PDF hosted at the Radboud Repository of the Radboud University Nijmegen

The following full text is a publisher's version.

For additional information about this publication click this link.
http://repository.ubn.ru.nl/handle/2066/128393

Please be advised that this information was generated on 2018-07-15 and may be subject to change.
Interaction of electronic excitations of Tm$^{3+}$ ions with acoustic vibrations in KTm(MoO$_4$)$_2$

D. Kamenskyi, I. S. Poperezhai, P. Gogoi, H. Engelkamp, J. C. Maan, J. Wosnitza, and V. Kut’ko

1 Radboud University, Institute for Molecules and Materials, High Field Magnet Laboratory, 6525 ED Nijmegen, Netherlands
2 B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine, 47 Lenin Ave., 61103 Kharkiv, Ukraine
3 Dresden High Magnetic Field Laboratory (HLD), Helmholtz-Zentrum Dresden-Rossendorf, D-01314 Dresden, Germany

(Electronic Excitations of Tm$^{3+}$ ions with Acoustic Vibrations in KTm(MoO$_4$)$_2$

Electron paramagnetic resonance spectra of KTm(MoO$_4$)$_2$ were measured as a function of magnetic field between 3 and 11.5 cm$^{-1}$ at $T = 2$ K. We found that in addition to the absorption line caused by the electronic excitation of Tm$^{3+}$ ions, the spectra contain sidebands. Far-infrared transmission measured with polarized light from 10 to 75 cm$^{-1}$ revealed vibration modes at 16.7 and 25.7 cm$^{-1}$ for polarizations $E^\parallel a$ and $E^\parallel c$, respectively. We show that sidebands in the spectra of paramagnetic resonance result from a parametric resonance between the electronic excitations of the Tm$^{3+}$ ions and the acoustic vibrations of the crystal lattice.

DOI: 10.1103/PhysRevB.89.014410 PACS number(s): 63.20.kd, 71.70.Ej, 76.30.—v, 76.30.Kg

I. INTRODUCTION

KTm(MoO$_4$)$_2$ belongs to a series of rare-earth compounds with a general formula $M R(MoO_4)_2$, where $M^+$ is an alkali-metal ion and $R^{3+}$ is a rare-earth ion. The characteristic feature of these materials is the strong coupling between the electronic excitations of the $R^{3+}$ ions and phonons; these electronic excitation energies fit to the lattice-vibrations energies near the maximum in the phonon density of states. Therefore structural phase transitions caused by the Jahn-Teller effect (including those induced by magnetic field) are quite frequent in these compounds.

In this paper, we discuss KTm(MoO$_4$)$_2$ for which previous measurements of the magnetic susceptibility and the specific heat have shown that neither structural phase transitions nor magnetic ordering occur down to 0.1 K. The absence of the heat capacity peak has shown that neither structural phase transitions nor magnetic ordering occur down to 0.1 K. The absence of the heat capacity peak has shown that neither structural phase transitions nor magnetic ordering occur down to 0.1 K.

II. EXPERIMENTAL DETAILS

Single crystals of KTm(MoO$_4$)$_2$ were grown from a melt by slow cooling. The crystallographic structure has the space group $P_{bnm}$ ($D_{4h}^+$) with the lattice constants $a = 5.05$ Å, $b = 18.28$ Å, $c = 7.89$ Å, and four formula units per unit cell. It consists of $[\text{Tm}(\text{MoO}_4)_2]^{-}$ layers which are built from Mo$_4$ tetrahedra and Tm$_2$O$_8$ octahedra and are separated by layers of K$^+$ ions (see Fig. 1). The weak bonding between the layers along the $b$ direction is responsible for the thin plates crystal shape. Important is that the K$^+$ ions are bonded to one of the $[\text{Tm}(\text{MoO}_4)_2]^{-}$ layers within cell somewhat stronger than to another one.

The samples investigated had typical dimensions of $9 \times 5 \times 0.2$ mm$^3$. This allows to measure the transmission spectra with the polarizations $E^\parallel a$ and $E^\parallel c$ axes ($E^\parallel$ is electric component of the microwave radiation).

FIR transmission spectra were measured using a commercial Fourier-transform infrared spectrometer (Bruker IFS113v) combined with a continuous-field 33-T Bitter magnet at 1.4 K at the High Field Magnet Laboratory in Nijmegen. A mercury lamp was used as a radiation source. The FIR radiation was detected using a silicon bolometer operating at 1.4 K below the field center with a maximal field <7 T. The data were collected between 10 and 75 cm$^{-1}$ with 0.1 cm$^{-1}$ resolution using a 200-μm mylar beamsplitter and a scanning velocity of 50 kHz. At each field, at least 50 scans were averaged.

The EPR measurements were performed at the Dresden High Magnetic Field Laboratory using a transmission-type spectrometer over the frequency range 3–11.5 cm$^{-1}$ (90–345 GHz) at $T = 2$ K. Virginia Diodes Inc. microwave sources were employed as radiation sources. The microwave radiation propagated along the $b$ axis of the crystal. The external magnetic field ($H$) was applied along the $c$ axis, which corresponds to the highest $g$ factor.

1098-0121/2014/89(1)/014410(5) 014410-1 ©2014 American Physical Society
III. RESULTS

The FIR transmission spectra of KTm(MoO$_4$)$_2$ at 1.4 K are shown in Fig. 2. We found absorption peaks at 16.7 and 25.7 cm$^{-1}$ for polarizations $E_{\omega} \parallel a$ and $E_{\omega} \parallel c$, respectively (arrows in Fig. 2). Standing waves within the plane-parallel sample cause interference in the spectra, which is visible as a Fabry-Perot type modulation of the transmittance in Fig. 2.

Figure 3 shows EPR spectra of KTm(MoO$_4$)$_2$ at different frequencies. We found an intensive absorption peak (marked by A in Fig. 3), which corresponds to the transition within the lowest quasidoublet with a zero-field gap of 2.33 cm$^{-1}$. The ground state of such systems is described by the conventional non-Kramers doublet spin Hamiltonian for an effective spin $S = 1/2$:

\begin{equation}
\mathcal{H} = g_z \mu_B H_z S_z + \Delta_x S_x + \Delta_y S_y. \tag{1}
\end{equation}

The terms $\Delta_x, \Delta_y$ are induced by the crystal field. They lead to a zero-field energy gap $\Delta = [\Delta_x^2 + \Delta_y^2]^{1/2}$ and mix the two lowest nondegenerate states. This mixing allows transitions within non-Kramers doublet when the oscillating magnetic field, $H_{\omega}$, has a parallel component along the $z$ direction ($H_{\omega} \parallel H$). Such an effect is not unique for Tm$^{3+}$ ions. Similar EPR properties were reported for Tm$^{3+}$ in a multicomponent fluorozirconate glass.

The frequency-field dependence of the peak A is shown in Fig. 4. Red points show data obtained by EPR, blue points by the FIR setup. The black line corresponds to a fit using the
formula
\[ \hbar \omega_0 = [\Delta^2 + (g \mu_B H)^2]^{1/2}, \] (2)
where \( \omega_0 \) is the radiation frequency. The values obtained for
\( g \sim 13.8 \) and \( \Delta \sim 2.33 \text{ cm}^{-1} \) are in agreement with previous
EPR investigations.12

At some frequencies, sidebands of the peak A appear
(shown by arrows in Fig. 3). Additionally, a number of weak
absorptions marked by asterisks have been observed. At some
frequencies, the peak A splits (6.9, 10.1, 11.5 cm\(^{-1}\)) and
the intensity of the anomalies increases (10.1 cm\(^{-1}\)). Since
the sidebands are situated quite far from the main resonance
peak A, they cannot be explained by the electrodynamic
effects near the resonance, e.g., by a change in the sample’s
refractive index. In the following, we argue that the observed
features in the EPR spectra are caused by the dynamic coupling
between the electronic excitations of Tm\(^{3+}\) ions and the lattice
vibrations.

IV. DISCUSSION

FIR acoustic spectra of K\( R(\text{MoO}_4)_2 \) compounds are formed
by the shear vibrations of the [R(\text{MoO}_4)_2]$^-$ layer as a whole along different crystallographic directions.12,20 Thus,
the dispersion of the vibration branches in the Brillouin zone,
\( \omega_{pb}(k) \), can be calculated using a one-dimensional model.
The dispersion relation of the vibrational branches of a linear chain
with two masses (\( M > m \)) is well-known:
\[ \omega_{ph}^2 = \alpha (1/m + 1/M) \]
\[ \pm \alpha [(1/m + 1/M)^2 - 4 \sin^2(ka/2)/mM]^{1/2}, \] (3)
where \( \alpha \) is the shear force constant, \( \omega = 2\pi v \) is the angular
frequency, \( a \) is the lattice parameter, and \( k \) is the quasi-wave-vector.21 Plus and minus correspond to the optical and acoustic
branches, respectively.

K\( \text{Tm(MoO}_4)_2 \) forms two nonequivalent layers,
[Tm(\text{MoO}_4)_2]$^-$ and ([Tm(\text{MoO}_4)_2]$^-$ + 2K$^+$), because,
as it has been mentioned above, the K$^+$ ions are bonded to
one of the [Tm(\text{MoO}_4)_2]$^-$ layers within cell stronger than
to another one (see Fig. 1).13 Thus, due to folding of the
Brillouin zone, new low-frequency optical branches appear.
Physically, they represent shear vibrations [Tm(\text{MoO}_4)_2]$^-$
versus ([Tm(\text{MoO}_4)_2]$^-$ + 2K$^+$) layers, and are observed by
us as the FIR absorption peaks at 16.7 and 25.7 cm\(^{-1}\) (see Fig. 2) for the \( a \) and \( c \) axes, respectively.

The frequency of the optical branch at \( k = 0 \):
\[ \omega_{opt} = [2 \alpha (1/m + 1/M)]^{1/2}, \] (4)
where \( M \) and \( m \) mases of [Tm(\text{MoO}_4)_2]$^-$ + 2K$^+$ and
[Tm(\text{MoO}_4)_2]$^-$ layers, respectively. We used the obtained
frequencies of the optical modes to determine \( \alpha \) from Eq. (4)
and calculate the dispersion of these modes, \( \omega_{pb}(k) \), using
Eq. (3). The results of calculations are shown in Fig. 5.

The sideband structure observed in the EPR spectra (see
Fig. 3) can now be explained by resonant dynamic coupling
between the electronic excitations of Tm\(^{3+}\) ions and the lattice
vibrations. The resonant dynamic coupling of these excitations is
possible if the following conditions are met: (a) the electronic
and phonon excitations must be of identical symmetry and
(b) the interacting excitations must have equal energies
and wave vectors.

The excitation spectrum of Tm\(^{3+}\) ions is determined by their
local symmetry, and the low-frequency vibration excitations
are dependent on the symmetry of the crystal. To check
whether condition (a) is fulfilled it is necessary to find out
the compatibility of the irreducible representations of the
corresponding symmetry groups. The local symmetry group
of Tm\(^{3+}\) ions is \( C_2 \) and the factor group is \( D_{2b} \). Table I contains
the irreducible representations of the local symmetry group
of Tm\(^{3+}\) ions and the factor group. The irreducible
representations of the symmetry group of the electronic excitations \( \Gamma_1, \Gamma_2 \) are compatible with the representations \( \Gamma^*_1, \Gamma^*_2, \Gamma_4, \Gamma_2, \Gamma_3, \Gamma_3, \Gamma_4, \Gamma_4 \) of the factor group, respectively. Vibrations
shown in Fig. 5 have the odd symmetry \( \Gamma^*_2, \Gamma^*_3, \Gamma^*_4 \). Thus
the coupling between the Tm\(^{3+}\) ions electronic excitations of
symmetry \( \Gamma_1, \Gamma_2 \) and the odd-symmetry lattice vibrations \( \Gamma^*_1, \Gamma^*_3, \Gamma^*_4 \) is allowed. The EPR spectra have been measured at
\( k \parallel b \), i.e., with \( E^o \perp \) \( C_2 \) axis (the local symmetry \( C_2 \) axis
of Tm\(^{3+}\) is parallel to the \( b \) axis), which is an excitation of
the symmetry \( \Gamma_2 \) compatible with the representations \( \Gamma^*_1, \Gamma^*_3, \Gamma^*_4 \). These representations characterize the transverse acoustic
vibrations of the [Tm(\text{MoO}_4)_2]$^-$ entities within the layer.

The lattice vibrations modulate the crystal field on the Tm\(^{3+}\)
sites. It leads to a modulation of the zero-field gap, \( \Delta \), in Eq.
(2). Usually, such a dynamic electron-phonon coupling leads
to a broadening of the EPR absorption peak.22 In
K\( \text{Tm(MoO}_4)_2 \), we found that the electron-phonon coupling
is resonant and induce nonlinear effects. The phonon energies
are quite low and coincide with the energies of electronic
excitations at certain magnetic fields. It leads to parametric
resonance between electronic excitations and phonons.

| TABLE I. The compatibility of irreducible representation of the symmetry group \( C_2 \) and the factor group \( D_{2b} \). |
|-------------|----------------|----------------|
| \( C_2 \)   | \( \Gamma_1 \) | \( \Gamma_2 \) |
| \( D_{2b} \) | \( \Gamma^*_1 \), \( \Gamma^*_1 \), \( \Gamma^*_2 \), \( \Gamma^*_2 \), \( \Gamma^*_3 \), \( \Gamma^*_3 \), \( \Gamma^*_4 \), \( \Gamma^*_4 \) |

FIG. 5. (Color online) Dispersion of acoustic and optic vibration branches of K\( \text{Tm(MoO}_4)_2 \). The horizontal dashed lines correspond
to the energies of phonons with wavelengths multiple of the lattice constant.
Parametric oscillator is described by the Mathieu equation. In the simple case of a pendulum in a time-dependent gravitational field:

$$\frac{d^2 \Theta}{dt^2} + \gamma \frac{d \Theta}{dt} + \omega_0^2 [1 + h \cos(2\omega t)] \Theta = 0,$$  \tag{5}

where $\Theta$ is an angular variable, $\gamma$ is the damping factor, $\omega_0$ is the eigenfrequency of the pendulum, $h$ is the relative amplitude of the modulation, and $\omega$ is the modulation frequency. The solutions of Eq. (5) are given by transcendental functions, called Mathieu functions, which we do not describe further. It is very important that Eq. (5) has stable solutions at certain conditions only. For an undamped system ($\gamma = 0$), the theory predicts instabilities at $\omega_0/\omega = 1/n$ ($n$ is integer). Such instabilities result in parametric resonances of the system. Figure 6 shows the stability diagram of Eq. (5) equation for $n = 1, 2$.

In our case, the electronic excitations play the role of the pendulum and the lattice vibrations are the external modulation. One can see in Fig. 6 that if the frequency of the electronic excitations, $\omega_{ph}$, coincide with the modulation frequency, $\omega_0$, and the amplitude of the oscillations increases. The modulation amplitude enhances when the energies of the electronic excitations coincide with phonon energies of wavelengths that are a multiple of the lattice constant (shown by vertical dashed lines in Fig. 5). The lattice vibrations with these wavelengths form standing waves and nodes are localized at weak interlayer bonds. Thus neighboring [Tm(MoO$_4$)$_2$]$^{-}$ layers move in antiphase, which modulates the crystal-field most strongly at the Tm$^{3+}$ sites. This leads to a resonant enhancement of the dynamic electron-phonon coupling and induces splitting and inhomogeneous broadening of the EPR peak.

The horizontal dashed lines in Fig. 5 show the energies of the acoustic phonons with wavelengths of a multiple of the lattice constant (3.2, 4.2, 4.8, 6.3, 6.4, 9.5, 11.4, and 12.0 cm$^{-1}$). Using the calculated phonon frequencies and Eq. (2), we can estimate the resonance magnetic fields for electronic excitations of same energy (0.33, 0.54, 0.66, 0.90, 0.92, 1.43, 1.73, and 1.83 T). When the resonance field is close to calculated fields (shown by vertical dashed lines in Fig. 3) the system falls into the instability area (see Fig. 6). It leads to the splitting of peak A and a very asymmetrical shape of it (see spectra at 6.9, 10.1, and 11.5 cm$^{-1}$ in Fig. 3). We believe that the additional features in spectra at 6.9, 10.1, and 11.5 cm$^{-1}$ are induced by nonlinear modulation of electronic excitation energy.

Since $\omega_{ph}$ is magnetic field dependent according to Eq. (2), the dynamic electron phonon coupling can be varied by the field. Outside the instability area, the EPR spectrum becomes noiseless and the sidebands appear (see the spectrum at 11.1 cm$^{-1}$ in Fig. 3). The parametric modulation in Eq. (5) leads to a low frequency modulation of the electronic excitation if system is close to instability area.\cite{24} It induces the sideband structure in the EPR spectra. The positions of the sidebands in the spectra are determined by the modulation frequency. Since the solutions of the Eq. (5) are strongly field-dependent, the positions of the sidebands are asymmetric respect to peak A. The sidebands in FIR spectra induced by electron phonon coupling reported also for other KRM(MoO$_4$)$_2$ compounds.\cite{1} We found the sideband structure survive in instability area as well (shown with arrows in Fig. 3).

Thus, in KTm(MoO$_4$)$_2$, we have the unique possibility to control the dynamic electron-phonon interaction by magnetic field. However, the strong field dependence of this coupling makes interpretation of the EPR spectra challenging. Additionally, the resonant parametric coupling is expected not only when the frequencies coincide, but also at the subharmonics of the lattice vibrations.\cite{24} This may lead to an additional structure of weak absorptions in EPR spectra (marked by asterisks in Fig. 3).

V. CONCLUSIONS

We investigated the transmission spectra of KTm(MoO$_4$)$_2$ by use of FIR and EPR techniques. Evidence of the parametric resonance between electronic excitations of Tm$^{3+}$ ions and acoustic phonons in form of sidebands has been observed in EPR signal. This nonlinear effect is induced by the dynamic electron-phonon interaction. We have shown that the electron-phonon coupling is enhance when the electronic level of Tm$^{3+}$ ions crosses the vibration branches with wave vectors multiples to the lattice constant.

The observation of the parametric resonance suggests KTm(MoO$_4$)$_2$ as a good model compound for the study of the nonlinear dynamical effects by varying the magnetic field and the microwave radiation power. At fields when the coupling is strong enough and the excitation energies coincide, the system may exhibit further nonlinear behavior when the radiation power is increased.

ACKNOWLEDGMENTS

This work is part of the research program of the Foundation for Fundamental Research on Matter (FOM), which is part of the Netherlands Organisation for Scientific Research (NWO). Parts of this work were supported by EuroMagNET II (contract No. 228043) and EMFL (contract No. 26211). The authors would like to thank A. V. Pronin, S. A. Zvyagin, and M. F. Kharchenko for fruitful discussions.

FIG. 6. Stability diagram of the Mathieu equation for $n = 1, 2$ (see text). Inside the hatched area, the Eq. (5) has no stable solution.