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Observation of spontaneous ferriquadrupolar order in KDy(MoO$_4$)$_2$

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Using Raman and infrared spectroscopies, spontaneous *ferriquadrupolar* ordering has been observed in the rare-earth-based system KDy(MoO$_4$)$_2$. Ordered quadrupoles in the electron subsystem attend nonequivalent distortions of rare-earth ions in the ordered phase. A mean-field theory explaining the onset of such a type of ordering has been constructed.

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Electronic correlations in condensed matter can change the behavior of electrons from a conventional metallic one to new, so-called liquid states, such as electronic liquid crystal ones in metals, valence bond solids, or spin-liquid states in insulating quantum spin systems [1]. For example, in the latter, the standard magnetic order (i.e., the ordering of magnetic dipoles) is suppressed down to the lowest temperatures due to the frustration of spin-spin interactions and/or enhanced quantum fluctuations in low-dimensional systems [2]. Individual magnetic moments (spins) remain disordered, while higher rank multipoles, first of all quadrupoles, that are caused by strong correlations between ions, can order under some special conditions. Unlike the order of magnetic dipoles, quadrupolar order does not break time-reversal symmetry. Quadrupolar ordering in insulating spin systems is often referred to as a "spin nematic" one, because that spin ordering is analogous to the known ordering of molecules in the nematic phases of liquid crystals [3]. For orbital electron moments the dipole moment of the orbital electron moment is frozen in most compounds [including the compound KDy(MoO$_4$)$_2$ discussed below], and the orbital order reveals itself first of all in the charge ordering or in the ordering of quadrupolar moments. The spin nematic order and the orbital/charge order breaks the rotational symmetry of electronic states. Strong nematic fluctuations were observed in Fe- and Cu-based superconductors [4] (nematicity is believed to be an essential property for Fe-based superconductors [5]), as well as in strontium ruthenates [6], and high fractional Landau levels [7]. Quadrupolar "hidden" order is often difficult to detect experimentally because most of the available techniques are sensitive to dipole moments only. Also, dipole moments are coupled to the electromagnetic field, while there is no simple field directly coupled to quadrupoles.

The cooperative Jahn-Teller (JT) effect [8] gives the possibility to observe quadrupolar ordering [9,10]. Here, quadrupolar orbital moments of the electron subsystem of a crystal interact with strains of the elastic subsystem, giving rise to a phase transition to the low-temperature phase, which is characterized by both quadrupolar electron ordering and nonzero distortions of the oxygen polyhedrons around the JT ions. Rare-earth-based JT compounds with strong coupling between the electron and elastic subsystems permit one to observe several kinds of quadrupolar hidden order. Ferroquadrupolar (by analogy with ferromagnetic) ordering (with a single sublattice of ordered orbital quadrupoles) was mostly observed in JT systems [8], however, some rare-earth-based compounds manifest antiferroquadrupole ordering, where at least two sublattices of ordered quadrupoles exist at low temperatures, as in antiferromagnets [11]. In this paper, we report a direct observation of spontaneous *ferriquadrupolar* (with two nonequivalent sublattices of quadrupoles) ordering. Using Raman and far infrared spectroscopy we observe clear features of the onset of two energetically nonequivalent ordered orbital quadrupolar moments in the rare-earth-based compound. That ordering is accompanied with the nonequivalent distortions of two groups of rare-earth ions, which reveal themselves in the onset of different electron optical lowest branches and phonons, also observed in our experiments.

KDy(MoO$_4$)$_2$ is the compound which represents the family of double molybdates with a general chemical formula MRe(MoO$_4$)$_2$, where M^+ is an alkali-metal ion and Re^{3+} is a rare-earth ion. The strong coupling between electronic excitations of Re^{3+} ions and phonons together with the strong anisotropy of Re^{3+} electronic states causes structural phase transitions, both spontaneous and induced by an externally applied magnetic field. Thus, the series of those compounds includes materials which are a perfect playground for studying the microscopic details of phase transitions related to the cooperative JT ones. In KDy(MoO$_4$)$_2$, previous investigations revealed a spontaneous phase transition at a temperature of the order of 10 K [12]. An external magnetic field being applied in a certain direction suppresses the phase transition [13]. In the high-temperature phase, KDy(MoO$_4$)$_2$ has the $Pbcn(D_{2h}^{14})$ structure with $Z = 4$. At present, low-temperature x-ray data are absent for KDy(MoO$_4$)$_2$, however, the phenomenological approach shows that the phase transition leads to the doubling of the unit cell with a lowering of the symmetry to monoclinic [14]. Nevertheless, the microscopic mechanism remains unclear. A series of studies [15] demonstrates that in the process of phase transformations, two phase transitions take place with close critical temperatures. There is a data spread in the definition of the value of the critical temperatures [12,13,15–22].

Besides, the question remains regarding how the distortions are ordered around nonequivalent ions of Dy^{3+}; there are four of those ions in the high-temperature phase, and eight in the low-temperature ones. One study [22] stresses that the standard soft mode has not been detected. The lowest multiplet of the Dy^{3+} ion, namely $^6H_{15/2}$, is split by the crystal field into eight doublets; the first excited level lies at 18 cm^{-1} above the ground state; the next one is at about 80 cm^{-1} [23].

To investigate the temperature behavior of the lowest-energy levels at temperatures 1.4–25 K, two spectroscopic methods, far infrared (FIR) and Raman spectroscopy, have been used. The goal of our study is to determine the type of ordering in a multisublattice JT system.

The studied $KDy(MoO_4)_2$ samples were grown from a melt by slow cooling. The samples have a typical plate shape with dimensions of 5×5 mm^2 with the b axis perpendicular to the plates. It allows for FIR transmission measurements with the polarizations of the electric component of the radiation $E_\omega \parallel a$ (B_{3u}) and $E_\omega \parallel c$ (B_{1u}). The FIR experiments have been performed using the Fourier-transform infrared spectrometer Bruker IFS113v. A mercury lamp has been used as a radiation source, and the liquid-helium-cooled silicon bolometer has been used as a detector. Raman scattering has been measured using a Nd:YAG (neodymium-doped yttrium aluminum garnet) solid-state laser ($\lambda_{exc} = 532$ nm) with 36-mW incident power. The sample heating has been estimated by relative intensities of the Stokes and anti-Stokes components of a phonon mode at 74 cm^{-1}. The scattered light has been collected in a 90° geometry, dispersed through a double-stage monochromator Ramanor U-1000, and then detected with a cooled photomultiplier.

The FIR spectra of $KDy(MoO_4)_2$ have a complicated structure. First of all, multiple reflections within the plane-parallel sample cause a Fabry-Pérot type of modulation of the transmittance, which appears as fringes in the spectra. The periodicity of the fringes [see Fig. 1(a), left panel] is determined by the thickness and the refractive index of the sample. The exact energies of the absorption modes were determined using the REFFIT script [24], which also simulated the fringes. Second, at the same range of energies besides electronic excitations, the spectra show low-energy phonons.

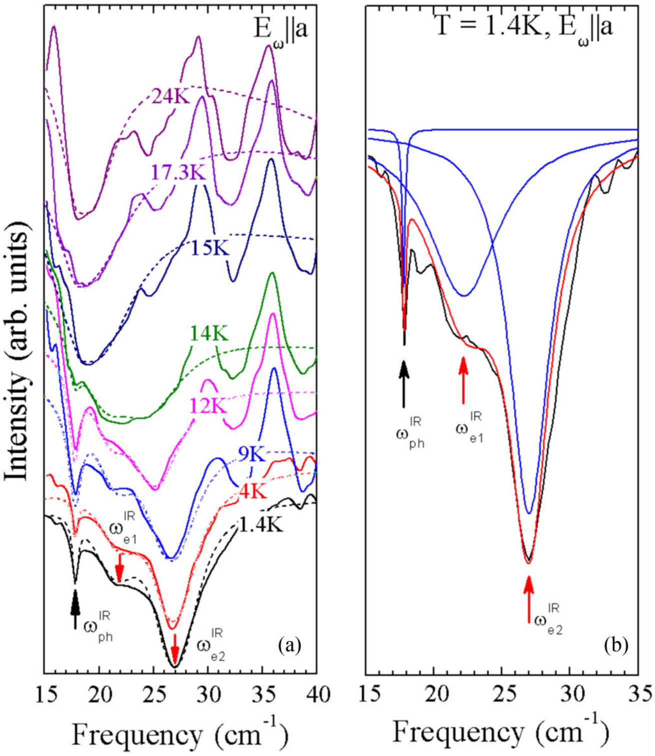

FIG. 1. Left panel: The temperature evolution of the transmission (FIR) spectra of $KDy(MoO_4)_2$ for $E_\omega \parallel a$ polarization. The black arrow shows the phonon mode ω_{ph}^{IR} and the red arrows show the electron modes ω_{e1}^{IR} and ω_{e2}^{IR}. Solid lines: Experiment. Dashed lines: Multiple reflections removed. Right panel: FIR transmission spectra for $T = 1.4$ K; the black line describes the data of the experiment; three blue lines describe the theoretical fitting within the Lorentz approximation for each of the three observed lines; the red line is the sum of all fitting contributions.

Figure 1 (left panel) displays the temperature evolution of the FIR spectra between 1.4 and 24 K for $E_\omega \parallel a$ polarization (experiments have been performed for other polarizations also). The lines in this temperature region have different half widths and different temperature dependences of their energy positions. Figure 1 (right panel) shows the positions and spectral half widths at 1.4 K; it was supposed that every line has a Lorentz profile. The most intensive line from the high-energy side is determined as the first excited level of Dy^{3+} ions; at higher temperatures (25–18 K) its energy is about 18 cm^{-1}. By lowering the temperature to 1.5 K its position is changed to ~27 cm^{-1}. Such a behavior was related [12,13] to the cooperative JT effect in $KDy(MoO_4)_2$, namely, to antiferroquadrupolar ordering with two equivalent quadrupolar sublattices [13]. The lowest-energy excitation in this group is presented by the very narrow shape (its half width is about 0.5 cm^{-1}). It is related [25] to the vibrations of the layers $\{Dy^{3+}(MoO_4)^{2-}\}^-$ as a whole. The energy does not depend on the temperature, at least in the temperature region where they are not overlapped with the wide electron line. Meanwhile, that phonon excitation close to 17.5 cm^{-1} does not demonstrate a noticeable broadening compared with lower temperatures. Note that at the external magnetic field the electron line shifts to higher energies [23]. Importantly, we observe weak electron excitation appears in the spectra near 22 cm^{-1} at temperatures below about 15 K. We suppose that the onset of this excitation is the result of enlarging the rhombic phase unit cell by at least twice [22]. The number of JT centers which are connected with Dy^{3+} ions is twice as many as in the high-temperature phase. If the symmetry of the crystal is also lowered to the monoclinic one, half of the JT centers in the common position are not connected by any symmetry elements with the other part. The distortions of the surroundings of the JT ions, which belong to different groups, provide different energies of nonequivalent rare-earth ions.

So, when the temperature is decreased, the electronic mode shifts towards higher energies and splits into two modes,

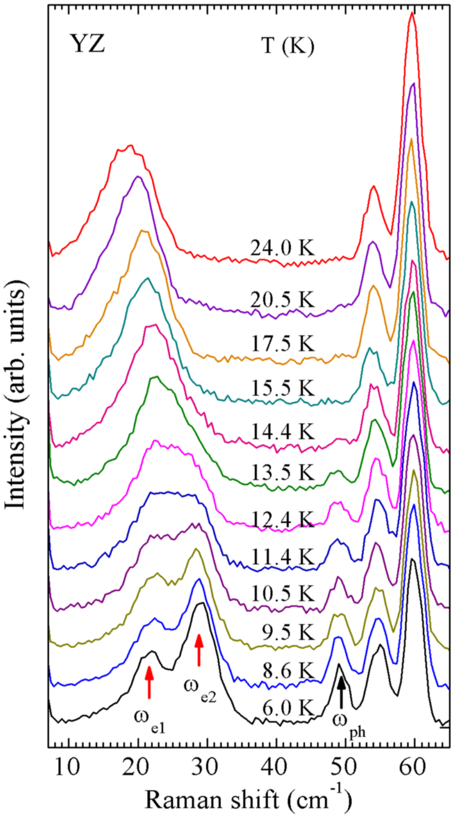

FIG. 2. The temperature behavior of the low-frequency part of the Raman spectrum of $\mathrm{KDy(MoO_4)_2}$. The geometry of the experiment is $Z(YZ)Y$ (B_{3g} symmetry). The black arrow shows the additional phonon line, and red arrows show the low-energy electron transitions (related to the ones between the levels of the main multiplet ${}^6H_{15/2}$ in the high-temperature phase) of the $\mathrm{Dy^{3+}}$ ion. The spectral resolution is 3 $\mathrm{cm^{-1}}$.

$\omega_{e1}^{\mathrm{IR}}$ and $\omega_{e2}^{\mathrm{IR}}$, with energies of 22 and 27 $\mathrm{cm^{-1}}$ of different intensities, respectively. The temperature-independent sharp peak at 17.5 $\mathrm{cm^{-1}}$ marked with $\omega_{\mathrm{ph}}^{\mathrm{IR}}$ is the phonon mode which corresponds to the shear lattice vibrations [25]. At high temperatures the electron excitation (as a broad line) basically superimposes on the phonon excitation. We think one can suppose that the infrared active phonons of that nature are not "triggers" of the phase transition. More preferable is the assumption about the participation in the mechanism of the JT transition of the A_u low-frequency phonons connected with the weak turns of the tetrahedral anions of $\mathrm{(MoO_4)^{2-}}$, which deform the local environment of the $\mathrm{Dy^{3+}}$ ions. Those excitations are nonactive either in the FIR or in the Raman spectra, and their low-frequency nature can be manifested only with the help of the modeling.

Figure 2 shows the temperature evolution of the Raman spectra between 6 and 24 K for the $Z(YZ)Y$ geometry (experiments have been performed for other geometries, too), which probes B_{3g} modes. There are three peaks with energies below 70 $\mathrm{cm^{-1}}$ at 24 K. The broad peak at 18 $\mathrm{cm^{-1}}$ corresponds to the electronic excitation within the ${}^6H_{15/2}$ multiplet and the peaks at 55 and 60 $\mathrm{cm^{-1}}$ are related to phonons [22]. Upon cooling below 14.5 K this phonon mode appears at 49.2 $\mathrm{cm^{-1}}$ (shown by the black arrow). The onset of the phonon modes below the critical temperature points towards the multiplication of the unit cell, because in the rhombic phase (above 14.5 K) the degeneracy of the phonons is already removed. A few more phonons were observed in the low-temperature phase [22]. The electronic mode with an energy of 18 $\mathrm{cm^{-1}}$ at 24 K shifts upon cooling to higher energies and splits to two peaks at 21.1 and 28.8 $\mathrm{cm^{-1}}$ (shown by red arrows). Two other polarizations show analogous behavior [22].

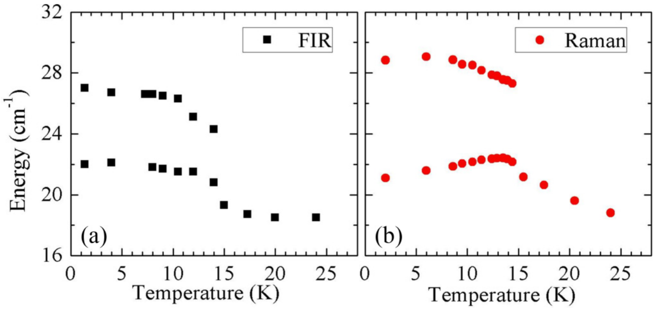

FIG. 3. The temperature dependence of the low-energy electronic excitations of $\mathrm{Dy^{3+}}$ ions in $\mathrm{KDy(MoO_4)_2}$ in the vicinity of phase transition(s). Left panel: FIR measurements; right panel: Raman measurements. Raman data for 2 K are used from Ref. [22].

Note that in Ref. [17] the observed excitation of an electronic nature of about 21–22 $\mathrm{cm^{-1}}$ was interpreted as a soft mode, however, without supporting experimental data. That softening of the mode is directly connected to the equivalence of two ordered quadrupolar sublattices [17]. Instead, in our experiment it is shown that both low-temperature lines do *not* shift to zero. Moreover, Raman experiments [22] of various polarizations and at various frequency ranges do not reveal any sorts of "soft" modes.

Figure 3 summarizes the results of our Raman and FIR studies. It shows the temperature dependence of the energies of electronic excitations. Below the phase transition the gap between two lowest electron energies increases. The mode splitting is clearly visible in both experiments. We assign the splitting of the electronic mode to the increase of the nonequivalent positions of the $\mathrm{Dy^{3+}}$ ions, which means that the symmetry in the low-temperature phase is not higher than monoclinic in the volume-doubled elementary cell of the rhombic phase [23,26]. We address the difference in energies of the electronic excitations in the Raman and FIR measurements to eight nonequivalent positions of $\mathrm{Dy^{3+}}$ ions. The interaction between those ions additionally splits the electronic levels. The schematic picture of the low-temperature phase unit cell is shown in Fig. 4. There are eight rare-earth ions which occupy the common

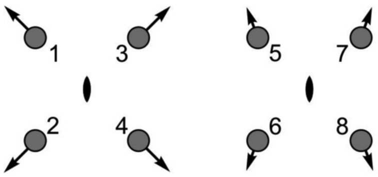

FIG. 4. The schematic picture of the distorted $\mathrm{Dy^{3+}}$ ions in $\mathrm{KDy(MoO_4)_2}$ below the phase transition to the ferriquadrupolar phase.

crystallographic positions. They consist of two groups, each of which includes four ions. Those four ions are connected with each other by an inversion operation, however, no symmetry operation exists which transfers one group to the other one.

Obviously, such a behavior evidences [27] the onset of ferriquadrupolar electron ordering, in which two ordered sublattices of orbital quadrupoles are nonequivalent [28]. It is accompanied with nonequivalent distortions of two groups of oxygen polyhedrons surrounding two groups of Dy^{3+} ions (see Fig. 4). To explain the observed behavior of the interacting electron and elastic subsystems of $KDy(MoO_4)_2$ via the JT effect, we develop the approach proposed in Refs. [8,9,13], modifying it according to the nonequivalence of two quadrupolar sublattices observed in our experiment. Such an approach has been successfully applied for the description of the features of the infrared and optical spectroscopy in rare-earth-based JT systems [8,9,13,17,21].

At high temperatures the first excited doublet of Dy^{3+} is situated 18 cm^{-1} above the ground-state doublet due to the crystalline electric field, hence for the description of the low-energy properties of the system we limit ourselves to those two doublets [8,9] (often called Ising pseudospins). Quadrupolar moments of Dy^{3+}, related to those doublets [9], interact with each other via phonons with a long-range Ising type of effective coupling [8], yielding quadrupolar ordering at low temperatures. That interaction is taken into account within the mean-field theory for quadrupolar ordering [13]. In our calculations the value of the interaction between quadrupolar moments, belonging to the same sublattice, is taken to be equal to the value of the interaction between quadrupoles, belonging to different sublattices (however, with a different sign). It has been used to avoid the additional magnetic-field-induced ordered phase, analogous to the spin-flop phase of antiferromagnets, not observed in the experiment [21] (that phase is necessarily predicted by the mean-field theory as in Ref. [13], if those interactions have different values).

Within such an approach the low-energy part of the free energy per site of quadrupolar moments (Ising pseudospins) coupled to the elastic subsystem in the simplest approximation can be written as $F = -(k_B T/2)(\ln[2\cosh(A_+/k_B T)] + \ln[2\cosh(A_-/k_B T)]) + Cx^2/2$, where T is the temperature, k_B is the Boltzmann constant, $A_\pm = [(\lambda L)^2(1 \pm x)^2 + \varepsilon^2]^{1/2}$ are the renormalized (half) splittings of energies of quadrupolar moments (namely, transitions between those low-energy electron states were observed in our spectroscopic experiments), λ is the parameter of the effective interquadrupole Ising-like interaction, ε is the crystalline electric field, which determines the high-temperature (half) splitting of 18 cm^{-1}, and L is the order parameter [13,21]. The first two terms are related to the energy gain of the quadrupolar electron subsystem due to the nonequivalence of quadrupoles due to the nonzero parameter of the nonequivalence x. On the other hand, the last term describes the energy loss of the elastic subsystem due to the nonequivalence of strains of two electron sublattices (cf. Fig. 4), with C being related to the elastic modulus. For $x = 0$, i.e., for equivalent quadrupolar sublattices (antiferroquadrupolar ordering), the order parameter L is the solution of the self-consistency equation $A = \lambda \tanh(A/k_B T)$, where $A = [(\lambda L)^2 + \varepsilon^2]^{1/2}$ (see Ref. [23]).

In the ground state the order parameter L is equal to $[1 - (\varepsilon/\lambda)^2]^{1/2}$, and it monotonically decreases to zero at $T = T_D = \lambda/k_B$. That type of ordering exists only for $\lambda \geqslant \varepsilon$. Then, to describe the nonequivalence of the quadrupolar sublattices, i.e., ferriquadrupolar ordering, we minimize the free energy F with respect to x. We obtain the equation for the determination of x,

$$\frac{2Cx}{(\lambda L)^2} = \frac{(1+x)}{A_+} \tanh\left(\frac{A_+}{k_B T}\right) - \frac{(1-x)}{A_-} \tanh\left(\frac{A_-}{k_B T}\right). \tag{1}$$

Obviously, for $T \gg A_\pm/k_B$ only the trivial solution $x = 0$ exists. We can see that a nontrivial solution $x \neq 0$, which describes ferriquadrupolar ordering with nonequivalent quadrupole sublattices $L(1 \pm x)$, exists only for $T < T_D$, where $L \neq 0$. Unfortunately, it is impossible to find the analytic solution to Eq. (1). Our analysis of the numerical solution shows that for given values of λ and ε the nontrivial solution for $x \neq 0$ exists, however, only for some range of values of C, which is reasonable for $KDy(MoO_4)_2$. Depending on the values of the used parameters, the model can describe the single transition from the disordered high-temperature phase to the ferriquadrupolar ordered phase directly. The other possibility is via two phase transitions, first from the disordered phase with $L = 0$ to the antiferroquadrupolar one (with equivalent sublattices $L \neq 0$, $x = 0$), and then to the ferriquadrupolar phase with nonequivalent sublattices $L \neq 0$, $x \neq 0$.

In summary, using FIR and Raman spectroscopies we have directly observed the spontaneous low-temperature ferriquadrupolar ordering of quadrupolar moments of the rare-earth ions in the rare-earth-based compound $KDy(MoO_4)_2$. Our FIR and Raman studies also manifest that such ordering is accompanied with a different optical phonon mode, related to the nonequivalent distortion of rare-earth ions, belonging to the observed nonequivalent quadrupolar sublattices. The developed mean-field theory explains the main mechanism of the transition(s) to the low-temperature ferriquadrupolar phase, observed in our experiments. Four nonequivalent Ising-like magnetic centers observed in the external magnetic field [29] in the low-temperature phase of $KDy(MoO_4)_2$ also support our conclusion about the ferriquadrupolar character of the low-temperature phase of the electron subsystem.

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[26] The results of Raman studies for different polarizations of light [22] also agree with our conclusions.

[27] There is no magnetic ordering in $KDy(MoO_4)_2$ in the considered range of the temperature. The magnetic ordering takes place below approximately 1.1 K (see Refs. [16,18]), and has nothing in common with the anomalies observed below approximately 15 K, related to orbital quadrupolar ordering (and simultaneous distorsive ordering, characteristic of the cooperative Jahn-Teller effect) in $KDy(MoO_4)_2$ (see Refs. [13–19,21]). The nature of the low-temperature magnetic ordering is related to magnetic dipole-dipole interactions, which are too weak to explain the observed features in the temperature range considered in our study.

[28] Ferroquadrupolar ordering is known to be excluded for $KDy(MoO_4)_2$ [13–19,21]. As for antiferroquadrupolar ordering, equivalent quadrupole sublattices would yield softening of the lower electron mode at the critical temperature [17]. Such a softening is obviously absent (see Fig. 3) in both the observed FIR and Raman data (also for other polarizations of light). The model with nonequivalent sublattices, i.e., the model of ferriquadrupolar ordering (see below), does not reveal such a softening.

[29] V. A. Bagulya, A. I. Zvyagin, M. I. Kobets, A. A. Stepanov, and A. S. Zaika, Fiz. Nizk. Temp. **14**, 493 (1988) [Sov. J. Low Temp. Phys. **14**, 270 (1988)].