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Observation of Raman Scattering of High-Frequency Phonons by Spin States

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High-frequency acoustic phonons in an Al_2O_3 crystal at low temperature were generated at one frequency (891 GHz) by excitation of V^{4+} impurity ions with a far-infrared laser, and detected at another frequency (874 GHz) by fluorescence from Cr^{3+} ions. A strong detector signal was observed, giving evidence that inelastic phonon scattering occurred. The dependence on magnetic field and temperature indicated that the effect was due to Raman scattering of phonons by spin states.

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In this Letter we report on a first direct observation of Raman scattering of phonons by spin states at low crystal temperatures. To observe a phonon frequency shift we have generated monochromatic phonons of one frequency, and detected phonons of another frequency. By application of recently developed techniques of high-frequency phonon spectroscopy, phonons were generated by use of a far-infrared laser¹⁻³ and detected by phonon-induced fluorescence.⁴ Since the cross section increases strongly with frequency,⁵ high-frequency phonons are most suitable for the study of Raman scattering.

The principle of our experiment, performed on an Al_2O_3 crystal containing V^{4+} and Cr^{3+} impurity ions, is shown in Fig. 1. Monochromatic phonons are generated by far-infrared excitation and relaxation of V^{4+} ions. Far-infrared laser radiation at a frequency ν_{FIR} (891 GHz) is absorbed in the wing of a broad absorption line^{6,7} which is due to an electronic transition between the ground state and the lowest excited state of V^{4+} . Since the V^{4+} ions are excited to forced electronic vibrations by the monochromatic far-infrared radiation, it is expected that the generated acoustic waves have exactly the same frequency ν_{FIR} as the far-infrared radiation.

Phonons at a detector frequency ν_{det} (874 GHz), which corresponds to the separation of the \bar{E} and $2\bar{A}$ levels⁴ of optically excited Cr^{3+} ions, are detected by R_2 fluorescence (Fig. 1). Since the \bar{E}

$\rightarrow 2\bar{A}$ absorption line is very narrow (0.5 GHz),⁸ the detector responds only to phonons in a very narrow frequency band. Surprisingly, phonon generation by excitation of V^{4+} ions with a far-infrared laser yielded an R_2 signal, even though the detector frequency ν_{det} was different (by 2%) from the generator frequency ν_{FIR} . This shows that inelastic scattering of the monochromatically generated phonons occurred.

Before we present further results the experiment will be described in more detail. The Al_2O_3 crystal (size $3 \times 3 \times 5 \text{ mm}^3$) contained 0.3 wt. %

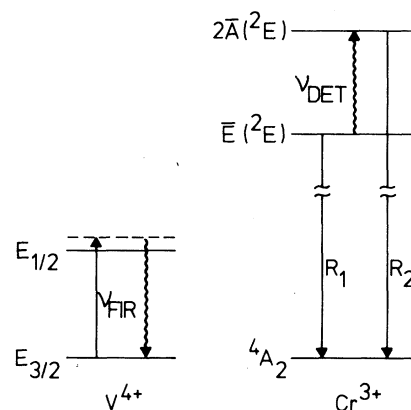


FIG. 1. Energy levels of V^{4+} and Cr^{3+} ions in Al_2O_3 and principle of monochromatic phonon generation and detection. Generator frequency ν_{FIR} and detector frequency ν_{det} are different.

V_2O_5 and 0.05 wt.% Cr_2O_3 .⁹ V^{4+} ions were obtained by x-ray irradiation.⁷ The crystal, which was immersed in liquid helium, was located in a superconducting magnet. Far-infrared radiation from a cw HCN gas laser was focused on the crystal. We estimated from the absorption curve⁶ that about 1% of the incident radiation was absorbed and that the phonon power at 891 GHz was 4×10^{-4} W. Excited Cr^{3+} ions in the \bar{E} level were obtained by optical excitation of the crystal with radiation from an argon ion laser (power 0.1 W). R_2 fluorescence radiation was separated from R_1 radiation with a double-grating monochromator and detected with a photomultiplier. The intensity of R_2 fluorescence due to far-infrared absorption was comparable with that caused by the optical excitation; for discrimination, the far-infrared radiation was chopped and the R_2 signal was detected by a lock-in technique. From the ratio of the modulated R_2 and the (unmodulated) R_1 fluorescence intensities the phonon occupation number n_D at the detector frequency ν_{det} was obtained. Therefore, n_D is a measure for the nonequilibrium phonon population generated by the far-infrared absorption.

The nonequilibrium phonon population was strongly influenced by a magnetic field (Fig. 2). At a crystal temperature of 1.7 K and for the field direction perpendicular to the crystalline c axis ($B \perp c$) n_D has a maximum at $B=0$ and decreases strongly with increasing field strength B . The result gives direct evidence that the inelas-

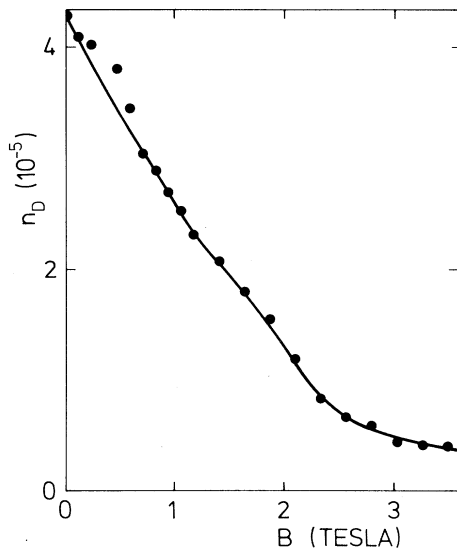


FIG. 2. Phonon occupation number n_D (at $\nu_{det}=874$ GHz) obtained by far-infrared excitation (at $\nu_{FIR}=891$ GHz) at a crystal temperature of 1.7 K and for $B \perp c$.

tic phonon scattering depends on the magnetic field strength. Therefore, we attribute the inelastic scattering to Raman scattering of phonons at spin states.

We note that, for our orientation $B \perp c$, level splittings are small for the generation levels (g factors $g_{\perp} < 0.2$ for $E_{3/2}$ and $E_{1/2}$ of V^{4+})¹⁰ as well as for the detection levels ($g_{\perp} < 0.02$ for \bar{E} and $2\bar{A}$ of Cr^{3+}).¹¹ A magnetic field $B \perp c$ is therefore expected to have only a small influence on phonon generation and detection. This is suggested by experiments for an orientation ($B \parallel c$) where the field dependences of generation and detection levels are stronger ($g_{\parallel} \approx 2$); we found that n_D decreases only slightly (by 20%) in a field range (0 to 0.3 T) where for $B \parallel c$ generation and detection levels become fully split. In the case of $B \perp c$, generation and detection levels become fully split only at high fields (> 3 T) in accordance with the small g factors ($g_{\perp} < \frac{1}{10} g_{\parallel}$). We think that it is therefore justified to attribute the strong $n_D(B)$ dependence (Fig. 2) mainly to a field dependence of the inelastic scattering.

The nonequilibrium phonon population depended also on temperature. While the occupation number at zero field and also the slope of the $n_D(B)$ curve at low fields (up to 1 T) were similar at 1.7 and 4.2 K, large differences were found at high fields (Fig. 3) where n_D increased by a factor of 3 between 1.7 and 4.2 K.

The $n_D(B)$ curves were smooth curves without fine structure. This indicates that the nonequilibrium phonons have a broad frequency distribu-

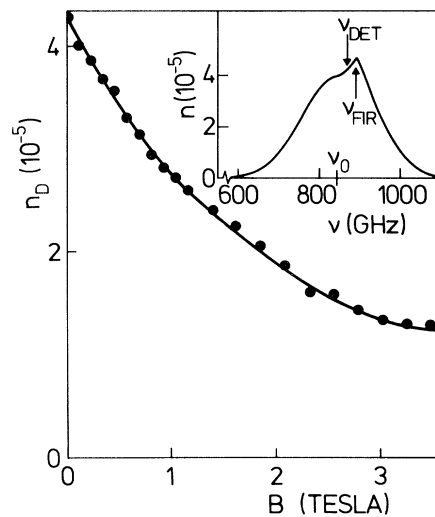


FIG. 3. Phonon occupation number n_D at 4.2 K and for $B \perp c$. Inset: A calculated frequency distribution of nonequilibrium phonons for $B=0$ (see text).

tion. We believe that Cr^{2+} ions are most likely the active inelastic scattering centers. These ions, present in ruby crystals irradiated by x rays,¹² have a Jahn-Teller ground state (5D) with strong electron-lattice interaction. Acoustic paramagnetic resonance experiments (at 8 GHz) showed¹³ that transitions between low-lying energy levels of Cr^{2+} in Al_2O_3 cause magnetic-field-dependent hypersonic absorption with broad absorption bands. It was concluded that Cr^{2+} ions occupy different lattice sites giving rise to a complicated scheme of low-lying energy levels which have magnetic-field-dependent separations, and that inhomogeneous level broadening occurred because of local strains in the crystal.^{13,14} We think that the inelastic phonon scattering observed in our experiment is due to Raman transitions between such low-lying energy levels.

Direct influence of x-ray irradiation on the lifetime of high-frequency phonons was observed for a ruby crystal which contained the same Cr_2O_3 concentration as our double-doped crystal, but no V_2O_3 doping. In this case no far-infrared absorption was found for $B=0$. By magnetic tuning (for $B \parallel c$) of the separation between \bar{E} and $2\bar{A}$ levels of excited Cr^{3+} ions to the far-infrared HCN laser frequency, far-infrared excitation and relaxation of excited Cr^{3+} ions led to generation of phonons directly at the detector frequency. The lifetime of these phonons was decreased by a factor of 5 by x irradiation¹⁵; for the irradiated ruby crystal a phonon lifetime of $\tau_{\text{in}} \simeq 10^{-7}$ s for inelastic scattering was obtained.¹⁵ R_1 fluorescence measurements before and after x-ray irradiation indicated that about 5% of Cr^{3+} ions were converted to Cr^{2+} ions, which is in agreement with other studies.¹² It follows therefore from τ_{in} that the total cross section for inelastic scattering of phonons at Cr^{2+} ions (concentration 10^{18} cm^{-3}) is of the order of 10^{-17} cm^2 (at 891 GHz). An estimate shows that Raman scattering of phonons at sublevels of the 4A_2 ground state of Cr^{3+} cannot explain our experiment; by means of theoretical arguments,⁵ it follows from spin-lattice relaxation times for Raman processes¹⁶ that the cross section for inelastic scattering at Cr^{3+} ions is very small (10^{-25} cm^2). We note that a difference in the electron-phonon interaction of several orders of magnitude between Cr^{2+} and Cr^{3+} as suggested by our analysis is known from other studies.¹⁷

According to the different low-lying energy levels of Cr^{2+} we expect a broad distribution of possible Raman frequency shifts. In a simplified

description, we introduce a mean Raman frequency shift ν_R and take as a mean inelastic scattering time τ_{in} the value obtained for the x-irradiated ruby crystal. We characterize the nonequilibrium phonon population by phonon occupation numbers $n(\nu)$. These are related with one another as a result of inelastic scattering processes with energy gain and loss, respectively. For the stationary conditions of our experiment we obtain the coupled rate equations

$$n(\nu)[\tau^{-1}(\nu) + 2\tau_{\text{in}}^{-1}] = [n(\nu + \nu_R) + n(\nu - \nu_R)]\tau_{\text{in}}^{-1}, \quad (1)$$

where $\tau(\nu)$ is the lifetime of the phonon population $n(\nu)$ at frequency ν for other than the inelastic scattering processes. We assume $n(\nu)$ to be constant in frequency intervals of width ν_R and describe the source term, which has to be added in Eqs. (1) for $\nu = \nu_{\text{FIR}}$, by $q/D(\nu_{\text{FIR}})\nu_R$ where q is the phonon generation rate and $D(\nu_{\text{FIR}})$ the density of states of phonons at ν_{FIR} . An upper limit for $\tau(\nu)$ is the time for diffusive escape of the phonons from the crystal volume. Diffusion occurs as a result of elastic resonance scattering at V^{4+} by transitions between $E_{3/2}$ and $E_{1/2}$ (Fig. 1). From diffusion theory we find

$$\tau(\nu) = \tau_0 [1 + (\nu - \nu_0)^2 / (\frac{1}{2} d\nu_0)^2]^{-1},$$

where $\tau_0 \simeq N\tau_F^2/D(\nu_0)$ is the escape time in the center of the Lorentzian line,⁸ N the concentration of V^{4+} ions, $D(\nu_0) \simeq D(\nu_{\text{FIR}})$, and τ_F a mean ballistic time of flight of the phonons to the crystal surfaces where the energy is transmitted to the helium bath.¹⁸ Considering that the total phonon loss is equal to the generation rate we obtain [with $q \simeq 2 \times 10^{19} \text{ cm}^{-3} \text{ s}^{-1}$, $N \simeq 10^{19} \text{ cm}^{-3}$, $D(\nu_0) \simeq 10^8 \text{ s cm}^{-3}$, $\tau_F \simeq 2 \times 10^{-7} \text{ s}$ and $n_D \simeq 4 \times 10^{-5}$ from Fig. 3] a mean Raman shift ν_R ($\simeq 4 \text{ GHz}$) and $n(\nu)$ shown in the inset of Fig. 3. The phonon population has a maximum at the generation frequency ν_{FIR} and extends over a range of 20% of ν_0 . It follows from our analysis that a single phonon undergoes during its average lifetime ($\langle\tau\rangle \simeq 5 \times 10^{-5} \text{ s}$) a large number of elastic collisions ($\langle\tau\rangle/\tau_F \simeq 10^3$) and also of inelastic collisions ($\langle\tau\rangle/\tau_{\text{in}} \simeq 500$), and that phonon escape occurs mainly via the far wings of the V^{4+} resonance line. We guess that anharmonic phonon decay¹⁹ is slower than diffusive escape and therefore does not influence $n(\nu)$ appreciably. This is in contrast to an extremely short anharmonic lifetime (10^{-7} s) assumed for the interpretation of phonon diffusion in x-irradiated Al_2O_3 containing V_2O_3 (Ref. 3); we think that also in this system low-lying energy

levels can be present and that inelastic scattering can strongly influence the phonon propagation.

We solved (for fixed τ_{in}) Eqs. (1) also for the values of n_D at different fields and found that the $n_D(B)$ curves (solid lines in Figs. 2 and 3) can be described by our model with Raman shifts ν_R which increase with increasing field (at 4.2 K ν_R increases by a factor of 2 and at 1.7 K by a factor of 5 between $B=0$ and 3 T). The field and temperature dependences of ν_R indicate that the separations of the low-lying energy levels of Cr^{2+} increase with increasing field, and that changes of the thermal populations of the levels lead (at 1.7 K) to a freezing out of Raman transitions which have very small frequency shifts. Our results are therefore consistent with spectral phonon diffusion caused by multiple Raman scattering at spin states.

In conclusion, a new spectroscopic technique with high-frequency phonons is demonstrated and first direct observation of Raman scattering of phonons is reported. Our results indicate that Raman scattering can lead to a strong broadening of the frequency distribution of monochromatically generated phonons. We think that Raman scattering of high-frequency phonons as observed in our experiment is a general phenomenon for crystals containing impurities and other defects, and also for glasses.

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