

1997

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Raman-scattering study of the order-disorder phase transition in KSCN

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(Received 9 May 1997)

Raman measurements were performed from room temperature to above the phase transition at 413 K on KSCN crystals. The internal mode spectra reveal a sideband above the internal CN stretching vibration which shows softening in frequency approaching the phase transition, while the CN mode shifts toward higher frequencies. Given that the sideband is a two-phonon process, involving an off-zone-center CN stretching mode and a lattice phonon, the substantial softening in its frequency shift indicates the possibility of an off-zone-center lattice instability related to the order-disorder phase transition. An anomalous temperature dependence was also found for the intensity of both the CN mode and the sideband. The relatively high intensity of the sideband was analyzed in terms of a substantial Fermi resonance coupling between the internal mode and the sideband. [S0163-1829(97)07546-2]

KSCN and other thiocyanates are of interest as systems containing triatomic linear SCN^- units which show orientational disorder at elevated temperatures.^{1,2} KSCN crystallizes at an ordered orthorhombic structure of $D_{2h}^{11}-Pbcm$ symmetry at room temperature. There are four KSCN molecules in the primitive cell in this phase and the four linear SCN^- clusters lie on the [001] plane. As the temperature is raised, the triatomic SCN^- ions are thermally activated to be able to flip between (110) and ($\bar{1}\bar{1}0$) directions within the [001] plane, which correspond to two minima in the orientational potential surface. When the temperature is increased to $T_c=413$ K, the SCN^- ions become able to reorient between these two minima, like the NO_2^- ions in NaNO_2 above the high-temperature phase transition,⁴ and the system undergoes a λ -type phase transition into a disordered tetragonal phase of $D_{4h}^{18}-I4/mcm$ symmetry (two units per primitive cell). The tetragonal symmetry of the high-temperature phase rests on, in addition to the equivalence of **a** and **b** lattice constants, a random distribution of the SCN^- ions between the two orientations of equal minimum energy.¹

There have been several spectroscopic investigations of the order-disorder transition in $R\text{SCN}$ systems (where R is either K, Rb, or Cs).^{3,5-10} These studies focused on the temperature dependence of the Γ -point vibrations and have shown that the phase transition in such systems is accompanied by anomalies in the vibrational spectra.^{3,8-10} The major concerns of these studies have been to address lattice effects on the transition, to determine the potential barrier for the reorientation of SCN^- ions, and to extract the critical exponent of the order parameter from the phonon data. However, other aspects, such as the possibility of an off-zone-center instability and the relation of the internal vibrations to the order-disorder phase transition, also deserve attention.

An off-zone-center phonon anomaly was discussed in the context of the order-disorder phase transition in systems such as NH_4Br .^{11,12} For KSCN such an instability was suggested in a recent review¹ from the form of the order parameter, but no more direct proof of this has been reported. However, the SCN^- bending and the CS stretching modes, at 480 and 750 cm^{-1} ,⁹ respectively, exhibit frequency softening approach-

ing T_c ,¹⁰ which indicates substantial coupling to the lattice motions and significant involvement in the order-disorder phase transition. Similarly, the CN stretching vibration at 2060 cm^{-1} (Ref. 10) shows hardening around the transition.

In this work, we will present a Raman study of single-crystal KSCN with emphasis on the lattice instability and anharmonicity. The temperature evolution of the spectra of the CN internal mode region was followed very closely, revealing anomalous changes of both the CN stretching mode and a sideband above it. The most interesting feature is that the sideband exhibits a substantial softening of ~ 12 cm^{-1} between 300 K and the phase transition. Assuming that the sideband is a two-phonon process involving an off-zone-center lattice phonon and an internal mode with the opposite wave vector, this softening indicates a possible off-zone center instability of the lattice accompanying the phase transition. Also, the relatively high intensity of the sideband suggests a substantial anharmonic coupling between the CN internal mode and the lattice vibration. As we should show, a simple two coupled oscillator model gives a nearly linear temperature dependence for this anharmonic coupling.

Single crystals of KSCN were grown by slow evaporation of a saturated acetone solution of commercially available KSCN powder.¹³ The crystals obtained were transparent and colorless. They are of cuboid shape with mirrorlike surfaces, and typically $2\times 2\times 4$ mm in size. As pointed out in Ref. 13, the long dimension direction of a crystal prepared this way indicates the c axis, and each rectangular surface is parallel either to the [110] or to the [$\bar{1}\bar{1}0$] plane. Assuming this is the case for the orientation of our crystals, we characterized our sample by measuring Raman spectra in various configurations. The spectra obtained agree very well with those of the same symmetry for KSCN reported in the literature.⁶

The Raman measurements were performed with a double monochromator, standard photon counting electronics, and a Spectra Physics Ar^+ laser as excitation source. A home-designed heating device was built for the high-temperature measurements. Because of the size of the crystals and their mirrorlike surfaces, no polishing was done on the measured samples. The spectra were recorded between 300 K and

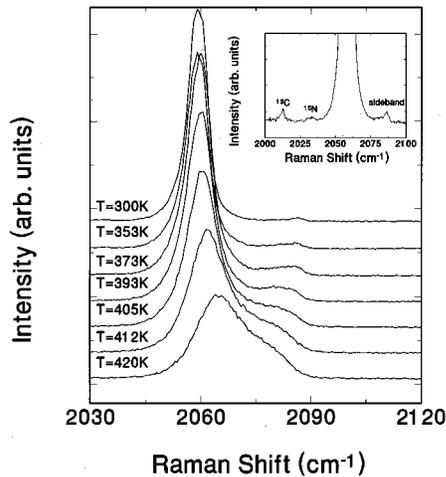


FIG. 1. Series of A_g Raman spectra taken at $T=300, 353, 373, 393, 405, 412,$ and 420 K, respectively. The curves are displaced upwards evenly along the intensity axis for clarity. Note the change of the line shape of the sideband with temperature. The inset is an enlargement of the weak peaks of the room-temperature spectrum for clarity.

above T_c in the 90° geometry with the 514.5 nm laser line. The temperature reading from the temperature sensor was calibrated using the anti-Stokes and Stokes intensities, and temperatures quoted below are the corrected values.

In this work we will focus on the CN internal mode region only. The remainder of the spectra will be discussed elsewhere. According to group-theory analysis,^{3,5} all three internal modes can appear in both the A_g and B_{1g} spectra of the crystal. The room-temperature spectra of various geometries have been well documented in literature, here we present only (X', Y') , where X' and Y' designate the **ab** diagonal and its perpendicular, geometry spectra which select the A_g symmetry component. Figure 1 shows a series of spectra taken at various temperatures between 300 and 420 K.

The strongest peak at 2059 cm^{-1} in the room-temperature spectrum is the CN stretching mode. In addition, weak peaks are observed at $2013, 2032,$ and 2086 cm^{-1} . The first two peaks are due to the ^{13}C and ^{15}N isotopes. Since, as already reported,^{3,7} the vibrational spectra of the KSCN are rich in multiphonon processes,^{6,7} the peak at 2086 cm^{-1} was reported in Ref. 7 among other multiphonon features and was considered to be a two-phonon scattering process involving the CN internal mode and a lattice phonon. Usually a two phonon process consists of phonons with wave vectors from some special points of the Brillouin zone where the density of state is high.³ Such points, called critical points, can occur at the center or the edges or in some case along the high-symmetry lines of the Brillouin zone. However, in the present case, assuming that the two-phonon argument is valid, the zone center possibility can be ruled out, since there is no match between the frequency of any of the lattice phonons¹⁴ and the frequency difference between the CN mode and the sideband, which is about 27 cm^{-1} at room temperature. Thus, the sideband must involve contributions from the points away from the zone center. However, since there is no experimental information on the phonon-dispersion curves of KSCN, it is hard to tell if the sideband is

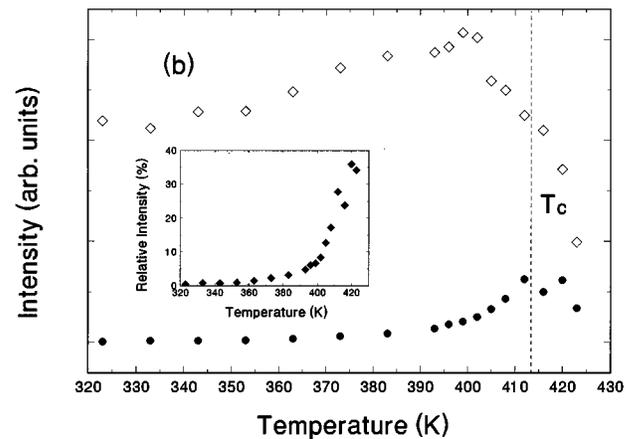
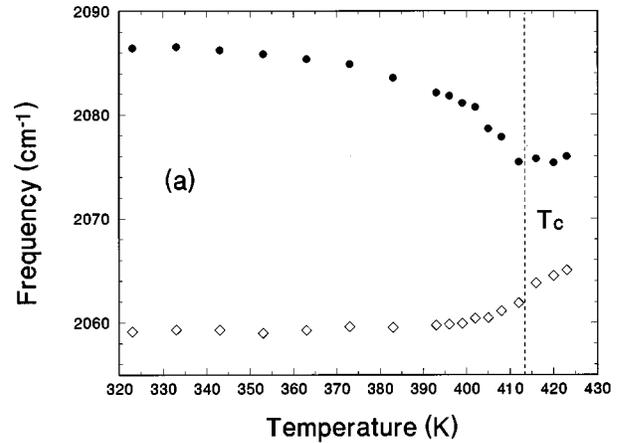


FIG. 2. The temperature dependence of the frequency (a) and the integrated intensity (b) of the CN internal mode (\diamond) and the sideband (\bullet). The softening of the sideband and the hardening of the CN mode are clearly seen in (a). The inset in (b) shows the change of the ratio of the intensity of the sideband to that of the CN mode with temperature.

a difference or a combination process. In addition, one has to note that usually a two-phonon process is rather weak because its intensity depends on the second derivative of the polarizability.¹⁵ This relatively high intensity of the sideband, especially at higher temperatures, we ascribe to anharmonic coupling to the neighboring CN mode as discussed below.

As the temperature is raised, one can see very marked changes in the two peaks as shown in Fig. 1, specifically: (1) the CN mode becomes less intense at higher temperature, while the sideband becomes stronger, (2) the two peaks become closer as the temperature rises, as the CN mode is shifting to higher frequency, while the sideband is softening, (3) while the line shape of the CN mode stays basically Lorentzian over the whole temperature range, the profile of the sideband changes with temperature: being quite asymmetric at room temperature and becoming symmetric at higher temperatures, (4) both peaks broaden markedly with increasing temperature.

In order to understand these changes, we fit the spectra with two Lorentzians plus a constant background, recognizing that a single Lorentzian may not be fully adequate for the sideband at the lower temperatures. In Figs. 2(a) and 2(b) we show the fitted frequencies and the integrated intensities, re-

spectively. The frequency of the CN mode does not seem to be influenced by temperature until about 400 K, then, it begins to increase, reaching 2064 cm^{-1} at T_c . This increase continues above T_c but with a reduced slope. On the other hand, the sideband starts to decrease in frequency just above room temperature, and softens by about 12 cm^{-1} at T_c . After the phase transition, the frequency of the sideband stays almost a constant. As regards the intensity change of the two peaks [Fig. 2(b)], one interesting feature is that the intensity of the CN mode, after increasing linearly from room temperature, begins to fall above 400 K. This is almost the same temperature at which the hardening of the frequency of the CN mode begins. This may indicate a precursor anomaly beginning about 15 K below T_c . The intensity of the sideband shows a continuous nonlinear increase toward T_c , from less than 1% of that of the CN mode at room temperature to about 30% at T_c . Such a dramatic change cannot be simply explained by the thermal occupation factors, as is usual for two-phonon processes in a harmonic system. The relative strength of the sideband in this case, as we mentioned above, is due to anharmonic coupling to the neighboring CN mode. Such a coupling, between a two-phonon process and a one-phonon state, is usually referred to as Fermi resonance previously observed in other solids.¹⁶ To treat this resonance we take a quasiharmonic mode coupling analysis by neglecting the damping¹² and assume that the phonon density of states does not change significantly with the temperature. With ω_s and ω_{CN} being the unperturbed frequency of the sideband and the CN mode, respectively, the new eigenfrequencies and eigenvectors, after allowing for the coupling, are determined by the following matrix equation:

$$\begin{pmatrix} \omega_s & V \\ V & \omega_{\text{CN}} \end{pmatrix} \begin{pmatrix} C_{s,\text{CN}}^1 \\ C_{s,\text{CN}}^2 \end{pmatrix} = \Omega_{s,\text{CN}} \begin{pmatrix} C_{s,\text{CN}}^1 \\ C_{s,\text{CN}}^2 \end{pmatrix}, \quad (1)$$

where $\Omega_{s,\text{CN}}$ represents the renormalized frequencies of the two coupled modes, V is the coupling constant, and $C_{s,\text{CN}}^1$ and $C_{s,\text{CN}}^2$ are the two coefficients describing the admixture of the two initial modes after the coupling. Equation (1) gives

$$\Omega_{s,\text{CN}} = \frac{(\omega_s + \omega_{\text{CN}})}{2} \pm \sqrt{\left(\frac{\omega_s - \omega_{\text{CN}}}{2}\right)^2 + V^2}, \quad (2)$$

and the new eigenvectors $|\Omega_{s,\text{CN}}\rangle = C_{s,\text{CN}}^1|\omega_s\rangle + C_{s,\text{CN}}^2|\omega_{\text{CN}}\rangle$ are given by

$$C_{s,\text{CN}}^1 = \frac{V}{\Omega_{s,\text{CN}} - \omega_s} C_{s,\text{CN}}^2, \quad (3a)$$

$$(C_{s,\text{CN}}^1)^2 + (C_{s,\text{CN}}^2)^2 = 1. \quad (3b)$$

If $\Delta\omega = \omega_s - \omega_{\text{CN}}$ and $\Delta\Omega = \Omega_s - \Omega_{\text{CN}}$ represent the frequency differences of the two modes before and after the perturbation, then Eq. (2) can be reduced to

$$\Delta\omega = \sqrt{(\Delta\Omega)^2 - 4V^2}. \quad (4)$$

Assuming the Raman activity of the sideband is negligible (≈ 0) compared to the CN internal mode before the pertur-

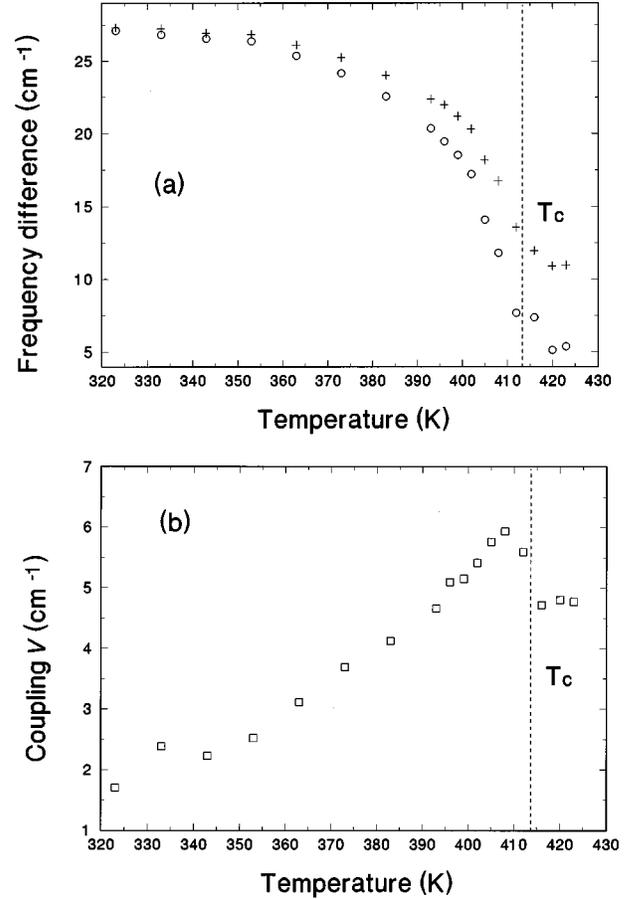


FIG. 3. The coupling between the CN mode and the sideband was estimated using a two coupled oscillator model. (a) The bare frequency difference (O) obtained from this mode coupling calculation is plotted, together with the observed value (+), against temperature. (b) shows the nearly linear temperature dependence found for the coupling parameter V .

bation, then the Raman intensity of the renormalized modes $I(|\Omega_{s,\text{CN}}\rangle)$ is proportional to the square of the eigenvector component of $|\omega_{\text{CN}}\rangle$, i.e., $I(|\Omega_{s,\text{CN}}\rangle) \propto (C_{s,\text{CN}}^1)^2$. The ratio of these intensities can be calculated using Eqs. (2)–(4) as

$$r = \frac{I(|\Omega_s\rangle)}{I(|\Omega_{\text{CN}}\rangle)} = \frac{V^2 + (\Omega_{\text{CN}} - \omega_s)^2}{V^2 + (\Omega_s - \omega_s)^2}. \quad (5)$$

From Eqs. (4) and (5) the coupling V then can be obtained

$$V = \frac{\Delta\Omega \sqrt{r}}{1+r}. \quad (6)$$

Note that both the ratio of intensity r and the frequency difference $\Delta\Omega$ of the two renormalized modes can be deduced from the experimental data, and therefore, the bare frequency difference $\Delta\omega$ and the coupling V can be obtained using Eqs. (4) and (6).

Using the experimentally determined values of r and $\Delta\Omega$, we obtain the values of $\Delta\omega$ and V and their temperature dependence which are plotted in Figs. 3(a) and 3(b). It can be seen that the bare frequency difference $\Delta\omega$ changes by more than 70% approaching T_c . Such a softening, about 20 cm^{-1} , is far larger than that observed previously^{1,3,8,9} for any mode

of KSCN. Also, the coupling V shows a nearly linear increase with temperature up to T_c with a slope of about $5.56 \times 10^{-2} \text{ cm}^{-1}/\text{K}$, and decreases after the phase transition. The magnitude of the coupling V is comparable to the frequency shifts of the CN mode and the sideband. However, it should be noted that even at $T \sim T_c$ V is only about 0.25% of the frequency of the CN mode. As regards to the specific origin of this coupling, one possibility we would suggest, is that it is due to rotational-librational interaction in the SCN^- molecule. Specifically the CN stretching mode causes a fluctuation in the rotational moment of inertia. Thus, in the crystal, it affects the frequency of the SCN^- librational motions involved in the various low-lying lattice modes. Hence the sideband and its dramatic softening probably reflects a strong

decrease in the librational frequency, to the point that, at T_c , the librations transform to hindered 90° rotations.

In summary, both the CN internal mode and the sideband were found to exhibit anomalous changes on approaching the order-disorder phase transition of KSCN. The sideband shows a substantial softening suggesting strong involvement of an off-zone-center lattice instability in the order-disorder transition. In addition, a quasiharmonic mode coupling model is employed to calculate the Fermi-resonance-type coupling between the CN mode and the sideband.

This work was supported by the U.S. Army Research Office under Grant No. DAAG-55-97-1-0106. We thank R. Kirby, W. N. Mei, R. Feile, and E. Sherman for helpful discussion.

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