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## Electronic and Magnetic Properties of the Rhodonite

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In this study, the electronic and magnetic properties of the mineral rhodonite ( $\text{MnSiO}_3$ ) are analysed, using both experimental and theoretical approaches. The investigation employs the experimental Faraday's method and theoretical DFT +  $U$  calculations. The inverse magnetic susceptibility  $\chi^{-1}(T)$  of rhodonite is found to follow the Curie–Weiss law. A distinct anomaly is observed in the  $\chi^{-1}(T)$  curve at 735 K, indicating a polymorphic phase transition from rhodonite to pyroxmangite, which is further confirmed by differential scanning calorimetry (DSC) analysis. The electron density of states is found to be asymmetric. Based on its electrical characteristics, rhodonite exhibits a wide band gap, indicating that it behaves as a dielectric mineral.

**Key words:** minerals, Faraday's method, magnetic susceptibility, Curie–Weiss law, magnetic moment, DFT +  $U$  calculations.

У даному дослідженні проведено комплексну аналізу електронних і магнетних властивостей мінералу родоніту ( $\text{MnSiO}_3$ ) із застосуванням як експериментальних, так і теоретичних методів. Експериментальна частина виконана методом Фарадея, а теоретичне моделювання — за допомогою розрахунків у рамках функціоналу густини із врахуванням кулонівської кореляції (DFT +  $U$ ). Обернена магнетна сприйнятливості  $\chi^{-1}(T)$  родоніту задовольняє закон Кюрі–Вайса. За 735 К у залежності  $\chi^{-1}(T)$  виявлено чітку аномалію, яку інтерпретують як поліморфний фазовий перехід від родоніту до пірохмангіту, що додатково підтверджено методом диферен-

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ційної сканувальної калориметрії (ДСК). Розподіл електронної густини станів виявився асиметричним. За своїми електричними характеристиками родоніт є широкозонним діелектриком.

**Ключові слова:** мінерали, метод Фарадея, магнетна сприйнятливість, закон Кюрі–Вайса, магнетний момент, DFT +  $U$ -обчислення.

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## 1. INTRODUCTION

Rhodonite, a manganese-rich mineral belonging to the pyroxenoid group, is characterized by a triclinic symmetry, similar to all other pyroxenoids. While the crystal lattice of rhodonite was initially studied in the conventional  $P1$  space group, a more comprehensive structural analysis by Ohashi and Finger [1] led to the adoption of the  $C1$  space group. This revised symmetry facilitates easier physical and chemical comparisons with pyroxenes and other pyroxenoids.

Rhodonite was first identified by Liebau and his research team [2], and four years later, its crystallographic data were refined and clarified by Peacor and Nisecki [3]. Although the mineral often contains several additional chemical elements, its ideal chemical formula is commonly represented as  $\text{MnSiO}_3$ . This stoichiometric composition was synthetically obtained by Ito [4]; however, a pure and well-ordered mineral of this kind has not been found in nature. Liebau *et al.* [2] proposed a more realistic formula,  $(\text{Mn,Ca})\text{SiO}_3$ , where Fe and Mg typically appear as minor substituents [5].

The heat capacity ( $C_p^0$ ) of rhodonite was measured by Richards and Huebner over the temperature range from 6 K to approximately 350 K, with no evidence of a  $\lambda$ -type anomaly (magnetic phase transition), indicating the mineral paramagnetic nature [6]. The unique magnetic behaviour of manganese-rich minerals, particularly, rhodonite, is of interest for both theoretical and practical research, potentially enabling various applications. The temperature dependence of magnetic susceptibility in minerals can be precisely studied using the Faraday's method, which allows for measurements over a wide temperature range [7, 8].

Density functional theory (DFT), a theoretical approach, whose computational results closely align with experimental observations, is increasingly utilized in the study of mineral properties. Investigating the electronic and magnetic characteristics of rhodonite, a manganese silicate mineral, through DFT calculations not only broadens the research scope, but also enhances the reliability of experimental findings. By employing DFT within the software packages such as Quantum ESPRESSO [9, 10], researchers can accurately model the electronic structure of rhodonite. This enables the elucidation of its band

structure and the density of states, which are critical for understanding its conductivity and other electronic properties. Reinforcing theoretical predictions with experimental validation significantly strengthens the credibility of the research.

## 2. METHODOLOGY

### 2.1. Experimental Details

The temperature dependence of the magnetic susceptibility,  $\chi(T)$ , of the rhodonite mineral was measured using the Faraday's method. The measurements were carried out in an inert helium atmosphere. The experimental values of the magnetic susceptibility at various temperatures were determined using the following expression:

$$\chi = \chi_r \frac{m_r (U_{h+s} - U_h)}{m_s (U_{h+r} - U_h)}. \quad (1)$$

In this context,  $U_{h+s}$  represents the compensating voltage measured for the combined sample and holder, while  $U_{h+r}$  corresponds to the compensating voltage for the standard reference and holder.  $U_h$  denotes the voltage drop of the empty holder (made of alumina,  $\text{Al}_2\text{O}_3$ ). The symbols  $m_r$  and  $m_s$  refer to the masses of the reference and the sample, respectively, and  $\chi_r$  indicates the magnetic susceptibility of the reference material. Mohr's salt was selected as the reference compound in the experiment.

The relative measurement uncertainty of the magnetic susceptibility in the setup does not exceed 3%.

### 2.2. Computational Details

For strongly correlated electron systems (particularly, those involving elements with occupied  $d$  and  $f$  orbitals such as Mn, Fe, Co, Ni and the lanthanides and actinides), the application of the extended density functional theory + Hubbard  $U$  (DFT +  $U$ ) method is considered appropriate. This approach accounts for the on-site Coulomb repulsion between localized electrons, thereby, producing results, which are more representative for the real physical behaviour of the material. The crystallographic data required for the DFT +  $U$  calculations were obtained based on the experimental results reported by Nelson and Griffen [5]. The DFT +  $U$  calculations were performed for the ferromagnetic (FM) phase, using the Quantum ESPRESSO package [11]. The Hubbard  $U$  parameters employed were as follow:  $U(\text{Mn}) = 4$  eV,  $U(\text{Si}) = 0$  eV, and  $U(\text{O}) = 0$  eV. Ultrasoft pseudopotentials were utilized

in all calculations.

### 3. RESULTS AND DISCUSSION

#### 3.1. Magnetic-Susceptibility Measurements

The temperature dependence of the magnetic susceptibility,  $\chi(T)$ , for the rhodonite ( $\text{MnSiO}_3$ ) mineral is illustrated in Fig. 1. As the temperature increases, the magnetic susceptibility decreases gradually. This behaviour is attributed to the enhanced thermal agitation, which leads to increasing disorder among the atomic magnetic moments. Figure 2 presents the inverse magnetic susceptibility ( $\chi^{-1}$ ) and the results of differential scanning calorimetry (DSC) analysis. In panel (a), the  $\chi^{-1}$  curve exhibits a linear increase with temperature, followed by a no-

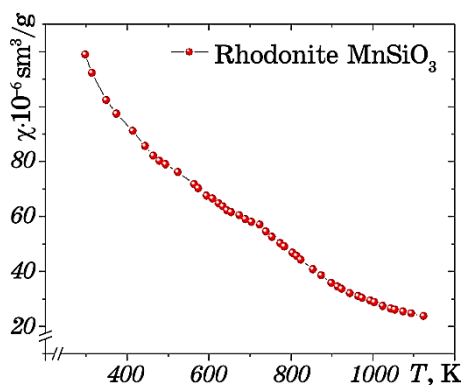


Fig. 1. The  $\chi(T)$  dependence graph for rhodonite.

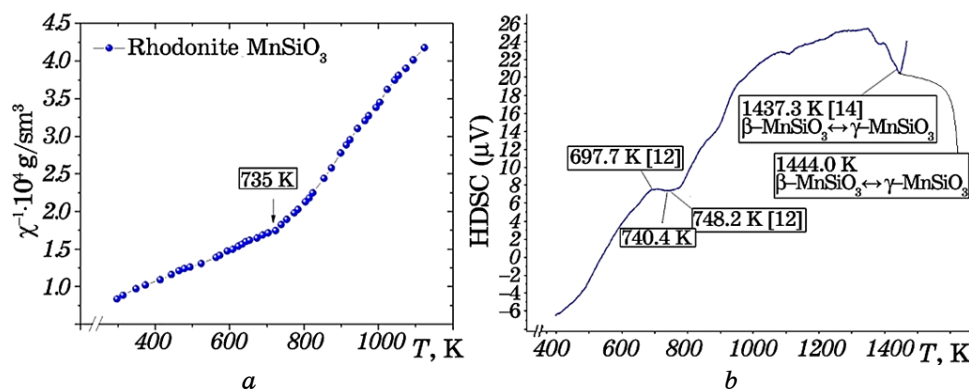


Fig. 2. The  $\chi^{-1}(T)$  dependence for rhodonite (a) and its DSC analysis (b).

ticeable inflection point at 735 K. This sharp change in magnetic susceptibility indicates the occurrence of a polymorphic phase transition. To verify the presence of this transition, DSC analysis was conducted and compared with findings from previous studies reported in the literature.

The temperature-dependent variation of the DSC signal shown in panel (b) was obtained using a STA PT1600 TG-DSC/DTA system. An endothermic effect was recorded at 740.4 K, indicating a thermal event. Similar anomalies in this temperature range were also reported by Maresch and Mottana [12], who identified the  $\alpha$ -rhodonite ( $\text{MnSiO}_3$ )  $\leftrightarrow$   $\beta$ -pyroxmangite ( $\text{MnSiO}_3$ ) polymorphic phase transition at closely related temperatures, specifically, at 697.7 K and 748.2 K, under different experimental conditions. This correspondence further supports the occurrence of a phase transition in the studied sample.

The  $\alpha$ -rhodonite ( $\text{MnSiO}_3$ )  $\rightarrow$   $\beta$ -pyroxmangite ( $\text{MnSiO}_3$ ) polymorphic phase transition is illustrated in Fig. 3. The observed endothermic effect within the 697.7–748.2 K range closely corresponds to the magnetic anomaly detected at 735 K, indicating a strong correlation between the magnetic transition ( $\chi^{-1}$ ) and the thermal response (DSC). At higher temperatures, a pronounced endothermic effect was observed at 1444.0 K, suggesting an additional significant thermal transformation.

This represents a second phase transition occurring at a temperature close to the  $\beta$ - $\text{MnSiO}_3 \leftrightarrow \gamma$ - $\text{MnSiO}_3$  transformation reported at 1437.3 K by Proidak *et al.* [14]. The transition temperature observed in our study (at 1444.0 K) shows excellent agreement with the findings of [14], with the minor discrepancy ( $\cong 7$  K) attributable to variations in experimental conditions such as scan rate, sample impurities, and instrument sensitivity.

As shown in Table 1, extrapolation of the linear region of the  $\chi^{-1}(T)$  dependence within the temperature range of 297–723 K yields a posi-

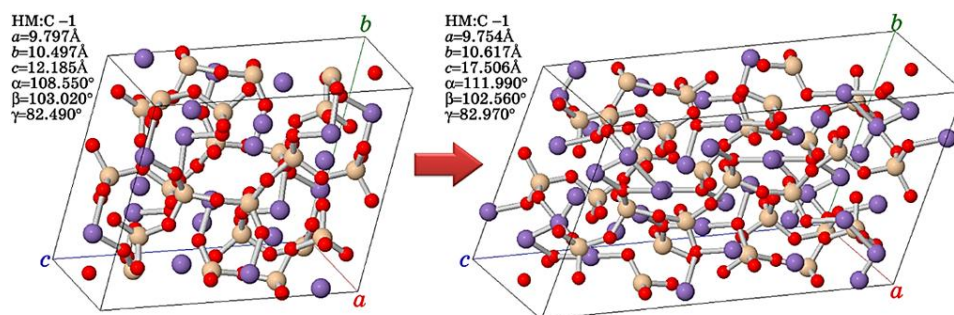


Fig. 3. Polymorphic phase transition from rhodonite ( $\text{MnSiO}_3$ ) to pyroxmangite ( $\text{MnSiO}_3$ ) [13].

**TABLE 1.** Calculation results.

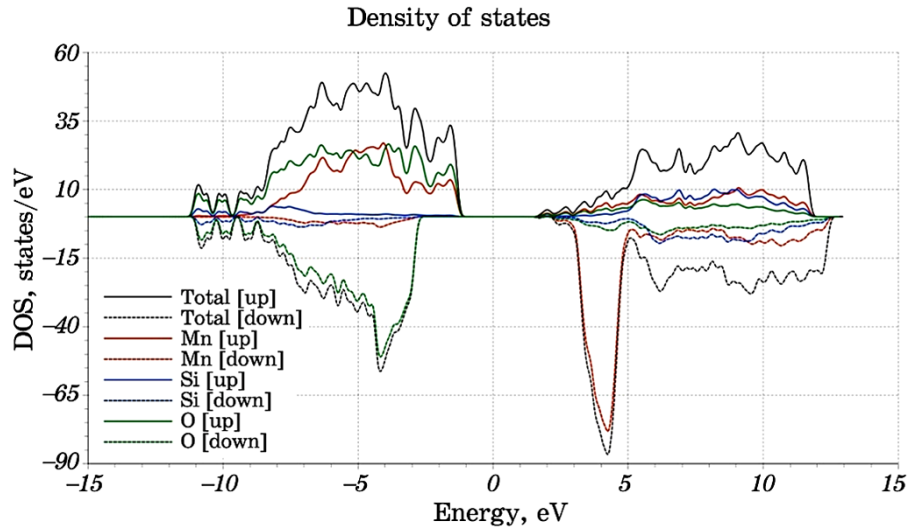
| Mineral               | Temperature interval, K | $\Theta$ | $C, 10^{-4} \text{ sm}^3 \cdot \text{g}^{-1} \cdot \text{K}$ | $\mu_{\text{eff}}, \mu_B$ | $\mu_{\text{eff}}, \mu_B$ |
|-----------------------|-------------------------|----------|--------------------------------------------------------------|---------------------------|---------------------------|
| rhodonite             | 297–723                 | 115      | 18                                                           | 4.53                      | 6.21                      |
| (MnSiO <sub>3</sub> ) | 738–1123                | 545      | 485                                                          | 2.68                      | 3.67                      |

tive Curie–Weiss temperature of  $\Theta = 115 \text{ K}$ , indicating the presence of ferromagnetic interactions between the magnetoactive atoms in the rhodonite crystal structure. At higher temperatures (738–1123 K),  $\Theta$  increases to 545 K. Concurrently, the effective magnetic moment ( $\mu_{\text{eff}}$ ) decreases from  $4.53\mu_B$  to  $2.68\mu_B$ , suggesting the influence of thermal effects and a possible phase transition within the crystal lattice.

### 3.2. DFT + $U$ Calculation

The DFT +  $U$  calculations based on the MnSiO<sub>3</sub> crystal structure of pure rhodonite (free of inclusions) were carried out for the ferromagnetic (FM) phase, using the Quantum ESPRESSO software package.

Figure 4 presents the calculated density of states (DOS), in which the asymmetrical distribution of the spin-up and spin-down states indicates spin polarization within the system. In particular, a pronounced difference is observed between the spin-up and spin-down densities of states for manganese and oxygen near the Fermi energy, indicating the presence of magnetic moments associated with the rho-

**Fig. 4.** Total and partial electron density of states of the rhodonite mineral.

donite atoms. Regarding the electronic properties, a significant band gap appears around the Fermi level, confirming the dielectric nature of rhodonite. As well known, DFT +  $U$  calculations tend to underestimate the band-gap energy ( $E_g$ ); therefore, to obtain values in closer agreement with experimental data, the HSE06 (Heyd–Scuseria–Ernzerhof 2006 hybrid functional) method is recommended.

Table 2 presents the magnetic moments (in Bohr magnetons,  $\mu_B$ ) of Mn, Si, and O atoms as calculated using the DFT +  $U$  method. The magnetic moments of all manganese (Mn) atoms range from  $4.0628\mu_B$  to  $4.0633\mu_B$ , indicating their dominant role in the magnetic behaviour of the system. In contrast, silicon (Si) atoms exhibit very small magnetic moments, between  $0.0043\mu_B$  and  $0.0050\mu_B$ , suggesting that they do not

**TABLE 2.** DFT +  $U$  calculated results.

| No. | Atom | Bohr<br>magne-<br>ton ( $\mu_B$ ) | No. | Atom | Bohr<br>magne-<br>ton ( $\mu_B$ ) | No. | Atom | Bohr<br>magne-<br>ton ( $\mu_B$ ) | No. | Atom | Bohr<br>magne-<br>ton ( $\mu_B$ ) |
|-----|------|-----------------------------------|-----|------|-----------------------------------|-----|------|-----------------------------------|-----|------|-----------------------------------|
| 1   | Mn   | 4.0628                            | 26  | Si   | 0.0045                            | 51  | O    | 0.0354                            | 76  | O    | 0.0233                            |
| 2   | Mn   | 4.0628                            | 27  | Si   | 0.0045                            | 52  | O    | 0.0354                            | 77  | O    | 0.0267                            |
| 3   | Mn   | 4.0628                            | 28  | Si   | 0.0045                            | 53  | O    | 0.0418                            | 78  | O    | 0.0267                            |
| 4   | Mn   | 4.0628                            | 29  | Si   | 0.0043                            | 54  | O    | 0.0418                            | 79  | O    | 0.0267                            |
| 5   | Mn   | 4.0633                            | 30  | Si   | 0.0043                            | 55  | O    | 0.0418                            | 80  | O    | 0.0267                            |
| 6   | Mn   | 4.0633                            | 31  | Si   | 0.0043                            | 56  | O    | 0.0418                            | 81  | O    | 0.0127                            |
| 7   | Mn   | 4.0633                            | 32  | Si   | 0.0043                            | 57  | O    | 0.0331                            | 82  | O    | 0.0127                            |
| 8   | Mn   | 4.0633                            | 33  | Si   | 0.0050                            | 58  | O    | 0.0331                            | 83  | O    | 0.0127                            |
| 9   | Mn   | 4.0599                            | 34  | Si   | 0.0050                            | 59  | O    | 0.0331                            | 84  | O    | 0.0127                            |
| 10  | Mn   | 4.0599                            | 35  | Si   | 0.0050                            | 60  | O    | 0.0331                            | 85  | O    | 0.0123                            |
| 11  | Mn   | 4.0599                            | 36  | Si   | 0.0050                            | 61  | O    | 0.0427                            | 86  | O    | 0.0123                            |
| 12  | Mn   | 4.0599                            | 37  | Si   | 0.0045                            | 62  | O    | 0.0427                            | 87  | O    | 0.0123                            |
| 13  | Mn   | 4.0299                            | 38  | Si   | 0.0045                            | 63  | O    | 0.0427                            | 88  | O    | 0.0123                            |
| 14  | Mn   | 4.0299                            | 39  | Si   | 0.0045                            | 64  | O    | 0.0427                            | 89  | O    | 0.0101                            |
| 15  | Mn   | 4.0299                            | 40  | Si   | 0.0045                            | 65  | O    | 0.0362                            | 90  | O    | 0.0101                            |
| 16  | Mn   | 4.0299                            | 41  | O    | 0.0454                            | 66  | O    | 0.0362                            | 91  | O    | 0.0101                            |
| 17  | Mn   | 4.0864                            | 42  | O    | 0.0454                            | 67  | O    | 0.0362                            | 92  | O    | 0.0101                            |
| 18  | Mn   | 4.0864                            | 43  | O    | 0.0454                            | 68  | O    | 0.0362                            | 93  | O    | 0.0127                            |
| 19  | Mn   | 4.0864                            | 44  | O    | 0.0454                            | 69  | O    | 0.0303                            | 94  | O    | 0.0127                            |
| 20  | Mn   | 4.0864                            | 45  | O    | 0.0378                            | 70  | O    | 0.0303                            | 95  | O    | 0.0127                            |
| 21  | Si   | 0.0053                            | 46  | O    | 0.0378                            | 71  | O    | 0.0303                            | 96  | O    | 0.0127                            |
| 22  | Si   | 0.0053                            | 47  | O    | 0.0378                            | 72  | O    | 0.0303                            | 97  | O    | 0.0168                            |
| 23  | Si   | 0.0053                            | 48  | O    | 0.0378                            | 73  | O    | 0.0233                            | 98  | O    | 0.0168                            |
| 24  | Si   | 0.0053                            | 49  | O    | 0.0354                            | 74  | O    | 0.0233                            | 99  | O    | 0.0168                            |
| 25  | Si   | 0.0045                            | 50  | O    | 0.0354                            | 75  | O    | 0.0233                            | 100 | O    | 0.0168                            |

significantly contribute to the magnetization and primarily participate in chemical bonding within the crystal lattice. Oxygen (O) atoms develop minor magnetic moments ranging from  $0.0127\mu_B$  to  $0.0418\mu_B$ . These results confirm that Mn atoms are the principal contributors to magnetism in the rhodonite mineral.

### 3.3. ELF Analysis

The electron localization function (ELF) map is a visual tool that illustrates the spatial localization of electrons and plays a crucial role in identifying interatomic electron densities and the nature of chemical bonding [15, 16]. It also reflects the electrical-conductivity characteristics within the molecular or crystal structures. Figure 5 shows the ELF map of the rhodonite ( $\text{MnSiO}_3$ ) mineral. A strong ionic character is observed between  $\text{MnI}^+$  and  $\text{OI}^-$  ions, although the valence electrons of oxygen also indicate partial covalence. Electrons are clearly local-

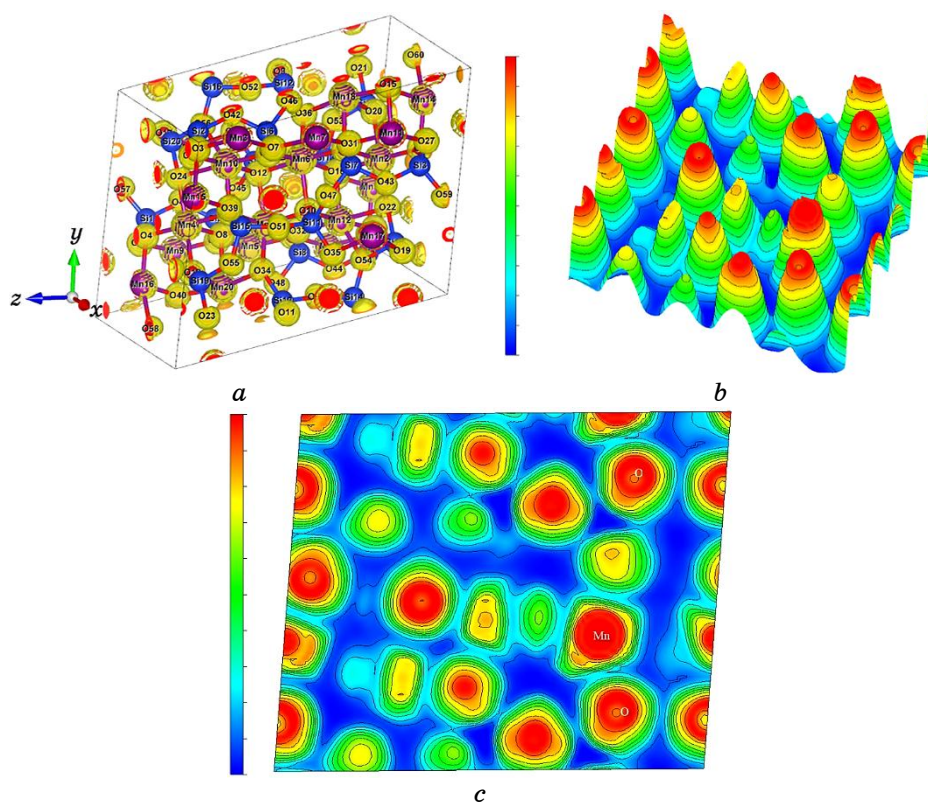


**Fig. 5.** ELF map of the rhodonite mineral, including 3D views (a), (b), and a 2D projection (c).

ized around Mn–O bonds, leading to the formation of electric dipoles, when an external electric field is applied. Such local dipole formations give rise to dielectric behaviour. The Si–O bonds exhibit polar and strongly covalent characteristics, with electron density skewed toward the oxygen atoms.

#### 4. CONCLUSION

Based on the combined experimental and theoretical (DFT +  $U$ ) investigations of the rhodonite mineral, the following conclusions were drawn. The  $\chi^{-1}(T)$  curve exhibits linear behaviour, confirming that rhodonite follows the Curie–Weiss law. A kink in the  $\chi^{-1}(T)$  plot at approximately 735 K corresponds to a polymorphic phase transition from rhodonite to pyroxmangite, consistent with the findings reported in Ref. [12]. At higher temperatures, the DSC analysis reveals a phase transition ( $\beta$ -MnSiO<sub>3</sub>  $\leftrightarrow$   $\gamma$ -MnSiO<sub>3</sub>) at 1444.0 K that agrees with the results in Ref. [14]. From the perspective of electronic properties, the presence of a wide band gap near the Fermi level indicates that rhodonite is a dielectric mineral. Magnetic-moment calculations for Mn, Si, and O atoms confirm that Mn atoms are the primary contributors to the magnetic behaviour of the mineral. The ELF (electron localization function) map further supports the dielectric nature of rhodonite, revealing localized electron regions consistent with strong Mn–O bonding. Although the heat capacity ( $C_p^0$ ) of rhodonite has been experimentally measured by Richard and Huebner over the temperature range from 6 K to  $\approx$  350 K, no  $\lambda$ -type peak indicative of a magnetic phase transition was observed [6], supporting the interpretation that rhodonite exhibits paramagnetic behaviour. However, to classify definitively rhodonite as an ideal paramagnet, additional experimental measurements below 6 K are required.

#### AUTHORS' CONTRIBUTIONS

O. K. Kuvandikov conceived the research idea and supervised the study. Z. M. Shodiev contributed to the interpretation of the results and manuscript editing. J. Sh. Akhtamov performed the theoretical calculations, conducted the experiments, analysed the results, and wrote the manuscript with input from all authors. All authors have read and approved the final version of the manuscript.

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