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The temperature dependence of the Raman T_{2g} lattice mode in K_2S crystals

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Abstract

The first-order Raman spectrum of K_2S was measured over the temperature range from 10 to 742 K. The temperature dependence of the linewidth can be explained using results from the anharmonic lattice dynamics approach. Both the cubic and the quartic anharmonic interactions are of importance for this system. At 293 K, the Raman line is at $\omega_{T_{2g}} = 128\ cm^{-1}$ with a full width at half maximum $\Gamma_{T_{2g}} = 2.9\ cm^{-1}$.

Keywords: Potassium sulfide; Ionic conductor; Raman effect; Thermal anharmonicity

PACS: 78.30.Hv; 66.70; 72.80.Ng

1. Introduction

Potassium sulfide, K_2S, is an ionic material crystallizing in the antifluorite structure. Compounds having this structure (e.g. Li_2O, Li_2S, Na_2S) or the antimorphous fluorite structure (e.g. CaF_2, SrF_2, BaF_2) are known to present a high temperature superionic phase with a characteristic temperature (T_c) often hundreds of degrees below their melting point ($T_c \leq 0.8T_m$) [1]. This transition, initially identified through heat capacity measurements versus temperature, where a broad peak was observed around T_c, has been confirmed by further numerous recent investigations using NMR, neutron diffraction, Brillouin and Raman scattering experiments (see Ref. [2] for a general survey). Potassium sulfide is probably the least studied member of this group and information about its thermal and optical properties is still largely absent. A diffuse transition was observed by Dworkin and Breding [3] with the aid of calorimetric measurements as a function of temperature. It begins at approximately 820 K and continues up to the melting point at 1221 K after showing a sharp specific heat maximum at 1050 K. This result was confirmed theoretically by Voronin [4], who analyzed several phenomenological thermodynamic models of superionic disorder using potassium sulfide and strontium chloride as examples. It was thereby confirmed that the temperature-dependent lattice disorder is related to the anharmonic ion–ion interaction potential.

Both the cubic antifluorite and fluorite structures have one Raman-active phonon mode of T_{2g} symme-

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try [the Brillouin-zone center representation is $\Gamma = T_{1u}(\text{acoustic}) + T_{1u}(\text{optic,IR}) + T_{2g}(\text{optic,Raman})$]. Experimental and theoretical studies (see, e.g. Ref. [5]) of the temperature dependence of the Raman spectrum of alkaline-earth fluorides have shown that the quasi-harmonic approximation is often suitable to explain the temperature dependence of the Raman frequency and linewidth. Recent Raman scattering experiments performed in our laboratory on Li_2S [6] were interpreted by using this model [5]. This allowed us to show that, above 850 K [well below the melting point ($T_c \leq 0.55T_m$)], a contribution due to lattice disorder was distinctly present, in addition to that arising from the anharmonic effects. K_2S has crystallochemical properties which are quite different from those of Li_2S. This should influence, among other things, the temperature dependence of the zone center optical vibrations. For these reasons a Raman study of the K_2S compound was performed as a function of temperature. This paper gives the results obtained from crystals and analyzes them with the aid of a model [7–10].

2. Experimental

2.1. Synthesis

Crystalline samples of K_2S were grown in a Bridgman furnace. They all exhibited an orange coloration indicative of the presence of several polysulfides with known low melting points ($T_m(K_2S_2) = 793$ K, $T_m(K_2S_3) = 565$ K). Samples of about 3 to 4 mm in diameter were used for the Raman experiments. Since K_2S is a very hygroscopic compound, preparation and crystal growth were realized under an ultrapure argon atmosphere in a glove box (residual oxygen partial pressure $<10^{-6}$ mmHg).

2.2. Raman scattering

The Raman setup consisted of a 5 W argon ion laser, a 1403 SPEX double monochromator and a cooled 31034-A20 Burle photomultiplier in conjunction with Stanford Research dual channel photon counting equipment. The spectrometer is fully computer controlled through home-built interfaces. Typically, the Raman experiments were made in the 180° scattering geometry with a laser output power of 20 mW at 488 nm and slits set to 100 μm. Low-temperature Raman spectra were recorded using an Oxford Instruments helium flow-through cryostat, whereas the high-temperature spectra were obtained with the aid of a home-built furnace (see Ref. [6], where experimental details are reported) under a 5N Ar atmosphere. The pressure was stabilized during the experiments with the aid of a cold finger immersed in liquid nitrogen. At high temperatures, slight depositions on the inner side of the quartz envelope of the Raman furnace were observed, probably due to the decomposition of the polysulfides present. Further, crystal surface changes were noted.

3. Results and discussion

First-order Raman spectra were obtained in the temperature range between 10 and 742 K. Fig. 1 shows typical spectra recorded at different temperatures. The Raman signal intensity decreased with increasing temperature, and sizeable broadening was observed. Over the whole range the Raman line was found to be Lorentzian. The position and width of the Raman line were accurately obtained by fitting the spectra with this function. The resulting experimental temperature-dependent line width, $\Gamma_{T_{2g}}$, and center frequency, $\omega_{T_{2g}}$, are depicted in Fig. 2. This latter quantity decreased linearly by approximately 15–20 cm^{-1} between room temperature (RT) and 700 K with slope $d\omega/dT = -0.0175$ cm^{-1}/K, while $\Gamma_{T_{2g}}$ increased almost exponentially. The RT values of the center frequency and the line width were: $\omega_{T_{2g}}(293\text{ K}) = 128$ cm^{-1} and $\Gamma_{T_{2g}}(293\text{ K}) = 2.9$ cm^{-1}. Note that the Li_2S zone center Raman line at RT has parameters: $\omega_{T_{2g}} = 372.6$ cm^{-1}, $\Gamma_{T_{2g}} = 10.8$ cm^{-1} [6]. The temperature dependence of the Raman line width must be accounted for by including cubic as well as quartic anharmonic contributions to the harmonic crystal potential (see, e.g. Ref. [8] for a general reference). K_2S (and Li_2S) has a rather low and consequently highly anharmonic potential barrier between normal and interstitial cationic sites in the antifluorite-type structure, which favors the

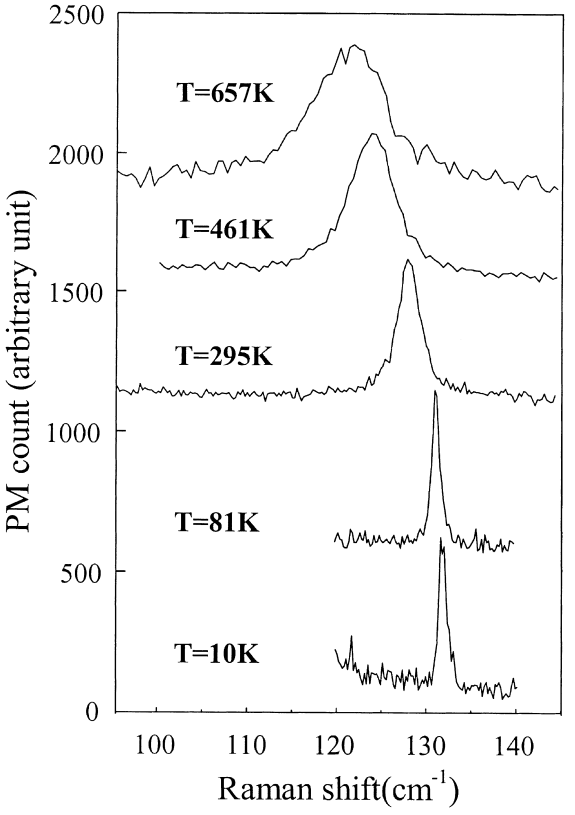

Fig. 1. Unpolarized Raman spectra of the T_{2g} phonon mode in K_2S as a function of temperature.

importance of these terms. Breakdown of the model of the harmonic crystal indeed produces the mechanisms which allow the optical phonon $h\omega_{T_{2g}}$, formally created by the light scattering process, to decay into several ones of lower energy. The following analytical expression for $\Gamma_j(T)$ is obtained by assuming thermal equilibrium of the phonons and under the simplifying hypothesis that the processes considered produce the decay of one optical phonon into two or three acoustical ones, respectively, of mutually the same frequency (i.e. $\omega_a = \frac{1}{2}\omega_{T_{2g}}$, $\omega_b = \frac{1}{3}\omega_{T_{2g}}$). It is based on second- and third-order perturbation contributions in the vibrational part within the quasiharmonic lattice dynamics model [7,8,10]:

$$\Gamma_j(T) = \Gamma_0 + a\left(n_a + \frac{1}{2}\right) + b\left[\left(n_b + \frac{1}{2}\right)^2 + \frac{1}{12}\right], \quad (1)$$

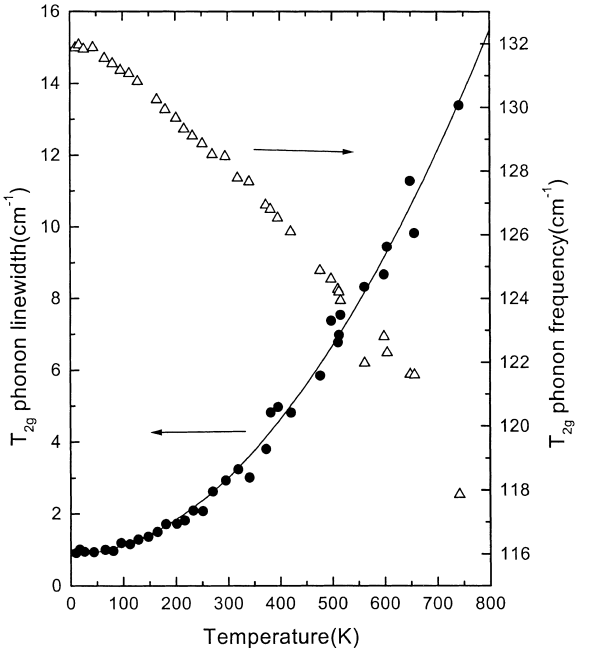

Fig. 2. Temperature dependence of the T_{2g} phonon frequency (△) and of the line width (●).

where Γ_0 is the residual broadening due to static lattice imperfections, $a/2$ and $b/3$ are constants, and the phonon occupation numbers $n_a = n_a(\omega_a)$, etc. are given by the Bose–Einstein statistics. The second term on the right-hand side of Eq. (1) is due to the cubic anharmonicity, while the third term arises from the quartic terms. A Matlab program using the Nelder–Mead simplex method was written to obtain the best fit between the model and the experimental data. Close agreement was obtained (model: solid line in Fig. 2) from 10 to 700 K. The values of the three parameters are given in Table 1, together with the corresponding quantities for Li_2S [6]. A second fit of the model was further performed by treating ω_a and ω_b as additional free parameters. The result is

Table 1
Least-square fitted parameters of Eq. (1)

Compound	Γ_0 (cm^{-1})	a (cm^{-1})	b (cm^{-1})	b/a
K_2S[a]	0.818	0.048	0.088	1.83
Li_2S[b]	4.21	0.572	1.862	3.26

[a] This paper.
[b] Ref. [6].

that the values of the constants Γ_0, a and b are very similar to those given in Table 1 and $\omega_a = 68.8\ \mathrm{cm}^{-1}$ and $\omega_b = 44.2\ \mathrm{cm}^{-1}$. This result is an additional argument for the applicability of the model initially developed by Wallis et al. [7]. The constants Γ_0, a and b (Table 1) relating to K_2S are significantly smaller than those for Li_2S. This may be related to the mass of the respective cations, but confirmation of this hypothesis has to await knowledge of the dynamical matrix. Comparison of the ratio b/a (see Table 1) for Li_2S and K_2S shows that the effect of the quartic anharmonicity is *reduced* by approximately a factor of 2 in the latter lattice. Possibly, this is related to the density of phonon states. The experimental Raman spectra show, even at RT, a broad low-frequency band due to slight breakdown of the $\vec{k}_{\mathrm{result}} \cong 0$ selection rule of the Raman process by static defects and anharmonicity. The peak of this feature is at around 64 cm^{-1} for K_2S. Li_2S has a maximum in the acoustic phonon part of the spectrum between 120 and 140 cm^{-1}. As these peaks correspond quite closely to a maximum in the density of acoustic phonon states the corresponding decay channels are probably favored. It is difficult, however, to make any quantitative progress as long as no experimental neutron scattering results are available for K_2S.

Finally, the remarkably smaller $T = 0$ K residual line width in K_2S in comparison with that in Li_2S may be due to the zero point energy of the host cation. Note that the eigenvectors of the harmonic zone center T_{2g} vibration are determined by the sole cation displacement coordinates. Lower zero point energy corresponds to less influence of the anharmonic potential. Additionally, the crystal quality of our Li_2S samples was always better than that of K_2S.

The strong broadening of the T_{2g} line as well as the rather low S/N obtained at temperatures above 700 K did not permit us to confirm unambiguously the existence of a diffuse phase transition around 820 K. Experiments with a very good S/N would be required in this temperature domain.

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