Neutron scattering studies of $(CN)^-$ defects in KBr

J. M. Rowe and J. J. Rush
National Measurement Laboratory, National Bureau of Standards, Washington, D.C. 20234

S. M. Shapiro
Brookhaven National Laboratory, Upton, New York

D. G. Hinks and S. Susman
Argonne National Laboratory, Argonne, Illinois 60439

(Received 8 January 1980)

We have studied both the librational and the tunneling excitations of $(CN)^-$ ions in a KBr matrix through the interaction of these modes with the acoustic phonons of the KBr host. From our measurements on a sample containing 0.00034 mole fraction of KCN in KBr, we find the A_{1g}-T_{2g} tunnel splitting to be 0.28 ± 0.05 meV (2.3 ± 0.4 cm^{-1}). From measurements on a more concentrated system, 0.0045 mole fraction of KCN in KBr, the A_{1g}-E_g librational excitation energy is found to be 1.6 ± 0.1 meV (13.0 ± 1.0 cm^{-1}). These values are consistent with the results of optical measurements.

I. INTRODUCTION

The rotational energy levels of $(CN)^-$ ion impurities in alkali halide hosts have been extensively studied[1] by optical techniques for many years. In recent years, the optical techniques have been extensively developed by Lüty, Beyeler, and co-workers[2–7] to allow definitive measurements from which the equilibrium orientations of the $(CN)^-$ ions could be inferred with a high degree of confidence. In addition,[4] assignments of the optical excitations to particular transitions were made by using relative intensities calculated from modifications of the Devonshire model.

The interaction of these rotational levels with the phonons of the host crystal were first studied by Walton *et al.*[8] using neutron scattering for 0.004 mole fraction of KCN in KCl. These data were first interpreted in terms of the [100] model for equilibrium orientations which was then generally accepted.[1] The data were later reinterpreted[9,10] in terms of the now generally accepted [111] model. The data and subsequent analysis showed that there was a strong resonant interaction which caused a large perturbation in the host modes, through which the librational level could be seen. Casella[11] has analyzed the neutron scattering and optical data, and has shown that the neutron scattering measurements are governed by strong selection rules dictated by the necessity for formation of coherent resonances. This approach will be utilized in the analysis of the present results.

The interaction of phonons and rotational levels has also been studied by Windheim[12] in KCl crystals containing 1 ppm of KCN using tuneable monochromatic phonons generated and detected by superconducting tunneling junctions. By measuring the stress dependence of the absorption, he was able to confirm the [111] orientations of $(CN)^-$ found by Lüty,[2] and also the tunnel splitting Δ was determined, which was in good agreement with the optical result. More recently,[13] the tunnel splittings for KCN in KCl have been measured by paraelastic resonance techniques. In this work, the different symmetry tunnel splittings were resolved, and the average splittings agreed well with previous measurements.

In the present paper, we present the first results obtained for the interaction of the tunneling modes with the equilibrium distribution of acoustic phonons as measured by neutron scattering. In addition, we have observed the interaction of librational modes with the [110] phonons in KBr.

II. EXPERIMENTAL DETAILS

The samples were large (approximately 5 cm^3) single crystals grown from the melt by the techniques[14] used earlier for pure KCN. Two crystals were grown for these measurements. The first, used for the tunneling studies, had a very small concentration of KCN in KBr. The analysis for CN concentration was performed by determining the infrared absorption constant to be 197 cm^{-1} at 2088 cm^{-1}. Using this number and a measured total path length for the crystal, we determined the average CN concentration to be 0.00034 mole fraction $(CN)^-$. In this crystal, infrared analyses show no impurities other than $(OCN)^-$, for which the concentration was less than 0.1 parts per billion.

The second crystal, which was used for the studies of librational modes, had a concentration of 0.0045 mole fraction KCN in KBr. This concentration was also determined by infrared analysis, and the level of impurities was similar to that quoted above for the low-concentration sample. The lattice parameter of both samples at $T=4.2$ K was measured to be 6.546 Å.

The experiments on the higher-concentration sample were performed on triple-axis spectrometers at the NBS reactor under varying conditions of energy resolution. In general, the scans were performed at constant momentum transfer with either the incident or scattered energy fixed at 5.025 meV. A typical collimation was 40-20-20-40 minutes of arc before and after the monochromator and analyzer, respectively. The sample was mounted in a fixed temperature cryostat at either 4 or 77 K, and measurements were performed along the [100] or [110] directions with a [001] axis vertical.

The experiments to study tunneling modes in the low-concentration sample were performed on a triple-axis spectrometer at the High Flux Beam Reactor at Brookhaven National Laboratory. The Be-filtered incident energy was fixed at 4.5 meV, with collimations of 20 min of arc before and after the monochromator and analyzer. The sample was mounted with an [001] axis vertical in a liquid-helium cryostat in which the temperature could be varied from 1.5 to 20 K by pumping on the bath or by heating, respectively.

III. THEORETICAL PREDICTIONS

The interaction of the rotational modes of isolated $(CN)^-$ defects with the normal modes of the host crystal have been studied by several authors.[10,11,15,16] We shall primarily use the results of Casella[11] in what follows. The principal result of this analysis is that the rotational excitations (both tunneling and librational) lead to *coherent* states mixed with the phonon (when the rotational states are otherwise well defined) and that by measuring the normal modes in particular directions by neutron inelastic scattering, one can directly measure the excitations to excited states of either T_{2g} or E_g symmetry from the A_{1g} ground state. In this case it is interesting to note that the selection rules for neutron scattering are very restrictive, more so than for light scattering. Thus, the neutron measurements can be used to assign some of the energy levels of the rotational system *unambiguously,* giving additional constraints on the interpretation of the optical data.

The key to this result is that, in contrast to the case for optical spectroscopy, neutron scattering couples so weakly to the defects themselves at low concentrations that the only observable effects are due to resonant perturbations of the host crystal lattice modes, as was first shown by Walton *et al.*[8] Casella[11] has showed that if one measures the phonon-dispersion relations for the $[110]T_{x\bar{y}}$ and $[100]T_y$ branches (where the subscript indicates the direction of the phonon polarization vectors) then the energy at which the phonon branches show evidence of strong interaction (i.e., where the neutron scattering line shape is resolved into two distinct peaks of equal intensity) gives directly the energy difference between the A_{1g} ground state and the E_g or T_{2g} excited states, respectively. The observations of a low-lying librational E_g state in KCl (Ref. 8) and KBr (present work) directly rule out the existence of [100] equilibrium orientations for the $(CN)^-$ ions, in good agreement with the conclusions of Lüty,[2] Beyeler,[3] and Windheim[12] that the $(CN)^-$ ions are oriented along [111] directions. However, Casella further predicts that *if* the T_{2g} librational state is close in energy to the E_g state, one should also see a strong interaction in the $[100]T_y$ mode, which we do not observe in KBr, although it was carefully looked for (see Sec. IV).

Thus, the experimental procedure is to study the $[100]T_y$ and $[110]T_{x\bar{y}}$ modes as a function of wave vector for energies near to those expected for the rotational energy levels. The existence of strong interactions is manifested by a splitting of the neutron scattering line shapes[9,10] due to the resonant nature of the mode coupling when the energy of the rotational modes in the absence of interactions equals the energy of the unperturbed phonon modes.

The measurements must be performed at low temperatures in order that only the tunnel-split ground states be occupied, and at low enough concentrations that defect interactions do not broaden the rotational states so much as to make them unobservable. Previous optical results[2,3] have shown that these limits are approximately 0.005 and 0.0005 mole fraction KCN for the librational and tunneling modes, respectively. From the earlier ultrasonics data of Byer and Sack[17] on the relative changes in ultrasonic velocities for E_g and T_{2g} symmetry strain modes for $(CN)^-$ in KBr, we estimated that at least the T_{2g} ground-state tunneling mode for a concentration of 0.0004 should be observable. Based upon the results of Walton[8] and Nicklow,[9] we chose a concentration of 0.0045 to study the librational modes. For this latter experiment we concentrated on a search for T_{2g} modes, although we also measured the E_g mode.

IV. RESULTS

The results of our scans on the 0.0045 sample at 5 K on the $[110]T_{x\bar{y}}$ branch are shown in Fig. 1 for a range of reduced momentum transfers (units of $2\pi/a$ where a is the lattice parameter) which spanned the

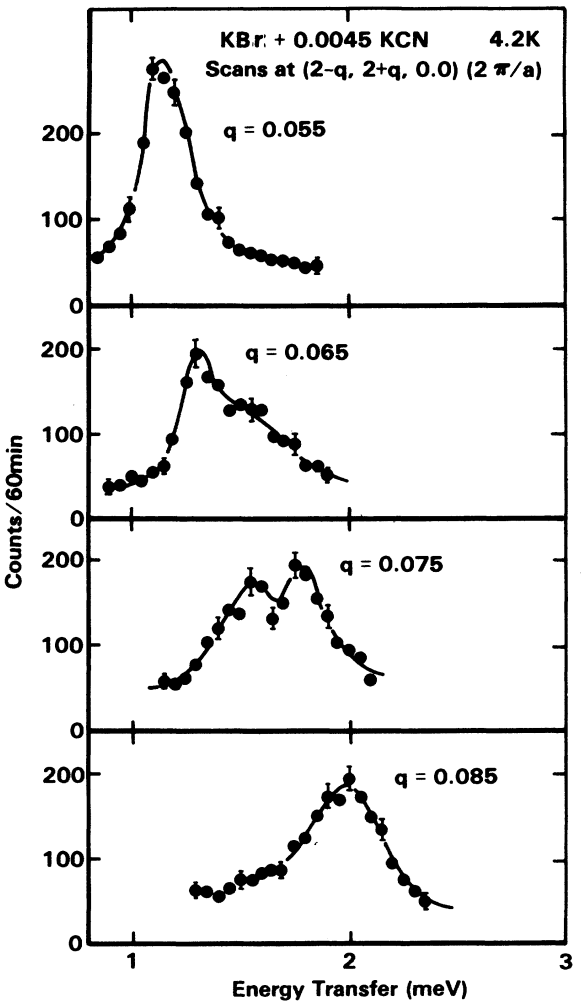

FIG. 1. Neutron scattering line shapes observed for KBr plus 0.0045 mole fraction KCN, measured at points $(2-q, 2+q, 0)(2\pi/a)$ at 4.2 K. This corresponds to the $[110]T_{x\bar{y}}$ branch of the phonon-dispersion relation. Solid lines are only a guide to the eye.

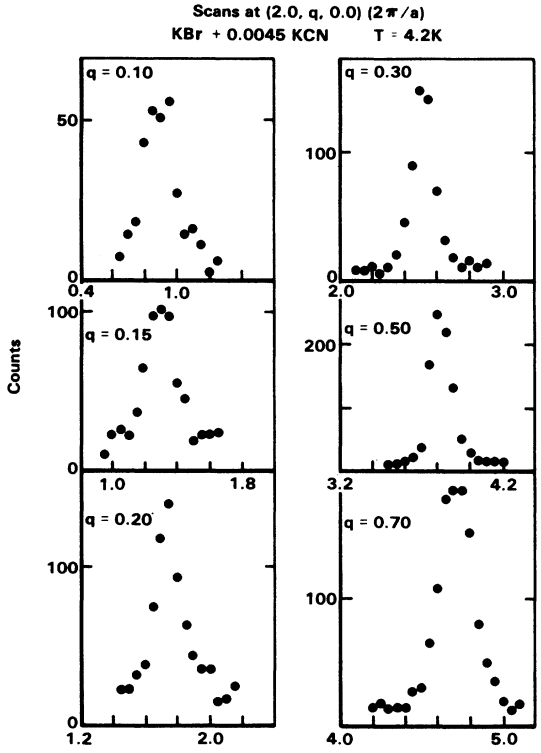

FIG. 2. Selected neutron scattering line shapes observed for KBr plus 0.0045 mole fraction KCN, measured at points $(2,q,0)(2\pi/a)$ at 4.2 K. This corresponds to the $[100]T_y$ branch of the phonon-dispersion relation.

energy region of strong interaction. From these data, we estimate the $A_{1g}-E_g$ librational energy splitting to be 1.6 ± 0.1 meV or 13.0 ± 1.0 cm^{-1}, in good agreement with the result quoted by Durand and Lüty[5] for crystals of concentrations of the order of 10^{-4} mole fraction. We have also made extensive, high-resolution scans over the entire $[100]T_y$ branch at 5 K in order to look for evidence of interactions. Some representative scans are shown in Fig. 2. None of the measured phonon resonances have widths significantly greater than the instrumental resolution. It should be noted that the scans for $q=0.10$, 0.15, and 0.20 cover the energy range where the E_g interaction was found (Fig. 1), while the scans at $q=0.3$, 0.5, and 0.7 are representative of scans taken at 0.05 steps in q for $0.05 \leq q \leq 0.8$. The changing width over the scan range is entirely due to resolution changes. Thus, there is no evidence of any resonant interactions in this branch, and therefore, according to the analysis of Casella,[11] there is no indication of a *well-defined* T_{2g} level close in energy to the E_g level. It is possible that the interaction with the phonons is simply too weak to be observed if the mode is significantly different in energy from the E_g or that the mode is high enough in energy to be either near the top of or above the potential "barrier" and thus significantly broadened. These results are similar to those of Nicklow[9,18] for $(CN)^-$ impurities in KCl.

In the second part of our experiments, we have studied the $[100]T_y$ branch in the low-concentration (0.00034 mole fraction KCN) sample in a successful attempt to measure the interaction of the phonons with the tunnel-split ground state. The results are shown in Figs. 3 and 4. The first point to be noted in these figures is the small value of wave vector at which measurements were made in order to cover the range of ground-state energy splittings. The greatest difficulty in these measurements arises from the scattering due to the "tail" of the resolution function intercepting the strong Bragg peak at (2,0,0). Careful

studies were made to optimize spectrometer conditions, and special care was taken to check the spectrometer alignment after each scan. The good vertical resolution of the BNL spectrometer (0.06 Å^{-1}) was essential to the success of this measurement. In Fig. 3, the temperature dependence of the neutron scattering group measured at $(2, -0.03, 0)$ is shown.

As can readily be seen the line shape is narrowest at higher temperatures, and at 20 K is almost equal to the calculated spectrometer resolution of 0.062 meV. However, as the temperature is decreased, the line broadens indicating the onset of an interaction, and at 1.5 K there is clearly structure observable. In Fig. 4, the momentum transfer dependence of the scattering at 1.5 K is shown. From the figure, it can be seen that the shape of the spectrum changes and narrows as q increases from 0.03 to 0.05, although there is still some *broadening* even at $q = 0.05$ (cf.

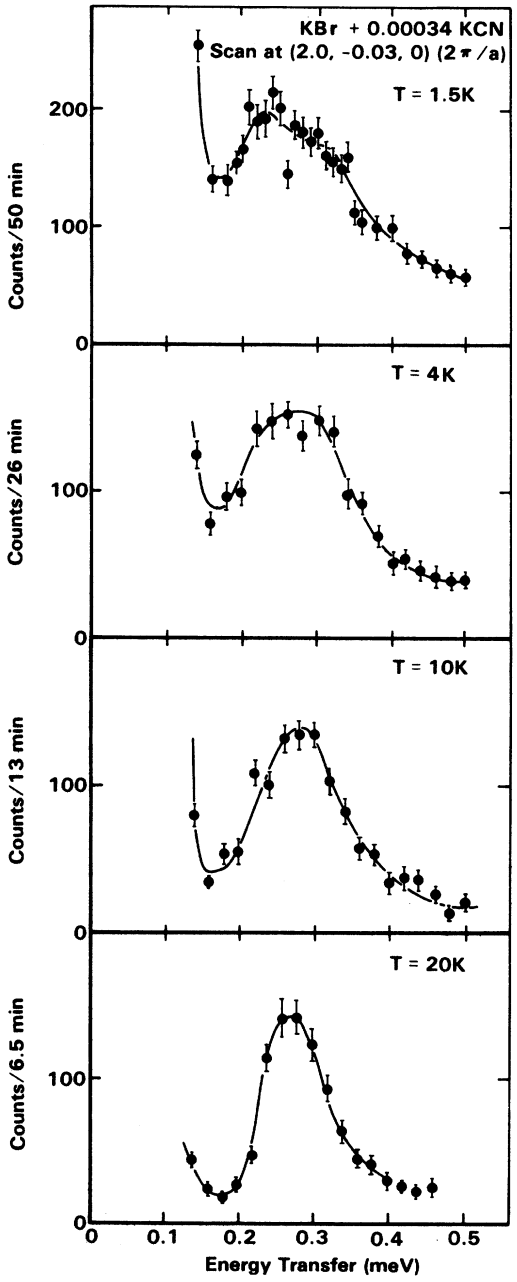

FIG. 3. Neutron scattering line shapes measured for the [100] T branch in KBr plus 0.00034 mole fraction KCN at a reduced wave vector of $0.03(2\pi/a)$ as a function of temperature. Measured about (2,0,0) reciprocal-lattice point. Solid lines are only a guide to the eye.

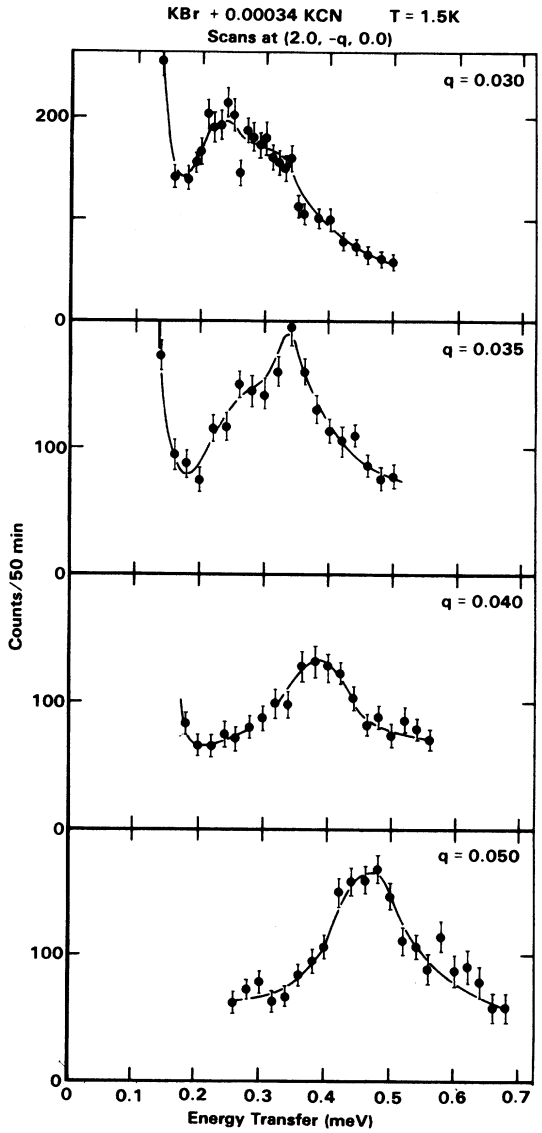

FIG. 4. Neutron scattering line shapes measured for the [100] T_y branch in KBr plus 0.00034 mole fraction KCN at 1.5 K as a function of reduced wave vector q. Measured about (2,0,0) reciprocal-lattice point. Solid lines are only a guide to the eye.

Fig. 3 at 20 K). The results in Figs. 3 and 4 represent the first observation of tunneling modes interacting with the phonons in equilibrium in a solid. From Fig. 3 we conclude that the splitting between the A_{1g} ground state and the T_{2g} tunnel level is 0.28 ± 0.05 meV or 2.3 ± 0.4 cm^{-1}.

V. DISCUSSION

The observation of a splitting in the $[110]T_{x\bar{y}}$ mode due to a resonant interaction with the $A_{1g} - E_g$ librational state transition in KBr is in agreement with earlier work on KCl.[8,9] The observed level spacing agrees well with the results of Raman studies quoted in Ref. 5. The absence of any splitting due to a resonant interaction with the $A_{1g} - T_{2g}$ librational state transition suggests that either the T_{2g} state has a short lifetime (because it lies near or above the local barrier) or that the coupling is much smaller for the T_{2g} mode than for the E_g mode. This latter is unlikely in view of the strong coupling to the T_{2g} tunnel states observed. The possibility that the relatively high $(CN)^-$ concentration broadens the T_{2g} state so that we do not observe it in the $[100]T_y$ branch cannot be ruled out, but the observations of Durand and Lüty[5] for KCN in KCl (Fig. 3 of their paper) on concentrations of 4×10^{-4} and 3×10^{-3} $(CN)^-$ offer some evidence that such concentrations do not strongly affect the librational modes.

The observation of a splitting in the $[100]T_y$ branch arising from $A_{1g} - T_{2g}$ excitations in the ground-state tunneling manifold is the first such measurement. The observed energy of the T_{2g} state is 0.28 ± 0.05 meV or 2.3 ± 0.4 cm^{-1} which is to be compared with the infrared absorption measurements of Beyeler,[3] which do not single out the $A_{1g} - T_{2g}$ splitting. Beyeler quotes an "average" tunnel splitting of 1.72 cm^{-1} (deduced from his value of $|\eta|$, the near-neighbor tunneling matrix element). The discrepancy is larger than our estimated error, but as Beyeler's measurements assume equal tunnel splittings for all states (an assumption known to be incorrect for KCl from the paraelectric resonance measurements[13]), one cannot comment further on the apparent discrepancy. In fact, from Fig. 18 of Ref. 3, one could assign a tunnel splitting of 1.9–2.0 cm^{-1}, which is within the error of our assigned value.

In considering all of the results for $(CN)^-$ ions in KCl and KBr, one is struck by the similarity of the values derived for various splittings in the two hosts. For example, in KCl Durand and Lüty[4] assign the $A_{1g} - E_g$ librational splitting as 13.8 cm^{-1} (see their Fig. 1), and Holuj and Bridges[13] find the $A_{1g} - T_{2g}$ tunnel splitting to be 2.36 cm^{-1}. (It should be noted that in the discussion of Ref. 5, a higher value for the $A_{1g} - E_g$ splitting in KCl is given when comparing the results for KBr and KCl hosts. We refer to the data shown in Figs. 1 and 3.) These should be compared to the values of 13.0 and 2.3 cm^{-1} found for a KBr host in the present study. However, the results of Walton *et al.*[8] indicate a somewhat higher value for the E_g librational mode in KCl (~ 15 cm^{-1}). Nonetheless, the similarity is striking, especially when the differences in lattice parameter of KCl and KBr are considered (6.274 and 6.586 Å, respectively). If one assumes, as is indicated by direct calculation, that the angular variation of the potential (but not the overall scale) are determined by overlap repulsion, the potentials should not be similar. A possible explanation, which can only be tested by Monte Carlo calculations, is that local relaxation of the host lattices leads to the similarity observed. In this case self-trapping must clearly occur, and the real potential will be quite unlike that derived from fitting the spectroscopic data to a Devonshire[19,20] model, or some extension of it.[5]

ACKNOWLEDGMENTS

The authors wish to acknowledge many stimulating discussions with R. C. Casella, K. H. Michel, and R. M. Nicklow. J. M. R. thanks the staff at Brookhaven National Laboratory for their hospitality during his stay there. Work at Argonne supported in part by the Division of Basic Energy Sciences, DOE. Work at Brookhaven supported by the Division of Basic Energy Sciences, DOE, under Contract No. EI-76-C-02-0016.

[1] A review article by S. V. Narayanamurti and R. O. Pohl, Rev. Mod. Phys. 42, 201 (1970) contains many references to early work on these systems.
[2] F. Lüty, Phys. Rev. B 10, 3677 (1974).
[3] H. U. Beyeler, Phys. Rev. B 11, 3078 (1975).
[4] D. Durand and F. Lüty, Phys. Status Solidi B 81, 443 (1977).
[5] D. Durand and F. Lüty, Ferroelectrics 16, 205 (1977).
[6] F. Lüty and A. Diaz-Gongora, Phys. Status Solidi B 85, 693 (1978).
[7] A. Diaz-Gongora and F. Lüty, Phys. Status Solidi B 86, 693 (1978).
[8] D. Walton, H. A. Mook, and R. M. Nicklow, Phys. Rev. Lett. 33, 412 (1974).
[9] R. M. Nicklow, in *Proceedings of Conference on Neutron Scattering, Gatlinburg, Tennessee, 1976* (National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia, 1976), Report No. CONF-760601-P1, p. 117.
[10] R. F. Wood and M. Mostoller, Phys. Rev. Lett. 39, 819 (1977).

[11]R. C. Casella, Phys. Rev. B 20, 5318 (1979).
[12]R. Windheim, Solid State Commun. 18, 1183 (1976).
[13]F. Holuj and F. Bridges, Phys. Rev. B 20, 3578 (1979).
[14]D. G. Hinks, D. L. Price, J. M. Rowe, and S. Susman, J. Cryst. Growth 15, 227 (1972).
[15]D. Walton, Phys. Rev. B 7, 3925 (1973).
[16]N. E. Byer and H. S. Sack, Phys. Status Solidi 30, 579 (1968).
[17]N. E. Byer and H. S. Sack, Phys. Status Solidi 30, 569 (1968).
[18]R. M. Nicklow (private communication) has also searched for evidence of interactions in the [100] branches of KCl containing $(CN)^-$ impurities without success.
[19]A. F. Devonshire, Proc. R. Soc. London Sect. A 153, 601 (1936).
[20]P. Sauer, Z. Phys. 194, 360 (1966).