Electromagnons in ferrimagnetic $\varepsilon$-Fe$_2$O$_3$ nanograin ceramics

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(Received 26 November 2012; revised manuscript received 8 August 2013; published 4 September 2013)

Electromagnons are known from multiferroics as spin waves excited by the electric component of electromagnetic radiation. We report the discovery of an excitation in the far-infrared spectra of $\varepsilon$-Fe$_2$O$_3$, which we attribute to an electromagnon appearing below 110 K where the ferrimagnetic structure becomes incommensurately modulated. Inelastic neutron scattering shows that the electromagnon energy corresponds to that of a magnon from the Brillouin-zone boundary. Dielectric measurements did not reveal any sign of ferroelectricity in $\varepsilon$-Fe$_2$O$_3$ down to 10 K, despite its acentric crystal structure. This shows that the activation of an electromagnon requires, in addition to the polar ferrimagnetic structure, a modulation of the magnetic structure. We demonstrate that a combination of inelastic neutron scattering with infrared and/or terahertz (THz) spectroscopies allows detecting electromagnons in ceramics where no crystal-orientation analysis of THz and infrared spectra is possible.

DOI: 10.1103/PhysRevB.88.104301 PACS number(s): 76.50.+g, 72.20.-d, 63.20.kd, 75.85.+t

I. INTRODUCTION

In past years, there has been an increasing interest in so-called multiferroic materials, displaying simultaneously spontaneous ferroelectric (FE) polarization and ferro- or antiferromagnetic (AFM) ordering. Multiferroics exhibit a rich variety of fundamental physical phenomena, and it is generally believed that they have a potential for novel applications in nonvolatile memories, magnonics, and magnetic sensors. It is generally believed that they have a potential for novel applications in nonvolatile memories, magnonics, and magnetic sensors. These applications would rely on the coupling of order parameters on various time scales from quasistatic to ultrafast. However, the understanding of the microscopic mechanism of the magnetodielectric coupling is still a fundamental problem of solid-state physics. The static and dynamic magnetoelectric (ME) couplings can have different origins. Owing to the static ME coupling, the macroscopic FE polarization emerges in the cycloidal or transverse conical modulated magnetic structures; this polarization can change with the magnetic field. In contrast, the dynamic ME coupling generates an oscillatory polarization and leads to a dielectric dispersion in the terahertz (THz) region. Indeed, THz studies of multiferroics revealed a new kind of electric-field-active spin excitations contributing to the dielectric permittivity $\varepsilon = \varepsilon' - i\varepsilon''$, called electromagnons (EMs). Their characteristic feature is a coupling with polar phonons, which manifests itself in the spectra by a transfer of dielectric strength from phonons to EMs on cooling. In contrast to ferromagnetic and AFM resonances, which are magnons from the Brillouin-zone (BZ) center contributing to the magnetic permeability $\mu = \mu' - i\mu''$, the EMs can also be activated outside of the BZ center. The understanding of this fact is not trivial because the photons which excite EMs have wave vectors much smaller than the EMs. Thus, to date, there are several different theories attempting to explain the observed properties of EMs in various materials.

EMs were discovered first in TbMnO$_3$ and GdMnO$_3$, which belong to multiferroics denoted as type II where the FE order is induced by a special magnetic ordering. Since then, EMs were confirmed in numerous type-II multiferroics. Other reports of EMs in type-I multiferroics [e.g., BiFeO$_3$ (Refs. 19–21) or hex-YMnO$_3$ (Ref. 22)] appear inconclusive since no transfer of the dielectric strength from polar phonons to EMs was observed. Also, recent infrared (IR) and THz studies did not confirm the EM in hex-YMnO$_3$. Here, we report experiments which reveal an excitation identified as an EM in the ferrimagnetic $\varepsilon$ phase of Fe$_2$O$_3$. Thanks to its chemical simplicity, this phase also appears as a suitable model system for theoretical studies of electromagnonic excitations. Although $\varepsilon$-Fe$_2$O$_3$ is quite rare and less known than the $\alpha$ (hematite) or $\gamma$ (magnhemite) phases of Fe$_3$O$_4$, its properties make it attractive for applications, such as electromagnetic-wave absorbers and memories. Owing to limited phase stability, it can be synthesized only in the form of nanoparticles tens of nanometers in size, epitaxial thin films, or nanowires a few micrometers long. Below 480–495 K, it is ferrimagnetic at room temperature, it has a collinear spin structure and exhibits a coercive field of $H_C \approx 2$ T (Ref. 31)—the highest known value among metal oxides. The crystal lattice has a temperature-independent noncentrosymmetric orthorhombic structure with the $Pn\bar{a}2_1$ space group (magnetic space group $Pn'\bar{a}2'_1$). It consists of three crystallographically nonequivalent FeO$_6$ octahedra, forming chains along the $a$ direction, and one type of FeO$_4$ tetrahedra. Compared to isostructural GaFeO$_3$, the low-temperature phase diagram of $\varepsilon$-Fe$_2$O$_3$ is complex—below 150 K, a series of magnetic phase transitions occurs. Below $T_m = 110$ K, an incommensurate magnetic ordering appears where the magnetic structure modulation has a periodicity of about ten unit cells. Near $T_m$, a drop in $\varepsilon'$ was observed,
and magnetocapacitive measurements revealed a quadratic coupling. Room-temperature microwave measurements provided evidence of a strong ferromagnetic resonance (FMR) near 0.74 meV (frequency of 180 GHz), which can be tuned by doping with Al, Ga, or Rh. In order to gain insight into the dynamic ME properties of ε-Fe$_2$O$_3$, we obtained THz, IR, and inelastic neutron-scattering (INS) spectra of ε-Fe$_2$O$_3$ nanograin ceramics upon cooling down to 10 K, providing information about polar and magnetic excitations.

II. SAMPLES AND EXPERIMENTAL METHODS

The nanoparticles of ε-Fe$_2$O$_3$ were synthesized by sol-gel chemistry. SiO$_2$-Fe$_2$O$_3$ composite gels containing 30 wt% of Fe$_2$O$_3$ were prepared from iron nitrate nonahydrate (Sigma-Aldrich > 98%) and tetraethoxysilane [(TEOS), Sigma-Aldrich 98%] in a hydroethanolic medium at a TEOS:H$_2$O:EtOH = 1:6:6 molar ratio. Iron nitrate was first dissolved, and then TEOS was added dropwise to the mixture under stirring. The sol was poured into 5-cm diameter Petri dishes that were closed with their covers, and gelation took place after 4 and 5 weeks. The sols were dried at 70 °C, were crushed, and were thermally treated in air atmosphere for 3 h at 1100 °C (heating rate of 80 °C/h). The resulting material was a composite of ε-Fe$_2$O$_3$ nanoparticles of about 25 nm in diameter dispersed in an amorphous SiO$_2$ matrix as checked by x-ray diffraction (XRD), which did not reveal any trace of other Fe$_2$O$_3$ polymorphs. The silica was removed by stirring the composite powder for 12 h in a 12 M aqueous NaOH solution at 80 °C under reflux. XRD patterns recorded after the silica removal revealed that the microstructure and the phase stability of ε-Fe$_2$O$_3$ nanoparticles were not affected by the etching process. The nanoparticles were further processed by spark plasma sintering (SPS) in order to prepare a pellet suitable for dielectric, THz, and IR measurements by pressing the ε-Fe$_2$O$_3$ powder in a graphite mold for 4 min at 350 °C under 100 MPa. The XRD analysis of the sintered pellet showed that the SPS process did not induce any grain growth or phase transformation. Finally, the SPS pellets were polished to thin disks with a thickness of 1.2 mm. Some IR and THz measurements were performed on ε-Fe$_2$O$_3$ pellets with a diameter of about 6 mm, which were prepared from powder at room temperature using a standard tabletop manual hydraulic press (Perkin Elmer). The spectra were qualitatively the same, only the value of the high-frequency IR reflectance was affected by the roughness of the sample surface, which could not be polished.

IR reflectance measurements with a resolution of 0.25 meV were performed using the Fourier-transform infrared spectrometer Bruker IFS-113v in near-normal reflectance geometry with an incidence angle of 11°. An Oxford Instruments Optistat optical cryostat with polyethylene windows was used for sample cooling down to 10 K, and a liquid-H$_2$-cooled Si bolometer operating at 1.6 K was applied as a detector. We also measured far-IR reflectivity with an applied magnetic field up to 13 T. To this aim, another Bruker IFS-113v spectrometer and a custom-made superconducting magnetic cryostat allowing measurements at 2 and 4 K were used. Time-domain THz spectroscopy was based on measurements of sample transmittance using custom-made spectrometers based on Ti:sapphire femtosecond lasers; one with an Optistat cryostat with mylar windows for measurements without a magnetic field but with a higher frequency resolution, enabling us to discern the FMR profile, and one with an Oxford Instruments Spectromag cryostat, enabling measurements with magnetic fields of up to 7 T. Here, the Voigt configuration was used with the external static magnetic field $B_{\text{ext}}$ perpendicular to the magnetic component of the THz radiation $B_{\text{THz}}$. Similar effects were also observed for $B_{\text{ext}} \parallel B_{\text{THz}}$.

INS experiments were performed between 10 and 190 K using about 3 g of loose ε-Fe$_2$O$_3$ nanopowder in the IN4 time-of-flight diffractometer at the Institut Laue-Langevin in Grenoble, France.

III. RESULTS AND DISCUSSION

A. Broadband study of the electromagnetic response

Figure 1(a) shows the far- and mid-IR reflectivity spectra displaying polar optical phonons of ε-Fe$_2$O$_3$ between 10 and 300 K. Figures 1(b) and 1(c) show the far-IR $\epsilon(E)$ spectra calculated from the fits of IR reflectivity together with the experimental THz data. For this purpose, we used a model that the microstructure and the phase stability of ε-Fe$_2$O$_3$ nanoparticles were not affected by the etching process. The nanoparticles were further processed by spark plasma sintering (SPS) in order to prepare a pellet suitable for dielectric, THz, and IR measurements by pressing the ε-Fe$_2$O$_3$ powder in a graphite mold for 4 min at 350 °C under 100 MPa. The XRD analysis of the sintered pellet showed that the SPS process did not induce any grain growth or phase transformation. Finally, the SPS pellets were polished to thin disks with a thickness of 1.2 mm. Some IR and THz measurements were performed on ε-Fe$_2$O$_3$ pellets with a diameter of about 6 mm, which were prepared from powder at room temperature using a standard tabletop manual hydraulic press (Perkin Elmer). The spectra were qualitatively the same, only the value of the high-frequency IR reflectance was affected by the roughness of the sample surface, which could not be polished.

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FIG. 1. (Color online) (a) Lines: IR reflectivity spectra showing polar phonons. Symbols below 8 meV: data calculated from THz spectra. The inset shows, in detail, the low-energy part where, below 8 meV, a new reflection band appears due to the EM. (b) and (c) Fits of the complex permittivity in the far-IR region, obtained from the IR reflectivity spectra using a sum of harmonic oscillators (lines), compared to data obtained from THz spectroscopy (symbols).
 involving 35 harmonic oscillators; this number is lower than the number of IR active modes provided by the factor group analysis (see the Appendix); apparently, a part of the modes is too weak to be observed. Upon cooling, all phonons above 12 meV exhibit the usual behavior—their intensity increases due to reduced phonon damping at low temperatures. The TO1 phonon near 11 meV exhibits an anomalous behavior: On cooling, its intensity increases only down to 115 K. Below this temperature, it markedly weakens, whereas a supplementary cooling, its intensity increases only down to 115 K. Below this temperature, it markedly weakens, whereas a supplementary cooling, its intensity increases only down to 115 K. However, this explanation cannot a priori exclude the hypothesis of activation of the TO1 phonon branch from the area of the BZ near its edge. This would require a folding of the structural BZ, which could be caused by a transfer of the magnetic BZ folding (linked to incommensurability) via magnetostriction. Nevertheless, in the x-ray diffraction studies, no appropriate satellite reflections were observed. Even supposing these satellite reflections to be very weak, one would expect the off-center phonons to also activate at higher energies, which we did not observe. This hypothesis, therefore, seems unlikely.

Based on further experimental evidence, especially in view of an analogous temperature behavior observed by INS, below we argue that the reflection band activated below $T_m$ is most probably an EM.

The temperature-dependent THz spectra (see Fig. 3) reveal the sharp FMR which was previously reported at room temperature. To quantify its temperature behavior, we used the harmonic-oscillator model for all phonons and one term accounting for the FMR in $\mu(E)$ while assuming a smooth dependence of $\varepsilon(E)$ in this interval. The resulting spectra, matching the measured data well, are shown in Figs. 3(c) and 3(d). From the fit parameters, we derived the temperature dependence of the magnon strength and FMR energy [see Fig. 3(e)]. We observe a sharp drop in the resonance energy between 150 and 75 K, very similar to that of the coercive field $H_c(T)$.

Furthermore, we measured THz time-domain spectra with an external magnetic field ranging from 0 to 7 T. Because of the high absorption of the EM, lying near 10 meV, the sample was opaque above 7 meV. Therefore, we could only measure the low-frequency wing of the EM. When the magnetic field is applied, two types of changes in the THz spectra can be observed: an increase in the FMR frequency corresponding to the peak of the $\kappa(E)$ spectra and a change in the slope of both real and imaginary parts of the index of refraction, indicating shifts in the EM frequency with a magnetic field. An example of the former behavior at $T = 100$ K is shown in Figs. 4(a) and 4(b); the FMR frequency, upon applying a static magnetic field, becomes more intense upon cooling [see the inset of Fig. 1(a)].

This transfer of strengths also involves the TO2 phonon (see Fig. 2), evidencing a coupling among these three polar modes. Despite the lattice distortions, which occur between 150 and 75 K, the crystal symmetry of $\varepsilon$-Fe$_2$O$_3$ does not change with temperature. This is further confirmed by our IR reflectivity spectra, displaying a temperature-independent number of phonon polarizations; should a structural phase transition occur, it would imply a change in the factor group analysis and different phonon selection rules. Given the high number of atoms in the unit cell, multiple new reflection bands throughout the IR range would be observed. Therefore, one can exclude the new mode from originating in a structural modification.

Another option to be considered is the polar phonon splitting due to exchange coupling below AFM phase transitions, which was reported in various transition-metal monoxides and chromium spinels; the mode splitting increased on cooling below the Néel temperature. However, this explanation cannot be valid as we observe an opposite temperature dependence—the new mode appears below $T_m$ at low energies and hardens towards the TO1 phonon energy on cooling, i.e., their energy difference decreases.

Finally, one cannot a priori exclude the hypothesis of activation of the TO1 phonon branch from the area of the BZ near its edge. This would require a folding of the structural BZ, which could be caused by a transfer of the magnetic BZ folding (linked to incommensurability) via magnetostriction. Nevertheless, in the x-ray diffraction studies, no appropriate satellite reflections were observed. Even supposing these...
field of $B = 7$ T, increases from 0.6 to 1.3 meV [see the inset of Figs. 4(a) and 4(b)]. The latter phenomenon is illustrated by Figs. 4(c) and 4(d), which trace the values of the complex refractive index at $E = 5$ meV as a function of temperature and applied magnetic field. Although changes only close to the sensitivity level were detected at temperatures of 10 and 300 K (not shown in Fig.4), there is a clear $B$ dependence of the spectra at intermediate temperatures. The highest sensitivity was observed at 100 K, close to the magnetic phase transition. Also, at $T = 75$ K, a marked hysteresis in $B$ occurs, similar to the temperature hysteresis observed by radio-frequency impedance spectroscopy techniques near this temperature (see Fig. 5); this observation will be discussed below. At $T \ll T_m$ where the magnetic structure is probably stable, the changes in $N$ with the magnetic field are smaller. This also explains why we did not detect any significant changes in the far-IR spectra with a magnetic field at $T = 2$ K.

In the frequency range from $f = 10$ Hz to 1 MHz, the complex permittivity $\varepsilon$ was measured by impedance spectroscopy as a function of temperature (see Fig. 6). No sign of a FE phase transition was detected. Above 200 K, both $\varepsilon'(T)$ and $\varepsilon''(T)$ increase due to the leakage conductivity and the related Maxwell-Wagner polarization. Between 100 and 200 K, we observed a steplike decrease in $\varepsilon'(T)$ towards lower temperatures and maxima in losses $\tan \delta(T, f) = \varepsilon''(T, f)/\varepsilon'(T, f)$, which is typical of a dielectric relaxation. The temperature dependence of the relaxation time $\tau(T)$, obtained from the peaks of $\tan \delta(T, f)$, follows an Arrhenius behavior, $\tau(T) = \tau_0 e^{E_0/\kappa T}$ with $\kappa_B$ denoting the Boltzmann constant, $\tau_0 = (1.5 \pm 0.2) \times 10^{-12}$ s, and $E_0 = (0.195 \pm 0.002)$ eV. The origin of this relaxation is not clear; however, similar effects are known from several perovskite rare-earth manganites, including the multiferroics TbMnO$_3$ and DyMnO$_3$. We attribute the relaxation to thermally activated vibrations of the FE domain walls or magnetic domain walls, which can be polar. The huge room-temperature coercive field $H_c$ is a consequence of a single-domain magnetic structure of the nanograins. Below 200 K, $H_c$ strongly decreases due to a transition to a polydomain structure, which explains why the dielectric relaxation exists only in this temperature range.

The inset of Fig. 6 shows the measured dependences of the polarization on an applied electric field. No open FE hysteresis loops nor signs of saturation were observed under the applied fields. Since the $P$n$a$2$_1$ crystal structure of $\varepsilon$-Fe$_2$O$_3$ corresponds to a pyroelectric space group, we cannot exclude that an applied electric field with an intensity higher than the one we used (beyond 5 kV/cm, our sample became leaky) would switch the polarization and that $\varepsilon$-Fe$_2$O$_3$ is, in fact, FE. Actually, one of us recently investigated strained epitaxial $\varepsilon$-Fe$_2$O$_3$ thin films and, under an applied electric field one order of magnitude stronger, observed a room-temperature FE switching. Since the crystal symmetry of $\varepsilon$-Fe$_2$O$_3$ does not change with temperature, one cannot exclude that the $\varepsilon$-Fe$_2$O$_3$ nanograins are also FE already above the ferrimagnetic phase transition occurring near 490 K; in any case, it is, at least, pyroelectric. Consequently, $\varepsilon$-Fe$_2$O$_3$ would belong to type-I multiferroics.

Near 75 K, a small peak in $\varepsilon'(T)$ was observed in our impedance spectroscopy measurements (as marked by the arrow in Fig. 6). This peak is rather weak on cooling, but it becomes more distinct on heating, and it exhibits a temperature hysteresis of $\approx 15$ K (see also Fig. 5). This is reminiscent of a dielectric anomaly typical for pseudoproper or improper FE phase transitions, such as those in perovskite rare-earth manganites. However, this hypothesis is not confirmed by the polarization measurements shown in Fig. 6, and the x-ray and neutron-diffraction investigations did not reveal any structural changes near 75 K. In type-II multiferroics, a narrow dielectric peak is seen at $T_c$ only at frequencies below 1 MHz, and its intensity strongly decreases with rising frequency. By contrast, in our impedance spectra, the peak is present at all frequencies up to the THz region [see Fig. 5(b)], although it is partly covered by the stronger dielectric relaxation at low frequencies. Therefore, this anomaly must originate from phonons or an EM. As the observed dielectric anomaly occurs...
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FIG. 5. (Color online) (a) Temperature hysteresis of the dielectric permittivity (black lines, left axis) and losses (red lines, right axis) observed at 300 kHz. (b) Temperature dependence of the permittivity at 1 THz measured on heating. The dashed line is a guide to the eyes. The values at 300 kHz are systematically higher than at 1 THz due to a small dielectric relaxation between these two frequencies; one can see a similar permittivity peak near 75 K in both experiments. (c) Temperature dependence of relative changes in the 1-kHz permittivity due to a magnetic field with $B = 9$ T (taken on heating).

at a temperature close to the lowest-temperature magnetic phase transition,$^{35}$ we propose that it arises from the transfer of the dielectric strength from the TO1 and TO2 phonons to the EM (see Fig. 2). We note that, in single-crystal multiferroics, often a steplike increase in the permittivity occurs below the temperature where the electromagnon activates.$^{13}$ Our observations on nanograin samples are somewhat different—whereas a steplike increase in $\varepsilon'$ below $\approx 130$ K, superimposed with the narrow-range anomaly near 75 K, was detected in the THz range [see Fig. 5(b)], only the anomaly near 75 K manifests itself in the kHz range [see Fig. 5(a)]. We suppose that the step in the low-frequency permittivity is screened by the observed dielectric relaxation in the microwave range.

We also investigated the dependence of the permittivity at 1 kHz on an external magnetic field up to 9 T. We found that $\varepsilon'(B)$ exhibits the highest changes (almost 2%) near 70 and 130 K [see Fig. 5(c)]. Both of these anomalies are clearly linked to the changes in magnetic structure.$^{35}$ We suppose that the lower-temperature change corresponds to the EM anomaly also observed in THz experiments, whereas that observed near 130 K is due to the relaxation linked to the magnetic and simultaneously polar domain walls.

B. Neutron scattering

In order to further explore the hypothesis of an EM, we performed time-of-flight INS experiments, which allow measuring the phonon and magnon density of states (DOS) in the meV energy range. As the nanopowder does not allow us to directly determine the phonon and magnon dispersion branches in the BZ, the data represent an orientation-averaged scattering function $S(Q,E)$, where $Q$ is the total momentum transfer and $E$ is the energy transferred between the crystal lattice and the neutrons (see Fig. 7). The data reveal a steep column of intense scattering, emanating from magnetic Bragg peaks at $Q = 1.4$ Å$^{-1}$ and extending up to $E \sim 10$ meV. The weaker columns at $Q > 2$ Å$^{-1}$ are due to scattering in higher-order BZs. The fact that the area of most intense scattering is located at low $Q$ unambiguously shows$^{44}$ that the dominant contribution to the low-$Q$ scattering comes from spin waves.

A qualitatively similar magnon response was recently observed in INS spectra of polycrystalline BiFeO$_3$;$^{45}$ the spin-wave character of the excitation was confirmed by INS on BiFeO$_3$ crystals where the magnon dispersion branch was directly measured.$^{46}$ Our scattering from the magnon waves becomes weaker on cooling due to the decreasing Bose-Einstein factor. Around 10 meV, a distinct scattering peak persists down to low temperatures, corresponding to a maximum of the
The inset of Fig. 7(d) shows a schematic of an acousticlike magnon dispersion branch in reciprocal lattice units, involving the FMR and EM near the BZ center and boundary, respectively.

TABLE I. Set of parameters used in the oscillator model to fit the IR reflectance data at 10 K. $\Delta \varepsilon$, $\Delta \Omega_0$, and $\Gamma$ mark the dielectric contribution, eigenfrequency, and damping of polar modes. The first row contains the parameters of the electromagnon, and the other rows describe 35 polar phonons. From mid-IR reflectivity, the high-frequency electronic contribution was obtained as $\varepsilon_{\infty} = 3.2$.

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a guideline for an unambiguous determination of EMs in materials where sufficiently large single crystals for polarized IR and THz measurements are not available.

ACKNOWLEDGMENTS

This work was supported by the Czech Science Foundation (Project No. P204/12/1163). The experiment in ILL Grenoble was carried out at the IN4 spectrometer within the project LG11024 financed by the Ministry of Education of the Czech Republic. M.G. acknowledges funding from the Spanish Ministerio de Economía y Competitividad (Projects No. RyC-2009-04335, No. MAT 2012-35324, and No. CONSOLIDER-NanoSelect-CSD2007-00041) and the European Commission (FP7-Marie Curie Actions, Grant No. PCIG09-GA-2011-294168). S.K. thanks P. Brázda for his stimulation of our ($\varepsilon$-Fe$_2$O$_3$) research and S. Artyukhin for a helpful discussion.

APPENDIX: PHONONS IN $\varepsilon$-Fe$_2$O$_3$

For the orthorhombic $Pna2_1$ crystal structure of $\varepsilon$-Fe$_2$O$_3$ with eight formula units per unit cell, the factor group analysis predicts the following phonon counts and symmetries in the BZ center:

$$\Gamma = 30A_1(z^2, y^2, z^2) + 30A_2(xy) + 30B_1(x, xz) + 30B_2(y, yz).$$  \hspace{1cm} (A1)

Here, $x$, $y$, and $z$ mark electric polarizations of the IR wave for which the phonons are IR active, whereas the rest of the symbols are components of the Raman tensor. After subtraction of the three acoustic phonons, 87 IR-active phonons are expected. We have observed 35 of them (see their parameters in Table I); the remaining ones cannot be identified, either because of low intensities or because they overlap with other ones.

\footnotesize
\begin{itemize}
\end{itemize}
43 D. Nižňanský (private communication). (No change in the Pna2₁ crystal structure was observed in XRD up to 800 K.)