Influence of O₂ molecular orientation on *p*-orbital ordering and exchange pathways in Cs₄O₆

D. Arčon,^{1,2,*} K. Anderle,¹ M. Klanjšek,^{1,3} A. Sans,⁴ C. Mühle,⁵ P. Adler,⁴ W. Schnelle,⁴ M. Jansen,^{4,5} and C. Felser⁴

¹Jožef Stefan Institute, Jamova c. 39, 1000 Ljubljana, Slovenia

²Faculty of Mathematics and Physics, University of Ljubljana, Jadranska c. 19, 1000 Ljubljana, Slovenia

³EN-FIST Centre of Excellence, Dunajska 156, 1000 Ljubljana, Slovenia

⁴Max-Planck-Institut für Chemische Physik fester Stoffe, 01187 Dresden, Germany

⁵Max-Planck-Institut für Festkörperforschung, 70569 Stuttgart, Germany

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The coupling of charge, lattice, orbital, and spin degrees of freedom was studied in a *p*-electron mixedvalence Cs_4O_6 compound by the electron paramagnetic resonance (EPR) and ¹³³Cs nuclear magnetic resonance (NMR). The dramatic differences in the evolution of the EPR and ¹³³Cs NMR spectra measured under different cooling protocols reveal two competing low-temperature phases: quenched high-temperature cubic and the low-temperature low-symmetry phases, respectively. They differ in the orientation of O_2^- anion axes, the ordering of π^* molecular orbitals, and the superexchange interactions through the Cs⁺ bridges. The transformation between the two phases involves large amplitude reorientations of O_2 groups and is extremely sluggish, thus explaining the coexistence of both phases and the deviations of the magnetic susceptibility from the simple Curie-Weiss dependence at low temperatures.

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I. INTRODUCTION

In transition metal oxides, the coupling of d-electron orbital degrees of freedom to the charge, spin, or lattice can lead to some highly intriguing phenomena, including reduced spin dimensionality or exotic spin ground states, nanoscopic phase segregation of competing phases, or colossal magnetoresistance.¹ Alkali metal superoxides AO_2 (A = Na, K, Rb, and Cs), one of the very few representatives that show low-temperature p-electron magnetism,^{2–5} were recently revisited in connection with the possible ordering of O_2^- antibonding π^* molecular orbitals.⁶⁻¹³ Orbital ordering was indeed experimentally observed in CsO₂, where it is responsible for the quasi-one-dimensional antiferromagnetic superexchange interactions between the O_2^- moments bridged by the Cs⁺ ions.⁶ The interplay between the orbital ordering and the *p*-electron magnetism in RbO_2 has been discussed in terms of the effective Kugel-Khomskii Hamiltonian¹⁴ in the limit of small spin-orbit coupling,⁹ while the sister compound KO₂ has been approached from the strong spin-orbit coupling limit.12,13

In mixed-valence compounds, charge degrees of freedom are an important additional parameter. For instance, ion vacancies in off-stoichiometric RbO_{1.72} facilitate a Jahn-Teller driven order-disorder transition of O_2^- anions resulting in a ferromagnetic glasslike state at low temperatures.¹⁵ On the other hand, sesquioxides A_4O_6 (Refs. 16–19) possess no such structural disorder while keeping mixed valences of closed shell peroxide O_2^{2-} and open shell hyperoxide O_2^{-} anions. The low temperature crystal structure of Rb₄O₆ has been studied by elastic and inelastic neutron scattering.¹⁹ Surprisingly, the structure remains cubic (space group $I\overline{4}3d$, inset to Fig. 1) at all temperatures with all the oxygen atoms being equivalent and forming O_2 units aligned along the cubic axes but with large atomic displacement factors perpendicular to the O-O bonds. The oxygen-oxygen distance in these O₂ units is in between those characteristic for peroxide and hyperoxide anions. On the other hand, the local density approximation (LDA + U)

calculations starting from the cubic Rb₄O₆ structure suggest a charge ordering of diamagnetic O_2^{2-} and paramagnetic O_2^- with a concomitant structural symmetry lowering.¹⁷ The apparent discrepancy between the experiment and theory can be explained either by static disorder of O_2^- and O_2^{2-} units or by valence fluctuations that globally restore the cubic symmetry.¹⁹ The latter seems to be a less likely possibility due to the large distances between anions (3.69 Å). On the other hand, the low-temperature static disorder is influenced by the anion dynamics at high temperatures and may be changed by the choice of a suitable cooling rate through the critical temperatures. The large anisotropic displacement factors even indicate that the axes of O_2 anions may at low temperatures tilt away from their cubic phase orientations. The rotation of anions breaks the degeneracy of antibonding π^* molecular orbitals and that typically leads to their orbital ordering.⁶ Moreover, since magnetic exchange interactions sensitively depend on molecular geometry, the rotation of anion axes should affect the magnetism too.

At present experimentally nothing is known about the orbital ordering and how such (dis)order couples to the structural and magnetic properties in these mixed-valence compounds. Here we report on a study of Cs₄O₆, which is isostructural to cubic Rb₄O₆ at room temperature and shows a similar lowtemperature magnetization dynamics.¹⁸ We employed the electron paramagnetic resonance (EPR), a very sensitive technique for the investigation of the $O_2^- \pi^*$ molecular orbitals,^{20,21} and ¹³³Cs nuclear magnetic resonance (NMR) being a powerful local probe of structural and electronic properties.²²⁻²⁴ We discovered a transition to a low-temperature low-symmetry orbitally ordered structure, which is avoided by rapid cooling that freezes-in the high-temperature orbitally disordered cubic phase. In this process, the orientational ordering of O₂ units is coupled to the orbital ordering that controls the superexchange interactions through the Cs⁺ bridges and therefore also the low-temperature magnetic properties of the two competing phases.



FIG. 1. (Color online) Temperature dependence of the inverse molar magnetic susceptibilities χ_m^{-1} of Cs₄O₆ powder measured on cooling (thin blue line) and on warming after rapidly cooling the sample (thick red line) in the field of 1 T. Insets: (bottom) the temperature dependence of the product $\chi_m T$ with arrows indicating the observed anomalies; (top) the crystal structure of cubic sesquioxides A_4O_6 , space group $I\bar{4}3d$ suggested in Ref. 19 from low-temperature neutron diffraction data on Rb₄O₆. Large gray and smaller red spheres represent Cs and O atoms, respectively.

II. EXPERIMENTAL METHODS

A. Sample preparation and characterization

The Cs_4O_6 powder was synthesized according to Ref. 18. All sample handlings were strictly carried out under inert conditions in the glovebox with O_2 and H_2O concentrations lower than 1 ppm because of the high sensitivity of reactants and products against air and moisture. Cesium was distilled twice before use in order to remove traces of peroxide or superoxide. Oxygen gas was carefully dried and the amount required for the synthesis of stoichiometric cesium oxide (Cs₂O) was controlled volumetrically with a dosimeter. For the formation of cesium superoxide (CsO_2) dried oxygen was supplied in excess. Both precursors were annealed at 473 K for two weeks in argon filled ampules under atmospheric pressure and subsequently ground five times. Cs₄O₆ was obtained by solid-state reaction of a mixture of CsO2 and Cs2O in a molecular ratio of 4 : 1 in a sealed glass tube containing argon atmosphere. The mixture was finally annealed for 24 h at 453 K.

To characterize the sample, Cs_4O_6 powder was placed in a sealed capillary filled with argon and inspected by x-ray diffraction using a Stoe & Cie PSD powder diffractometer with Mo $K_{\alpha 1}$ radiation. The lattice parameter a = 9.847(3) Å for the cubic structure with the space group $I\overline{4}3d$ was derived from a LeBail fit and matches the published data.¹⁸

B. Magnetic susceptibility measurements

The temperature dependence of the magnetization of the Cs_4O_6 powder sealed under helium in a Suprasil quartz tube was measured with a superconducting quantum interference device magnetometer (MPMS XL-7, Quantum Design) between 1.8 and 350 K in a magnetic field of 1 T. First, the

sample was cooled as rapidly as possible in zero magnetic field down to 1.8 K (within 15 min down to 100 K; within about 10 min down to 5 K). Data were collected during warming to 350 K with a rate of 2 K/min [zero-field-cooled (ZFC) up]. In a subsequent run, the sample was cooled under the same conditions in the magnetic field and the data were collected subsequently during warming (FC up). Finally, the data were collected during cooling in the selected magnetic field (FC down). For deriving the magnetic moment we corrected the data for a diamagnetic contribution of -168×10^{-6} emu/mol estimated from Pascal increments.

C. Electron paramagnetic resonance

For the temperature-dependent (4–320 K) X-band (9.6 GHz) continuous wave (cw) electron paramagnetic resonance (EPR) experiments, the powder sample (32 mg) was sealed under dynamic vacuum in a 4 mm diameter silica tube (Wilmad Lab Glass). The EPR spectrometer was equipped with a Varian E-101 microwave bridge, a Varian rectangular TE102 resonance cavity, and an Oxford Cryogenics continuous-flow helium cryostat. The temperature stability was better than ± 0.1 K over the entire temperature range. The EPR signal intensity was determined from the spectral fitting to a Lorentzian line shape and was calibrated at 120 K with the CuSO₄ · 5H₂O standard.

In slow-cooling experiments, the cooling time from 320 K to 180 K was approximately 24 h. From 180 to 4 K, the experiment took additional 10 h. EPR spectra were taken continuously during the cooling. In a rapid cooling experiment, the sample was directly immersed from 320 K into the liquid nitrogen, then transferred to the pre-cooled cryostat at 50 K and finally cooled to 4 K. The measurements were then performed on warming.

D. Nuclear magnetic resonance

¹³³Cs nuclear magnetic resonance (NMR) experiments on Cs₄O₆ powder were carried out in a superconducting 4.7 T magnet. The ¹³³Cs Larmor frequency as determined from a CsNO₃ standard is $v_L = 26.2345$ MHz. The ¹³³Cs NMR spectra were measured by solid-echo technique with $\pi/2$ pulse length of 3 μ s and interpulse delay of 40 μ s. At low temperatures the ¹³³Cs NMR spectra span over the frequency range of several MHz and were thus collected by changing the irradiation frequency in 40 kHz steps and glueing the contributions together. The transverse nuclear relaxation time T_2 was measured using a standard two-pulse sequence $\beta - \tau - \beta - \tau$ -echo, with pulse length $\tau_{\beta} = 3 \mu s$ and variable delay τ ranging from 10 μ s in steps of 2 μ s to the point of vanishing signal. The signal intensity as a function of the evolution time $t = 2\tau$ was fitted with an exponential function $\exp[-t/T_2]$, to obtain T_2 . Before the sample was cooled down using helium gas, either in a slow or in a rapid manner, the temperature was first raised to 320 K to delete any possible thermal history of the sample (like in EPR and magnetization measurements described above). In a slow-cooling experiment, the temperature was stabilized at each selected temperature, then the NMR spectrum as well as the T_2 measurement were taken, together lasting 2 h. In a rapid-cooling experiment, the sample was first rapidly cooled down to 10 K, which we were typically able to achieve in 30 min. After that the NMR spectra and T_2 measurements were taken upon warming, stabilizing the temperature at each selected value, where the measurement typically lasted 2 h.

III. RESULTS AND DISCUSSION

The temperature dependent molar magnetic susceptibility of Cs₄O₆ powder, $\chi_m(T)$, confirms the absence of long-range magnetic order, but suggests magnetic correlations in the low-temperature range, similarly as for related Rb₄O₆.^{17,18} In the temperature range 350 to 200 K the inverse magnetic susceptibility χ_m^{-1} obtained on slow cooling (Fig. 1) follows a Curie-Weiss behavior, $\chi_m(T) = 2C/(T - \Theta)$. Here the Curie constant is $C = g^2 \mu_B^2 S(S+1)/3k_B$ with S = 1/2 and the g factor corresponding to O_2^- and μ_B is the Bohr magneton. The factor of 2 accounts for two paramagnetic O_2^- units per formula unit Cs_4O_6 . Fitting of the magnetic susceptibility in this temperature range yields for the effective magnetic moment $\mu_{\text{eff}} = g\mu_B \sqrt{S(S+1)} = 2.05\mu_B$ per O₂⁻ ion and a Curie-Weiss temperature $\Theta = -36$ K. The μ_{eff} value is in good agreement with $\mu_{\rm eff} = 2.01 \mu_B$ reported earlier,¹⁸ while the Θ value ($\Theta = -5$ K in Ref. 18) appears to depend on the sample and the measurement conditions. The fact that μ_{eff} is somewhat larger than the spin-only value of $1.73\mu_B$ suggests the importance of orbital contributions to μ_{eff} .

Below 200 K χ_m^{-1} deviates from the linearity. Even more pronounced anomalies in χ_m^{-1} —particularly apparent in the temperature dependence of the product $\chi_m T$ (inset to Fig. 1) were observed between 200 and 250 K and at 320 K, when the measurements were taken on warming after rapidly cooling the sample. In alkali metal superoxides a strong link between the magnetism, the structural anomalies, and the orbital ordering has been established recently.^{6–13} We note at this point that due to the particular orbital order superexchange interactions mediated through the Cs⁺ bridges—and thus also Θ —may change. Moreover, in such cases the splitting of the electronic levels of O₂⁻ should change too, and this is very sensitively picked up by the electronic g factor. Therefore, the observed anomalies attributed here to changes either in g or in Θ may probe a degree of O₂⁻ orbital order that is strongly thermalhistory dependent.

The electronic g factor is directly measured in EPR experiments. The X-band EPR spectrum of Cs₄O₆ powder is at 320 K composed of a weak narrow line around g = 2and a very broad component that spans as a background signal over the entire experimentally accessible field range. The narrow line is fitted to an axially symmetric g tensor with $g_{\perp} = 2.130(5)$ and $g_{\parallel} = 2.050(5)$, while its intensity is equivalent to the spin susceptibility of $\sim 4 \times 10^{-6}$ emu/mol. Such small spin susceptibility of the narrow component corresponds to $\sim 0.3\%$ of the intensity coming from the O₂ units-it is thus attributed to some unidentified paramagnetic impurity. On cooling the broad component remains extremely broad so that it is, for instance at 220 K [Fig. 2(a)], still impossible to analyze it. However, below 215 K it dramatically narrows to a clearly resolved line with a Lorentzian line shape and a full width at half maximum (FWHM) of 407 mT at 120 K [Fig. 2(a)]. Although it is difficult to precisely



FIG. 2. (Color online) X-band EPR spectra of Cs_4O_6 powder measured on cooling (blue) at 220 K (dashed line) and 120 K (solid line). For comparison we show the spectrum measured on warming at 120 K (red solid line) after rapidly cooling the sample from 320 to 4 K (a). Temperature dependence of the EPR broad component *g* factor (b), EPR signal intensity (c), and full width at half maximum of EPR spectra (d). The experimental data-set acquired during the slow cooling is represented by solid blue circles, while data taken on warming after rapid cooling is shown by solid red squares. In the inset to (c) we show the temperature dependence of the EPR signal intensity multiplied by temperature. The solid line in (d) is a fit to the thermally activated temperature dependence with $\Delta E = 0.13$ eV.

determine the EPR intensity of such broad signals, an estimate of $\chi_{\text{EPR}} \approx 5 \times 10^{-3}$ emu/mol at T = 120 K confirms that the broad component is an intrinsic O₂⁻ signal of Cs₄O₆.

The explicit formulas for the g factors of O_2^- centers,

$$g_{zz} = g_e + 2\sqrt{\frac{\lambda^2}{\lambda^2 + \Delta^2}}l,$$

$$g_{yy} = g_e \sqrt{\frac{\Delta^2}{\lambda^2 + \Delta^2}} - \frac{\lambda}{E} \left[1 - \sqrt{\frac{\lambda^2}{\lambda^2 + \Delta^2}} - \sqrt{\frac{\Delta^2}{\lambda^2 + \Delta^2}}\right],$$

$$g_{xx} = g_e \sqrt{\frac{\Delta^2}{\lambda^2 + \Delta^2}} - \frac{\lambda}{E} \left[1 + \sqrt{\frac{\lambda^2}{\lambda^2 + \Delta^2}} - \sqrt{\frac{\Delta^2}{\lambda^2 + \Delta^2}}\right],$$
(1)

were first derived in Ref. 20. Here $g_e = 2.0023$ is the free electron value, $l \approx 1$ a correction to the angular momentum, and $\lambda = 226 \text{ cm}^{-1}$ an effective spin-orbit splitting. *E*, which is the separation between the $O_2^- \sigma$ and π^* levels, is much larger than the splitting of π^* orbitals described by Δ . For the free O_2^- anion a double degeneracy of the π^* states, i.e., $\Delta = 0$, gives the eigenvalues of the g tensor $g_{xx} = g_{yy} = g_{\perp} = 0$ and $g_{zz} = g_{||} \approx 4$ [thus $g = \frac{1}{3}(2g_{\perp} + g_{||}) = 4/3$], rendering the powder EPR signal practically immeasurable.^{25,26} This limit explains the extreme broadness of the experimental EPR signal at high temperatures where large amplitude librations of $O_2^$ units average out Δ in the cubic phase. However, as soon as O_2^- librations freeze out on cooling on the EPR time scale, the π^* orbital degeneracy is removed, *i.e.*, $\Delta \neq 0$, and the g-factor values for $\Delta \gg \lambda$ approach g_e .²⁰ The emergence of the EPR signal with $g \leq 1.984(8)$ therefore clearly speaks



FIG. 3. (Color online) ¹³³Cs NMR spectra of the Cs₄O₆ powder (blue) taken upon slow cooling at 320 K (upper panel) and 200 K (lower panel). The spectrum at 320 K is perfectly reproduced by a Lorentzian line shape (green). The spectrum at 200 K exhibits a slight asymmetry, but apart from that, it is better reproduced by a Gaussian line shape (green) as evident on the high-frequency side of the spectrum. The vertical black line indicates the position of the Larmor frequency v_L .

for the symmetry lowering of the crystal structure below 215 K associated with the freezing-out of O_2^- . To quantitatively account for g = 1.984(8) with Eqs. (1), a splitting between π_x^* and π_y^* of less than 10 meV is required thus suggesting that the orbital moment may not be completely quenched even in the low-symmetry structure in striking contrast to AO_2 compounds.^{9,20} The transition shows a large thermal hysteresis as the broad Lorentzian component disappears again on warming at 250 K. The thermal hysteresis of the transition to the low-symmetry phases is best observed in the temperature dependence of the product $\chi_{EPR}T$ [inset to Fig. 2(c)].

The ¹³³Cs NMR line at 320 K is shifted by $\delta = 86$ ppm from the Larmor frequency ν_L and exhibits a perfect Lorentzian line shape (Fig. 3) with a FWHM of $\Delta \nu = 25.1$ kHz indicating that the quadrupole interaction is negligible. On slow cooling from 320 K the ¹³³Cs NMR signal almost completely disappears below ~280 K (Fig. 4), but then reemerges again below ~220 K. Although the ¹³³Cs NMR peak is still found close to ν_L for $T \leq 220$ K, it has broadened to $\Delta \nu = 76.6$ kHz at 200 K and changed to the Gaussian line shape (Fig. 3). Moreover, the transverse ¹³³Cs relaxation rate, $1/T_2$, which is very sensitive to the low-frequency dynamics, clearly diverges below room temperature [Fig. 5(a)]. In particular, T_2 becomes extremely short between 280 and 220 K, with $T_2 \ll 10 \ \mu s$, resulting in the strong suppression of the ¹³³Cs NMR signal intensity, i.e., the wipeout effect.

The maximum in $1/T_2$ reflects a strong thermally activated transverse spin fluctuation mechanism with a correlation time τ_c becoming very long on the NMR time scale below $\sim 200 \text{ K.}^{22}$ The ¹³³Cs NMR line shape evolution from the



FIG. 4. (Color online) Temperature dependence of 133 Cs NMR spectra of Cs₄O₆ powder measured on slow cooling (blue) and on warming after rapid cooling from 320 to 4 K (red). The shaded gray area under the spectrum at 10 K represents the contribution of the frozen-in cubic phase that is fitted with the rectangularlike spectral line shape (solid green line). It is obtained after subtracting the contribution of the low-symmetry phase amounting to 40% of the total spectral intensity. The weak narrow line around the Larmor frequency apparent only at low temperatures is due to an unidentified impurity.

Lorentzian (typical for solids with rapid dynamics) to the Gaussian (i.e., frozen dynamics) fully supports this conclusion. We thus model the temperature dependence of $1/T_2$ with the ansatz $1/T_2 \propto \delta h(0)^2 \tau_c / [1 + (\omega_L \tau_c)^2]$, where $\delta h(0)$ is the magnitude of the fluctuating local field and $\omega_L = 2\pi v_L$.²² Assuming $\tau_c = \tau_0 \exp(E_a/k_BT)$ the fit [Fig. 5(a)] gives the attempt frequency $\tau_0^{-1} \sim 2 \times 10^{14} \text{ s}^{-1}$ (precise value is difficult to obtain since the maximum in $1/T_2$ is not reachable) and the activation energy $E_a = 200(40)$ meV. The obtained E_a is larger than the libration frequency of O_2^- units in NaO₂, for instance.²⁷ The increase in E_a is a manifestation of the larger size of Cs⁺ ions, which limit the rotational freedom of O₂ and force them to freeze out already at 215 K, i.e., at much higher temperature than in NaO₂.

As O₂ librations freeze out on slow cooling through the structural phase transition, the degree of orientational ordering of O_2^- anions and the accompanying suppression of orbital fluctuations is monitored by the ¹³³Cs hyperfine shift, which is found to be positive but extremely small [Fig. 5(b)]. Namely, the O₂⁻ orientational and orbital ordering are closely related as the lobes of π_x^* and π_y^* molecular orbitals point perpendicularly to the O–O bond. In the high-temperature cubic phase, O₂ units on average orient along the unit cell axes.¹⁷ However, in the low-symmetry phase, the smallness of the ¹³³Cs hyperfine shift reflects the reduced π^* electronic overlap with Cs⁺, which likely signals the tilting of the O_2^- anions away from the unit cell axes, a direct manifestation of the Jahn-Teller effect.^{9,28} The fact that the π^* molecular orbitals avoid Cs⁺ in the lowsymmetry phase also implies that the superexchange pathway between O_2^- via Cs^+ may be broken.

A particular orbital ordering defines the magnetic response, so we turn now to the low-temperature data. On cooling, χ_{EPR} increases with decreasing temperature approximately



FIG. 5. (Color online) Temperature dependence of the ¹³³Cs transverse relaxation rate $1/T_2$ (a), the shift (b), and the width of the line (c). The solid blue circles stand for the data taken on slow cooling, while the solid red squares stand for the data taken on warming after rapid cooling procedure. Insets to (b) and (c) show the zooms to the high-temperature dependences where a transition at 150 K is recognized. The light-blue shaded area indicates the ¹³³Cs NMR wipeout temperature interval.

following the Curie-Weiss law [Fig. 2(c)], similarly as χ_m (Fig. 1). The temperature dependence of the *g* factor, which even reduces to g = 1.883(6) at 30 K [Fig. 2(b)], is consistent with the weakly temperature dependent $\chi_{EPR}T$ [inset to Fig. 2(c)] and nonlinear $\chi_m^{-1}(T)$ (Fig. 1). Changes in all EPR parameters below ~30 K—most notably in the *g* factor, which sharply increases on cooling—are reminiscent of the short-range order effects developing either due to low-dimensional effects or partly frustrated exchange interactions.²⁹

Although the isotropic part of the ¹³³Cs hyperfine interaction is very small, as argued above, the 1/T dependence of the ¹³³Cs NMR linewidth [Fig. 5(c)] speaks for the electron-nuclear mechanism of the NMR line broadening. The ¹³³Cs NMR linewidth is related to the second moment of the electron-nuclear interactions $\Delta v = \sqrt{M_2}$, which can be in the case of electron-nuclear dipolar interactions calculated from $M_2 = \frac{1}{3} \frac{\mu_0}{4\pi} \gamma_I^2 \gamma_S^2 h^2 S(S+1) \langle \frac{(1-3\cos^2 \theta_{ij})^2}{r_{ij}^6} \rangle$. Here S = 1/2for the electron spin of O_2^- and γ_I and γ_S are the ¹³³Cs and electron giromagnetic ratios, respectively. We performed the powder averaging $\langle \cdots \rangle$ over the angle θ_{ij} , which is the angle between the external magnetic field and the vector connecting the electron at *i*th O₂⁻ and the *j*th ¹³³Cs site. There are two closest contacts between Cs⁺ and O₂⁻ ions at r = 3.03 Å and two at r = 3.15 Å finally giving $\sqrt{M_2} = 3.8$ MHz, i.e., almost perfectly matching the measured ¹³³Cs NMR linewidth. Therefore, the absence of any additional broadening of the ¹³³Cs NMR spectra as well as the absence of any critical behavior in the temperature dependence of the EPR linewidth rule out any long-range magnetically ordered state at low temperatures.

In an attempt to change the O_2^- orientational and orbital ordering we rapidly cooled the sample from 320 to 4 K and then measured the EPR and ¹³³Cs NMR spectra on warming. After rapid cooling the intensity of the broad Lorentzian EPR component representing the low-symmetry phase is only about ~30% of that measured during the slow cooling experiment [Fig. 2(a)]. The large majority, i.e., ~70%, of the sample thus indeed remains frozen in the high-temperature cubic phase with degenerated $\pi^* O_2^-$ molecular orbitals and contributes to the extremely broad background signal. We can conclude that rapid cooling leads to a structural phase separation with a majority of the sample in the high-symmetry cubic and the minority in the low-symmetry phase.

The minor low-symmetry phase shows qualitatively similar behavior as in the slow-cooling experiment although there are some notable differences, like larger g factors or the characteristic temperature where EPR linewidth is at its maximum and the g factor at its minimum (Fig. 2). Slightly different orientation of O_2^- anions or the interaction between the cubic and the low-symmetry phases are among plausible explanations for these differences. Near 150 K the g factor of the low-symmetry phase suddenly drops and approaches the values of the phase stabilized by slow cooling (Fig. 2). A similar feature in the $\chi_m T$ data (Fig. 1 inset) is shifted to higher temperature, which may be due to kinetic effects. The anomalies in the heating-mode magnetic properties are attributed to the relaxation of the frozen phase into the thermodynamically stable low-symmetry phase near 150 K and the subsequent full transformation back to the cubic phase above 250 K. The concomitant large broadening of the EPR spectra for T > 200 K shows a thermally activated temperature dependence $\frac{1}{T} \exp[-\Delta E/k_B T]$ [Fig. 2(d)] with the activation energy of $\Delta E = 0.13$ eV for the large amplitude motions necessary for the reestablishment of the π^* degeneracy. The instability of the frozen cubic phase near 150 K is also directly evident from the anomalies in all NMR parameters [insets to Figs. 5(b) and 5(c)]. The memory for the thermal effects is finally erased by complete disordering of the O₂ units above 320 K, which is reflected in additional minor anomalies in the $\chi_m T$ and NMR data.

¹³³Cs NMR allows us to investigate the magnetism of the cubic phase at low temperatures. After rapid cooling, the ¹³³Cs NMR spectral intensity is largely shifted to lower frequencies (Fig. 4), i.e., at 10 K the shift amounts $\delta = -2.6\%$. The shift is strongly temperature dependent and, just like the linewidth [Figs. 5(b) and 5(c)], follows a Curie-Weiss–like dependence between 10 and 120 K with $\Theta = -6(1)$ K. Since the shift is towards the negative frequencies, we conclude that the transferred hyperfine interaction is nonzero in the cubic phase. Such interaction is operative when the lobes of the



FIG. 6. (Color online) ¹³³Cs NMR shift plotted against the magnetic susceptibility. A linear relation (red solid line) is observed for the frozen cubic phase in the temperature range from 150 K to 30 K.

electronically active O_2^- orbitals overlap with the neighboring Cs^+ ions making superexchange pathways via Cs^+ possible, in striking contrast to the low-symmetry phase. Therefore, the very different temperature dependence of the NMR shifts in the cubic and in the low-symmetry structure of Cs_4O_6 arises from the different orientations of nearest neighboring paramagnetic O_2^- units with respect to the Cs^+ ions. The fact that the exchange pathways are sensitively determined by the molecular orientation^{6,15} also rationalizes that the low temperature magnetism depends on the cooling protocol (Fig. 2 and Ref. 18).

The shift scales linearly with the magnetic susceptibility (Fig. 6) from 150 K down to 30 K, allowing us to write ${}^{133}\delta(T) = (A/N_A\mu_0)\chi_m(T)$. Here N_A and μ_0 are the Avogadro number and the vacuum permeability, respectively. A linear fit in the corresponding temperature range leads to the isotropic hyperfine coupling constant A = -3.1 kOe/ μ_B . A slight departure from the linear behavior below 30 K is most likely due to the underestimated negative shift in this range, as a consequence of the large linewidth.

Similarly as in the EPR experiment, we see the coexistence of both competing phases in ¹³³Cs NMR spectra too. The pronounced shift of the ¹³³Cs NMR intensity to lower frequencies in the rapid-cooling experiment indicates that the spectral intensity coming from the cubic phase is concentrated in the low-frequency wing of the spectrum, while the remaining high-frequency wing corresponds to the residual low-symmetry phase. The 133Cs NMR spectrum of the low-symmetry phase is known from the slow-cooling experiment. Hence its presence in the ¹³³Cs NMR spectra of the rapid-cooling experiment can be eliminated by multiplying the ¹³³Cs NMR spectrum of the low-symmetry phase by a properly chosen factor and subtracting it. This procedure is illustrated in Fig. 4 for the ¹³³Cs NMR spectrum taken at 10 K. The high-frequency wing is completely eliminated by setting the corresponding factor to 0.4. This implies that 40% of the ¹³³Cs NMR spectral intensity in the rapid-cooling experiment at 10 K is due to the low-symmetry phase, in good agreement with the above EPR estimate. Strikingly, the obtained spectrum has the rectangularlike spectral line shape,³⁰ which is more compatible with the frozen and ordered O_2^- moments. The coexistence of both the cubic and the low-symmetry phases is a direct consequence of an extremely sluggish transformation between the two phases and involves large amplitude reorientations of O2 groups. Moreover, since superexchange interactions between O_2^- through the Cs⁺ bridges depend on the orientation of π^* molecular orbitals, such coexistence explains the deviations of the temperature dependence of the magnetic spin susceptibility (Fig. 1) from the simple Curie-Weiss dependence and the history dependence of χ_m below 15 K (Fig. 1).

IV. CONCLUSIONS

In conclusion, we have presented a comprehensive EPR and ¹³³Cs NMR study of a mixed-valence Cs₄O₆ compound. The richness of this system stems from the simultaneous presence of orientational, charge, orbital, and spin degrees of freedom that are strongly coupled. This is most spectacularly demonstrated when samples are treated under different thermal protocols. Cubic and low-symmetry structures can coexist at low temperatures and their physical properties depend on the O₂ orientational order that affects the degree of ordering of O₂⁻ π^* molecular orbitals as well as the superexchange interactions through the Cs⁺ bridges.

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*denis.arcon@ijs.si

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