroxene group and occurs in different places of the world (Prewitt & Burnham, 1966; Rossman, 1974; Khomenko & Platonov, 1985). Good quality jadeite is highly appreciated in jewellery and for this reason jadeite has been also synthesized artificially by a high-pressure technique (Zhao *et al.*, 1994 and refs. therein).

The unit cell of jadeite is monoclinic, space group C_{2h}^6 (C2/c) with the lattice parameters $a = 0.942$, $b = 0.856$, $c = 0.522$ nm and $\beta = 107.6°$ (Prewitt & Burnham, 1966). The crystal structure contains two inequivalent metal cation sites M1 and M2 occupied by Al and Na ions, respectively, and these sites may be substitutionally replaced by the ions of the transition metal elements.

The typical green color of jadeite follows from the presence of a sufficient amount of Cr and/or Fe, depending on the place of origin. For example, the chemical analysis of jadeite from Kazakhstan shows that this mineral contains comparable quantities of both elements (reported as Cr_2O_3 of 0.68, Fe_2O_3 of 0.45 and FeO of 0.24 wt.%) and much smaller amounts of other magnetic elements, such as Ti and Mn, reported as TiO_2 of 0.04 and MnO of 0.02 wt.%, respectively (Khomenko & Platonov, 1985). On the other hand, the electron microprobe analysis performed on jadeites

from Burma demonstrates that Fe is the only dominant magnetic element (reported as Fe_2O_3 of $0.4 - 0.9$ wt.%); other magnetic elements, first of all Cr, as well as Mn and Ti, are of much lower concentration (reported as Cr_2O_3, MnO and TiO_2 of $0.02 - 0.09$ wt.%) and occur in various combinations in different samples (Prewitt & Burnham, 1966; Rossman, 1974). Moreover, the color of natural jadeite crystals from Burma, which have been studied also in this work, can vary from white through lavender to green, being mainly dependent on the magnitude of Fe content with a possibility of simultaneous presence of both Fe^{3+} and Fe^{2+} ions as deduced from spectroscopic studies (Rossman, 1974). On the other hand, similar studies of jadeite from Russia have revealed the presence of Fe^{3+} ions only (Bakhtin & Manapov, 1976).

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

Experimental

We have investigated magnetic properties of two samples of jadeite, *i.e.* a white sample J1 and a green sample J2, both
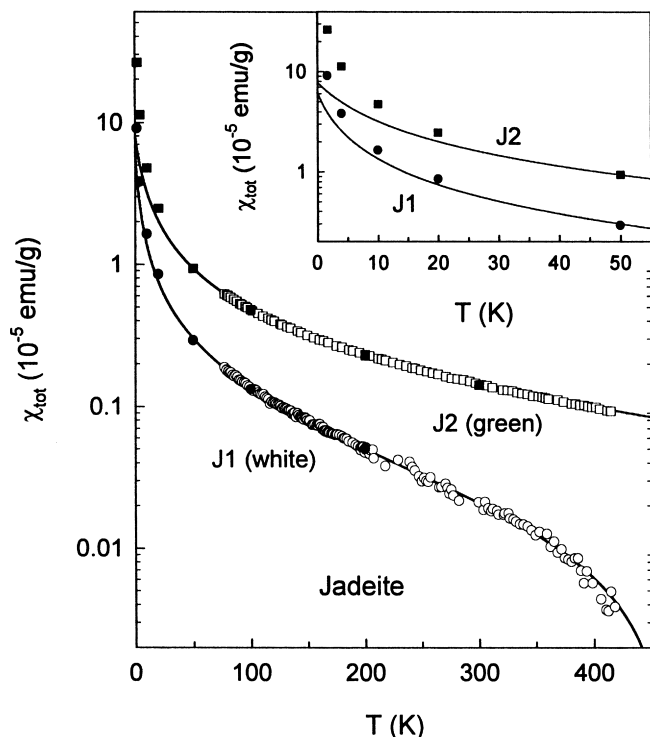
Fig. 1. Temperature dependence of the total magnetic susceptibility of two jadeite samples, J1 (white) and J2 (green). The inset shows the same dependence in greater detail at low temperatures. Full and open symbols represent the experimental data determined from the linear part of magnetization measured by the sample extraction method and by the Faraday method, respectively. The solid curves represent the sum of the high-temperature paramagnetic susceptibility of interacting magnetic ions described by the Curie-Weiss law [Eq. (1)] and the diamagnetic susceptibility of the jadeite matrix.

originating from Burma (now Myanmar). As examined by a microscope, the minerals studied were optically homogeneous, almost translucent and without any inclusions. Both samples were pieces of unoriented single crystals in the form of a slab with dimensions of the order of 2×10 mm^3; their masses were equal to 340 and 275 mg for sample J1 and J2, respectively. For magnetic studies the samples were taken as they were without crushing or milling.

The magnetization measurements have been performed at several temperatures $T \geq 1.7$ K in dc magnetic fields up to 14.5 T by the sample extraction method (Picoche *et al.*, 1989). 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 careful susceptibility measurements at low fields ($H \leq 0.2$ T) with an electronic microbalance by the Faraday method (see *e.g.* Smith *et al.*, 1970) in the temperature range $77-420$ K.

Results and discussion

The temperature dependence of the total magnetic susceptibility for the jadeites studied is presented in Fig. 1. The y-

axis of this figure is logarithmic because susceptibility changes over three orders of magnitude in the investigated temperature range; on the other hand, to better visualize the low-temperature behavior of both jadeites, their susceptibility at $T \leq 50$ K is shown in greater detail in the inset of Fig. 1.

It can be observed that the magnetic response of green jadeite (sample J2) is higher than that of white jadeite (sample J1) with its susceptibility decreasing quickly at higher temperatures which indicates that the negative diamagnetic contribution χ_d of the matrix becomes comparable with the positive paramagnetic contribution χ_p of magnetic ions. Nevertheless, on the whole, the measured signal of the investigated jadeites is stronger than that of the previously studied kunzites with non-interacting Mn^{2+} ions as the dominant ones (Bartkowska *et al.*, 2000). This difference indicates that the studied jadeites contain more magnetic ions than kunzites making possible an interaction between the ions present in jadeites which, at high temperatures, can be described by the Curie-Weiss law for the paramagnetic susceptibility (Morrish, 1965):

$$\chi_p = \frac{C}{T-\theta} \qquad (1)$$

where C is the Curie constant and θ is the Curie-Weiss temperature. Adding the diamagnetic susceptibility of the jadeite matrix χ_d to Eq. (1), one gets the formula for the total high-temperature susceptibility χ_{tot} which has been fitted to the experimental data in the range $77-420$ K, treating C, θ and χ_d as adjustable parameters. The result of this fitting for both samples studied is shown in Fig. 1 as solid curves, yielding $\chi_d = -(3.8 \pm 0.2) \times 10^{-7}$ emu/g together with $C = (1.80 \pm 0.07) \times 10^{-4}$ K·emu/g and $\theta = -(3 \pm 1)$ K for sample J1, and $C = (5.57 \pm 0.08) \times 10^{-4}$ K·emu/g and $\theta = -(7.1 \pm 0.8)$ K for sample J2. Low and negative values of θ obtained for both jadeites indicate the onset of the antiferromagnetic (AFM) interaction between magnetic ions which is further supported by the low-temperature experimental data lying considerably higher than the solid curves representing the high-temperature Curie-Weiss law, as demonstrated in the inset of Fig. 1. A similar behavior of susceptibility is observed in diluted magnetic semiconductors (DMS) and is explained as being due to superexchange (Spalek *et al.*, 1986; Furdyna *et al.*, 1988).

Bearing in mind that the main magnetic element contained in natural jadeites from Burma is Fe (Prewitt & Burnham, 1966; Rossman, 1974), the low-temperature behavior of the measured susceptibility indicates the presence of Fe^{3+} ions (with spin $S = 5/2$ and the orbital momentum $L = 0$) as the dominant ones in the minerals studied, similarly as in jadeite from Russia (Bakhtin & Manapov, 1976). Our data confirm also that in jadeites from Burma (Rossman, 1974), Fe^{2+} ions would constitute a minor proportion of total Fe content, since Fe^{2+} ions (with $S = 2$ and $L = 2$) exhibit van Vleck paramagnetism leading to saturation of their susceptibility at low temperatures (Slack *et al.*, 1969; Mahoney *et al.*, 1970, Twardowski *et al.*, 1988; Arciszewska *et al.*, 1990).

Fig. 2 and 3 show the paramagnetic magnetization (M_p) of jadeites studied at various temperatures, subtracted from the measured total magnetization $M_{tot} = M_p + \chi_d H$, with $\chi_d = -3.8 \times 10^{-7}$ emu/g as determined from the susceptibility
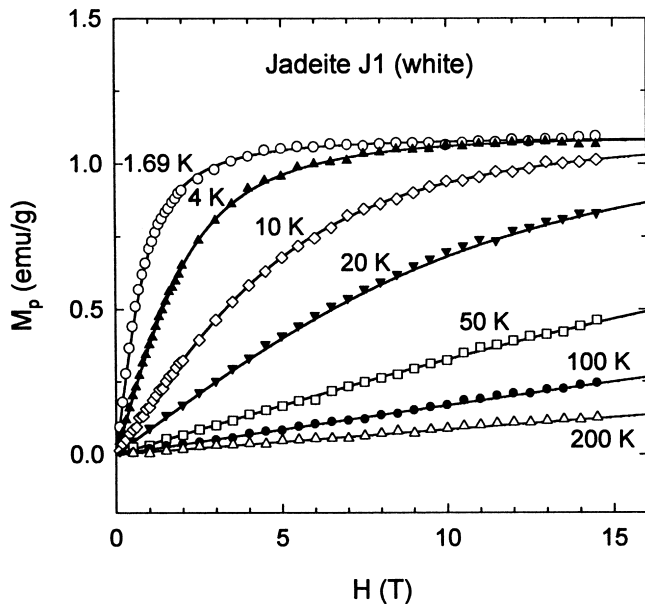
Fig. 2. Field dependence of the paramagnetic magnetization of white jadeite sample J1 at different temperatures. The solid curves represent the cluster model of Nicholas *et al*. (1995) and are calculated according to Eqs. (2) and (3).
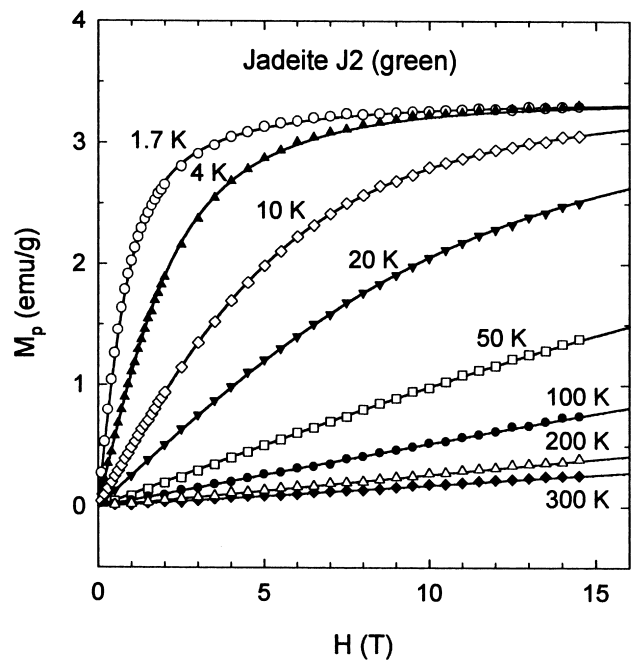

Fig. 3. Field dependence of the paramagnetic magnetization of green jadeite sample J2 at different temperatures. The solid curves represent the cluster model of Nicholas *et al*. (1995) and are calculated according to Eqs. (2) and (3).

data. It can be seen that magnetization of both samples resembles the Brillouin behavior expected for isolated Fe^{3+} ions with, however, an important difference; namely, even at the lowest temperature, magnetization does not saturate at high fields but continues to increase monotonically for $H > 5$ T, though much slower than at low fields.

The magnetization data from Fig. 2 and 3 are strongly temperature dependent even at the lowest temperatures which indicate, similarly as the susceptibility data from Fig. 1, that Fe^{2+} ions constitute a minor proportion of total Fe content in the studied jadeites, since magnetization of these ions does not depend on temperature below 5 K (see *e.g.* Testelin *et al*., 1992). Thus, the lack of saturation of magnetization at high fields and at low temperatures supports the susceptibility results indicating the onset of AFM interaction between the neighboring Fe^{3+} ions present in jadeites. Such an interaction leads to the formation of clusters, first of all pairs, triples, *etc.*, which results in reduction of the mean spin of the magnetic ion with respect to its free ion value.

Another characteristic feature of the lowest temperature (1.7 K) experimental data from Fig. 2 and 3 is that magnetization changes smoothly with field and does not exhibit any step-like structure in the investigated field range following from discrete spin-flip transitions within the magnetic ion pairs, as observed in cubic DMS (see *e.g.* Shapira *et al*., 1984). Observation of magnetization steps in these materials, with relatively simple crystal structure, is connected with a discrete spectrum of cation-cation distances, *i.e.* a given host cation (which can be replaced in DMS at random by a magnetic ion) has 12 nearest neighbors (NN) at distance $a\sqrt{2}/2$ (with *a*, the lattice constant), 6 next-nearest neighbors (NNN) at distance *a*, *etc.* (de Jonge & Swagten, 1991). On the other hand, a much more complicated, monoclinic

crystal structure of jadeite (Prewitt & Burnham, 1966) is characterized by a quasi-continuous spectrum of cation-cation distances with a great variety of pairs that, on the whole, may give no observable steps in the investigated field range.

In order to describe our magnetization data, we use therefore the cluster model of Nicholas *et al*. (1995) providing a smooth increase of magnetization at high fields. Within this model, the mean spin projection $<S_z>$ on the magnetic field direction of an ion with spin $S = 5/2$ is written as

$$<S_z> = \left[S_0 + \left(\frac{5}{2} - S_0 \right) B_{5/2} (y_2) \right] B_{5/2} (y_1) \qquad (2)$$

where S_0 denotes the effective spin at $H = 0$, $B_{5/2}(y)$ is the Brillouin function for $S = 5/2$ with $y_i = g\mu_B SH//k_B T_i$ (where the Landé factor $g = 2$, μ_B is the Bohr magneton and k_B is the Boltzmann constant) with T_i being the effective temperatures. The first term in Eq. (2) represents the contribution to $<S_z>$ of an isolated ion, while the second simulates the behavior of all the clusters which dissociate at high fields. It turns out that T_1 corresponds to the lattice temperature T, while T_2 is associated with the mean cluster size which increases with increasing the magnetic ion concentration x and can be expressed as $T_2 = T + T_c$, with T_c being proportional to x (Nicholas *et al*., 1995; Zehnder *et. al*., 1996). For magnetic ions of the molar concentration $x = N_m/N_A$ (with N_m, the number of magnetic ions per mol and N_A, the Avogadro number), their magnetization (in emu/g) is given by

$$M_p = x N_A g\mu_B <S_z> /m \qquad (3)$$

where *m* is the molar mass.

The fitting procedure of magnetization data demonstrat-

ed in Fig. 2 and 3 has been performed as follows. First, Eqs. (2) and (3) were fitted to the experimental data at the lowest measured temperatures (1.7 K) for both jadeites, treating x, S_0 and T_c as adjustable parameters. Then, at higher temperatures, S_0 was the only adjustable parameter, while the values of x and T_c were those determined at 1.7 K. The results of calculations, shown by solid curves in Figs. 2 and 3, appear to describe very well the magnetization data in all investigated temperatures for both jadeites.

The fitting procedure at 1.7 K yields the value of T_c, which may be related to the AFM interaction strength within the clusters, as being equal to 7.6 and 8.7 K, as well as the molar concentration of Fe^{3+} ions $x_M = 0.79$ and 2.41% for sample J1 and J2, respectively. These values of x_M found from the magnetization data can be compared with the molar concentration x_C calculated from the Curie constant, given (in K·emu/g) by

$$C = \frac{x_C N_A p_{eff}^2}{3 k_B m} \qquad (4)$$

where p_{eff} is the effective magnetic moment, equal to 5.9 μ_B for Fe^{3+} ion (Morrish, 1965). Using this formula, we get $x_C = 0.83$ and 2.57% for samples J1, J2, respectively, which are in satisfactory agreement with the values of x_M quoted above, bearing in mind small measured signals, possible presence of trace amounts of other magnetic ions and uncertainty of fitting procedures. Thus, the average Fe^{3+} concentration in the jadeites studied is 0.8% in sample J1 and 2.5% in sample J2 which is indeed reflected by their color changing from white to green. These concentrations appear to be correlated to the Curie-Weiss temperatures (–3 and –7 K for sample J1 and J2, respectively), that can be written as $\theta = C_0 x$, with $C_0 \approx -300$ K, being comparable with values obtained for various DMS (Spalek *et al.*, 1986; Furdyna *et al.*, 1988).

The temperature dependence of the effective spin S_0, obtained from analysis of magnetization data, is shown in Fig. 4. As could be expected, S_0 increases with increasing temperature, because thermal disordering decreases the AFM coupling within the clusters, increasing thus their magnetic moment. S_0 reaches its free ion value $S = 5/2$ at about 20 and 100 K for sample J1 and J2, respectively, which follows from the difference in the Fe^{3+} ion concentration of both samples and is consistent with the susceptibility data from Fig. 1.

A small Fe^{3+} ion concentration x found in the studied jadeites allows one to assume that the majority of these ions are isolated ones, almost all the rest of ions forms the AFM coupled NN pairs which at $H = 0$ and at low temperatures do not contribute to the effective spin S_0 (Fatah *et al.*, 1994; Nicholas *et al.*, 1995), and contribution of triples and higher clusters may be neglected. In such a case, S_0 is determined by probability P_1 that a given magnetic ion has no NN. This probability is expressed as (Shapira *et al.*, 1984; Nicholas *et al.*, 1995)

$$P_1 = (1 - x)^n \qquad (5)$$

where n is the number of NN cation sites in the crystal lattice; then $S_0/S = P_1$, with S, the free ion spin. Analyzing the crystal structure of jadeite (Prewitt & Burnham, 1966) with
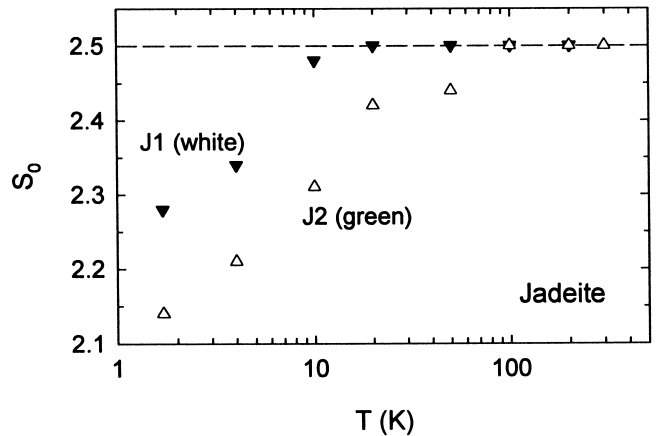

Fig. 4. Temperature dependence of the effective spin of Fe^{3+} ions for two jadeite samples J1 and J2 obtained from fits shown in Fig. 2 and 3, respectively.

a quasi-continuous spectrum of cation-cation distances, we have found 6 cation sites which are situated at the shortest- and close to each other distances (lying in the range 0.295 – 0.334 nm) from a chosen cation site (M1 or M2). Applying Eq. (5) with $n = 6$ to sample J1 ($x = 0.8\%$) and J2 (2.5%), one gets $S_0 = 2.38$ and 2.15, respectively, which is comparable with the values 2.28 and 2.14 (see Fig. 4) obtained from fitting of magnetization data at 1.7 K.

Conclusions

Studies of the magnetic properties of two jadeites of different colors from Burma have shown that these minerals behave like paramagnetic materials and their total magnetic susceptibility and magnetization is a sum of the positive temperature-dependent Brillouin-type contribution of dominant and interacting Fe^{3+} ions and negative temperature-independent diamagnetic contribution of the jadeite matrix. The analysis of the experimental data has allowed us to determine the diamagnetic susceptibility of jadeite $\chi_d = -3.8 \times 10^{-7}$ emu/g and the molar concentration of Fe^{3+} ions being equal to 0.8% in the white jadeite (sample J1) and 2.5% in the green jadeite (sample J2).

Summarizing, the present investigations of natural jadeites, together with our previous studies of natural kunzites (Bartkowska *et al.*, 2000), demonstrate the usefulness of careful magnetic measurements as an efficient and nondestructive method to characterize various minerals containing small amounts of magnetic ions.

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