J. Phys. C: Solid State Phys., **15** (1982) 1143–1150. Printed in Great Britain

Temperature dependence of halfwidth and frequency shift of the gap mode of the NO_3^- ion in KI

S S Khatri and A L Verma
Department of Physics, North-Eastern Hill University, Shillong-793003, India

Received 20 May 1981, in final form 20 July 1981

Abstract. The temperature dependence of the halfwidth and centre frequency of the ν_3 fundamental and its combination with the low-frequency gap mode of the NO_3^- ion doped in KI single crystal has been investigated from 1.7 to 77 K. From this study, detailed information about the variation of halfwidth and centre frequency of the gap mode as a function of temperature has been obtained which can be satisfactorily explained in terms of anharmonic interactions of the gap mode with lattice phonons.

1. Introduction

Introduction of impurities in ionic crystals destroys the periodicity of the lattice and this may modify the vibrational characteristics of the host crystal. Weakly coupled or lighter impurities may induce non-propagating vibrational modes at frequencies where the normal lattice vibrations of the host crystal may not occur. These are called local modes if they occur at higher frequencies than the highest frequency phonon mode, gap modes if they occur in a forbidden gap between the acoustic and optical phonon branches, and resonant modes if they fall within an allowed frequency band of lattice phonons.

Temperature-dependent studies of the localised modes can provide useful information about the interactions between the local mode and the lattice phonons. There have been numerous studies, both experimental and theoretical, on the temperature dependence of the width, position and intensities of local and resonant modes of several substitutional impurities in alkali halides using infrared absorption techniques as reviewed by Barker and Sievers (1975). In contrast, hardly any temperature-dependent measurements of the infrared active gap modes have yet been possible. The reason is that the difference band absorption of the host lattice dominates the spectral region near the gap and thus masks the impurity-induced absorption in the gap above about 15 K. Although there are no phonons in the forbidden gap at very low temperature, the eigenvectors of gap mode involve motion of nearest neighbours along with that of the impurity. It would, therefore, be of considerable interest to study the temperature dependence of gap modes in a suitable system and see whether similar mechanisms can explain the temperature-dependent effects for gap modes which are responsible for local modes.

When an impurity is substituted in a crystal lattice, the relevant symmetry for the vibrational transitions of the impurity is determined by both the symmetry of the impurity

0022-3719/82/061143 + 08 $01.50

and the symmetry of the lattice site. In the case of an NO_3^- ion with D_{3h} symmetry substituted in KI, its threefold axis coincides with the cube diagonal of the KI unit cell resulting in a C_{3v} symmetry. The original triply degenerate gap mode in the O_h symmetry splits into A and E components and induces two gap modes at 72.92 ± 0.05 and $87.93 \pm 0.05\ cm^{-1}$ in the phonon gap of KI. Due to the anharmonicity of the oscillator potential, these gap modes may appear as side bands to the strong ν_3 internal vibration of the NO_3^- ion in KI and have indeed been observed in the near infrared (Metselaar and Van der Elsken 1968) as well as in the far-infrared absorption directly (Eijnthoven 1970, Renk 1965). From an experimental point of view, it is a great advantage that the gap modes can be observed as combination bands in the near infrared and are amenable for temperature variation studies without interference from background absorption. Moreover, the high resolution attainable in this frequency region can allow observation of very small frequency shift and bandwidth rather easily.

The ν_3 fundamental (antisymmetric stretch) vibration of the nitrate ion ($^{14}NO_3^-$) in KI appears as a very strong and sharp band at $1372.50\ cm^{-1}$ even at room temperature. We have measured the temperature dependence of the bandwidth and centre frequency of the ν_3 fundamental of $^{15}NO_3^-$ and combination of the $73\ cm^{-1}$ gap mode with the ν_3 fundamental of $^{14}NO_3^-$. From these studies we have extracted information about the temperature dependence of the gap mode of the NO_3^- ion in KI and results are discussed in the light of the anharmonic interactions between the gap mode and the lattice phonons.

2. Experimental procedure and results

Single crystals of nitrate-doped KI were pulled from the melt by the Kyropoulos method by adding 0.02–0.05% KNO_3 by weight in KI under the atmosphere of dry oxygen gas. The concentration of the nitrate ions in the resulting crystals was of the order of 10^{17}–10^{18} ions cm^{-3}. Samples of $10 \times 10 \times 8$ mm were cut from the boules and polished thoroughly. To avoid interaction effects among impurities, samples of large thickness and lower concentration were used.

The optical measurements were made using a Perkin–Elmer Ebert-14 spectrophotometer equipped with a helium-cooled copper-doped germanium bolometer as a detector. The infrared radiation after dispersion from the monochromator was chopped mechanically and then focussed at the sample held in a cryostat in a modified optical arrangement between the exit slit of the monochromator and the detector. Low-temperature absorption measurements were made with a resolution of $0.05\ cm^{-1}$. At sample temperatures above 25 K, absorption lines become relatively broad and spectra were measured with a resolution between 0.1 and $0.15\ cm^{-1}$. Variable temperature measurements between 1.7 and 4.2 K were made with the help of an immersion cryostat by pumping on the liquid helium and temperatures were determined from the vapour pressure of the helium gas. For measurements between 5 and 77 K, a variable temperature conduction cryostat of conventional design was used. Sample temperature was adjusted by passing a regulated current through a nichrome wire heater wrapped around the sample ring. The temperature was measured by determining the resistance of a $\frac{1}{10}$W Allen-Bradley carbon resistor of either 1000 or 4700 Ω nominal resistance which were calibrated at boiling temperatures of liquid helium and nitrogen at atmospheric pressure. Temperature measurements above 5 K are accurate to better than ±0.50 K.

The near infrared spectrum of nitrate ion in KI between 1300 and $1500\ cm^{-1}$ at 4.2 K has been reported and its complicated structure has been interpreted satisfactorily

(Eijnthoven and Van der Elsken 1969). For the sake of present work, the important features of the spectrum are the ν_3 fundamental of the $^{14}NO_3^-$ ion at 1372.50 cm^{-1}, that of the $^{15}NO_3^-$ ion at 1340.60 cm^{-1}, appearing in the spectrum due to natural occurrence of ^{15}N, and the combination of the former band with the 72.92 cm^{-1} gap mode at 1442.42 cm^{-1}. We have measured the temperature dependence of the bandwidth and centre frequency of the last two bands. The low intensity sharp band due to the ν_3

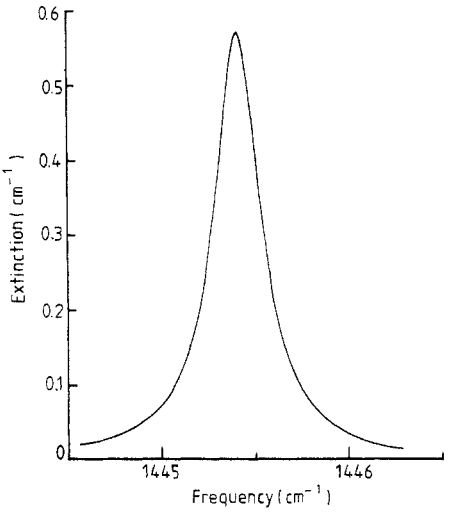

Figure 1. Infrared absorption spectrum of a 10 mm thick KI crystal containing approximately 10^{17} NO_3^- ions cm^{-3} at 4.2 K in the ν_3 and gap mode region; spectral resolution is about 0.05 cm^{-1}.

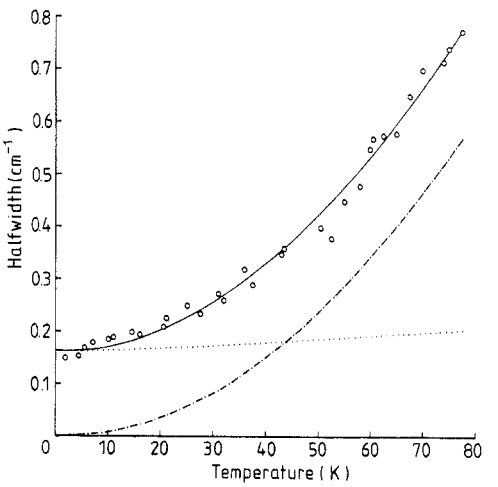

Figure 2. Temperature dependence of the halfwidth of the gap mode. The dotted curve represents the calculated contribution of the two-phonon decay along with the temperature-independent contributions due to local strains etc. The chain curve represents the contribution from the phonon-scattering process with θ_D = 24 K. The full curve is the resultant of the other two curves.

fundamental of $^{15}NO_3^-$ monitors the frequency shift and bandwidth of the internal vibration especially when the 1372.5 cm^{-1} band of $^{14}NO_3^-$ is too intense to be measured accurately with the same crystal. Figure 1 shows the spectrum of the NO_3^- ion in KI in the combination band region at 4.2 K recorded with a resolution of 0.05 cm^{-1}. The water vapour band at 1465.01 cm^{-1} was used to monitor the frequency shift of the combination band. Both the combination and internal vibration bands show Lorentzian lineshapes and gap modes are known to give rise to Lorentzian lineshapes.

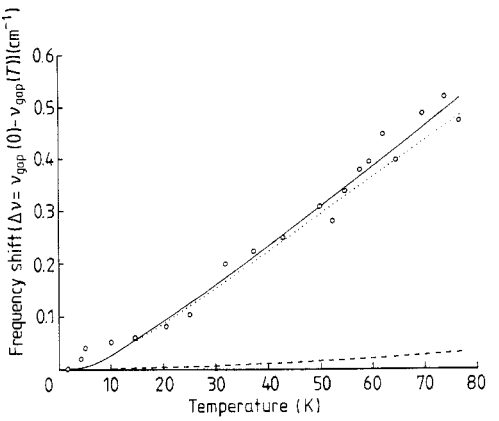

Figure 3. Temperature dependence of the frequency shift $\Delta\nu = \nu_{gap}(0) - \nu_{gap}(T)$ for the 73 cm^{-1} gap mode. The broken curve represents the contribution from lattice thermal expansion. The dotted curve represents the contribution from the phonon-scattering process with $\theta_c = 24$ K. The full curve is the resultant of the other two curves.

We have attributed the temperature-dependent characteristics of the combination band to the sum of the characteristics of the ν_3 fundamental and the gap mode. The linewidth and frequency shift of the ν_3 fundamental of $^{15}NO_3^-$ were subtracted from that of the combination band (1442.52 cm^{-1}) at the same temperature to get these quantities for the gap mode. The temperature dependence of the halfwidth and the frequency shift are shown in figures 2 and 3 respectively. The frequency and bandwidth of the ν_3 fundamental of $^{15}NO_3^-$ at a particular temperature are taken as the zero point for the frequency shift and bandwidth of the combination band at the same temperature and the difference is taken as arising from the temperature-dependent effects on the gap mode. Another implicit assumption here is that the residual linewidth at 0 K is also Lorentzian and the temperature dependent characteristics of the ν_3 fundamentals of $^{14}NO_3^-$ and $^{15}NO_3^-$ are identical.

3. Discussion

The temperature-dependent characteristics of local and resonant modes of several substitutional impurities in different lattices (Elliott *et al* 1965, Klein 1968, Ivanov *et al* 1966) have been interpreted as arising from the dynamical coupling of the local mode with the perturbed normal modes of the host lattice. The anharmonic terms in the potential energy involving the coordinates of the local mode and the host-lattice phonons serve as the coupling mechanism. We shall adopt a similar approach to explain the

temperature-dependent effects on gap modes and estimate the relative importance of different mechanisms responsible for these changes for local and gap modes.

Anharmonic terms involving normal coordinates of gap mode such as Q^3 and Q^4 affect the energy of the gap mode and induce higher harmonics and side bands etc while terms involving only the lattice modes such as $q_iq_jq_k$ give rise to thermal expansion of the lattice. Excluding these contributions, the Hamiltonian for the gap mode oscillator involving coupling between the gap mode and lattice phonons can be written as (Bauerle 1973):

$$H = H_0 + H_3 + H_4 \tag{1}$$

where H_0 is the harmonic part of the Hamiltonian for the gap mode, H_3 and H_4 are the cubic and quartic terms respectively of the Hamiltonian. In terms of normal coordinates of gap mode Q_g and lattice phonons q_i, q_j etc they can be expressed as:

$$H_3 = \tfrac{1}{6}\left(\sum_{g,i,j} \frac{\partial^3 V}{\partial Q_g \partial q_i \partial q_j} Q_g q_i q_j + \sum_{g,i} \frac{\partial^3 V}{\partial^2 Q_g \partial q_i} Q_g^2 q_i\right) + \ldots$$

and

$$H_4 = \tfrac{1}{24}\left(\sum_{g,i,j,k} \frac{\partial^4 V}{\partial Q_g \partial q_i \partial q_j \partial q_k} Q_g q_i q_j q_k + \sum_{g,i,j} \frac{\partial^4 V}{\partial^2 Q_g \partial q_i \partial q_j} Q_g^2 q_i q_j\right) + \ldots \tag{2}$$

which can be written in terms of creation and annhilation operators as (Bauerle 1973)

$$H_3 = \tfrac{1}{6}\left(\sum_{g,i,j} V_3(g,i,j)\,(a_g + a_g^\dagger)\,(a_i + a_i^\dagger)\,(a_j + a_j^\dagger) + \sum_{g,i} V_3(g,i)\,(a_g + a_g^\dagger)^2 (a_i + a_i^\dagger)\right) + \ldots$$

$$H_4 = \tfrac{1}{24}\left(\sum_{g,i,j,k} V_4(g,i,j,k)\,(a_g + a_g^\dagger)\,(a_i + a_i^\dagger)\,(a_j + a_j^\dagger)\,(a_k + a_k^\dagger) + \sum_{g,i,j} V_4(g,i,j)\,(a_g + a_g^\dagger)^2 (a_i + a_i^\dagger)\,(a_j + a_j^\dagger)\right) + \ldots \tag{3}$$

where g refers to the eigenvectors of the gap mode and i, j, k of lattice phonons. V_3 and V_4 represent the coupling coefficients of the cubic and quartic terms respectively in the potential energy coupling gap mode with lattice phonons. Since these processes depend on the thermal occupation number $n_i = [\exp(\hbar\omega_i/kT) - 1]^{-1}$ of phonons involved in the interactions, temperature dependence is contained in this factor.

As the terms H_3 and H_4 in equation (1) are small compared with H_0, the contributions of these anharmonic terms to the energy and damping of the gap modes can be calculated using perturbation techniques. The difference processes contributing to the width and shift of energy levels can be divided into two broad categories: decomposition processes and scattering processes. Both of these processes modify the lifetime of the excited gap mode state and consequently affect the width of the levels through the uncertainty principle (Alexander *et al* 1970).

In a decomposition mechanism for the width of the gap mode, the gap mode excited state decays into one or more phonons. Requirement of conservation of energy makes the one-phonon decay of gap modes unfeasible. For the low-frequency gap mode ($72.92\ \mathrm{cm}^{-1}$) of NO_3^- in KI, the most probable mode of decay will involve two phonons through the terms $V_3(g,i,j)\,a_g a_i^\dagger a_j^\dagger$ in expression (3). The temperature dependence for this mode of decay can be calculated by using the properties of boson operators $a_i^\dagger$ and

a_i and the contribution to halfwidth is given by (Bauerle 1973):

$$\Delta\Gamma_g = 18\pi \sum_{i,j} |V_3(g, i, j)|^2(\bar{n}_i + \bar{n}_j + 1)\, \delta(\omega_g - \omega_i - \omega_j) \tag{4}$$

where the delta function expresses the necessary energy conservation. The temperature dependence of equation (4) in the Debye model can be expressed as

$$\Delta\Gamma_g = C\left(\frac{kT}{\nu_m ch}\right)^5 \int_0^{\nu_m ch/kT} X^3(\Omega ch/kT - X) \times \left(\frac{1}{e^X - 1} + \frac{1}{\exp(\Omega ch/kT - X) - 1} + 1\right) dX \tag{5}$$

where $\nu_m = 69.7\ \text{cm}^{-1}$ is the maximum frequency of the acoustic band and $\Omega = 72.92\ \text{cm}^{-1}$ is the gap mode frequency and $X = h\nu/kT$.

This predicts a constant value at low temperatures and a linear dependence on T at higher temperatures. Similarly, a three-phonon decay process through the terms $V_4(g, i, j, k)\, a_g a_i^\dagger a_j^\dagger a_k^\dagger$ shows a temperature dependence of the form

$$[(\bar{n}_i + 1)(\bar{n}_j + 1)(\bar{n}_k + 1) - \bar{n}_i\bar{n}_j\bar{n}_k]$$

and predicts a constant linewidth at low temperatures and T^2 dependence at higher temperatures. We calculated the contribution of the frequency-dependent part from equation (5) in terms of constant C which gave a significant contribution to the linewidth in the temperature range of interest.

At slighly higher temperatures, another fourth-order process takes over which may be described as scattering of lattice phonons by the gap mode leading to fluctuations in the gap mode state (Elliott *et al* 1965). This broadens the absorption line by limiting the lifetime of the overall excited state consisting of gap mode excitation plus phonons and the process involved can be depicted as (Barker and Sievers 1975, Alexander *et al* 1970):

$$|g\rangle|\ldots n_i, n_j, \ldots\rangle \rightarrow |g\rangle|\ldots n_i \pm 1, n_j \mp i, \ldots\rangle \tag{6}$$

and can be brought about by anharmonic terms like $V_3(g, i)$ (taken to second order in perturbation theory) or $V_4(g, i, j)$ (taken to first order). In the Debye approximation for phonon distribution, both of these processes give a contribution to the linewidth which can be expressed as:

$$\Delta\Gamma_g' = \beta\left(\frac{T}{\theta_D}\right)^7 \int_0^{\theta_D/T} \frac{X^6 e^X}{(e^X - 1)^2}\, dX \tag{7}$$

where β is a coupling constant and is positive, $X = h\nu/kT$ and $k\theta_D/h$ is the effective Debye cut-off frequency. This process predicts a T^2 dependence above θ_D and a T^7 dependence at temperatures below θ_D. We computed the integral in equation (7) for various values of θ_D. Then we added the contributions from expressions (5) and (7) for different values of θ_D and adjusted the constants C and β in a least-squares fitting to match the sum of these contributions to the observed results. Values of $C = 0.191\ \text{cm}^{-1}$, $\beta = 0.275\ \text{cm}^{-1}$ and $\theta_D = 24\ \text{K}$ gave the best fit to the experimentally determined linewidth (figure 2). The dotted curve in figure 2 shows the contribution from two-phonon decay along with the temperature-independent contributions due to local strains etc which have been taken equal to halfwidth extrapolated to 0 K [$\Gamma(0\ \text{K}) = 0.15\ \text{cm}^{-1}$]. The chain curve shows the contribution from scattering and the full curve is the sum of the contributions due to scattering and decay processes which is in reasonable agreement with experiment.

4. Frequency shift

The temperature dependent frequency shift of a gap mode may arise from direct anharmonic coupling to lattice phonons and the thermal expansion of the lattice. The frequency shift from the latter effect can be expressed as (Bauerle 1973):

$$\Delta\nu_{\text{th}} = \frac{3\Delta a}{a(0)}\,\alpha(A_{1g}) \tag{8}$$

$a(0)$ is the lattice parameter at 0 K, $a(T)$ that at temperature T and $\Delta a = a(T) - a(0)$. Data for lattice parameters was taken from Landolt–Börnstein (1973). $\alpha(A_{1g})$ is the hydrostatic strain coupling constant related to the uniform dilation of the lattice and is responsible for the shift of the energy level of the gap mode. This can be calculated from the frequency–stress derivatives for the ν_3 fundamental of $^{15}NO_3^-$ in KI and the combination band under uniaxial stress (Bruining and Van der Elsken 1975, Bauerle 1973) and a value of $\alpha(A_{1g}) = 7.273\ \text{cm}^{-1}$ for the gap mode has been obtained.

Using these values the contribution of lattice thermal expansion to the frequency shift of the 73 cm^{-1} gap mode has been calculated from equation (8) and is shown as a broken curve in figure 3 and shows an increase in the frequency shift [$\Delta\nu_{\text{th}} = \nu_{\text{gap}}(0) - \nu_{\text{gap}}(T)$] with increasing temperature. Since $\nu_{\text{gap}}(0)$ is constant, it is obvious that the frequency of the gap mode decreases with increase in temperature.

The major contribution to the shift in centroid frequency of the gap mode with temperature can be attributed to the elastic scattering of lattice phonons by the gap mode. In the Debye approximation for lattice phonons, which is described by an expression (Barker and Sievers 1975, Alexander *et al* 1970):

$$\Delta\nu_{\text{sc}} = \nu_{\text{gap}}(0) - \nu_{\text{gap}}(T) = \delta\left(\frac{T}{\theta_c}\right)^4 \int_0^{\theta_c/T} \frac{X^3\,\mathrm{d}X}{\mathrm{e}^X - 1} \tag{9}$$

where δ is a coupling coefficient and θ_c an effective Debye temperature. In the regions of low and high temperatures, this gives the limiting behaviour as:

$$\Delta\nu_{\text{sc}} \propto T^4 \qquad \text{for low } T$$

$$\Delta\nu_{\text{sc}} \propto T \qquad \text{for high } T.$$

The values of δ and θ_c needed to predict the additional frequency shift as shown by the dotted curve in figure 3 to agree with the experiments are $\delta = 0.511\ \text{cm}^{-1}$ and $\theta_c = 24$ K. The full curve (figure 3) shows the sum of contributions due to scattering and thermal expansion which is in reasonable agreement with the experimentally observed behaviour.

5. Conclusions

In the gap mode vibration, the first nearest-neighbours move in phase with the defect and the amplitude is not localised at the defect site. The coupling of the NO_3^- gap mode to lattice phonons of KI is evident in the temperature-dependent halfwidth and frequency shift of this mode. This coupling is mainly of anharmonic nature leading to change in volume and interactions between gap mode and lattice phonons which change the self-energy of phonons and also give finite lifetime to gap modes.

Out of the two line-broadening mechanisms for the gap mode of the NO_3^- ion in KI

discussed, the scattering mechanism dominates at higher temperatures while the two-phonon decay mechanism contributes significantly at low temperatures. Major contribution to the frequency shift of the gap mode comes from scattering mechanisms at all temperatures while the contribution from thermal expansion is very small up to 77 K. Both of these processes decrease the frequency of the gap mode with increase in temperature.

The effective Debye temperatures needed to fit the calculated values of different contributions to the linewidth and frequency shift with the experimental data indicate a limit to the distribution of phonons which take part in the particular mechanism under consideration. The best value of the effective Debye temperature to explain the frequency shift and halfwidth of the 73 cm^{-1} gap mode in the $KI:NO_3^-$ system is obtained as 24 K. This implies a participation of similar types of phonon distributions in the contributing physical processes. The values of the coupling coefficients to explain the data are obtained as $\beta = 0.275$ cm^{-1} and $\delta = 0.51$ cm^{-1}. For comparison purposes with the in-band resonant modes in systems like $KBr:Li^+$, $NaCl:Cu^+$, $KI:Ag^+$ etc (Alexander *et al* 1970), the values of effective Debye temperatures for these systems vary from 25 to 33 K, coupling constant β from 2 to 12 cm^{-1} and δ from 1 to 3 cm^{-1}. Smaller values of the coupling coefficients β and δ for the gap mode of NO_3^- in KI compared with the in-band resonant modes of these quoted systems indicate that the resonant modes couple more strongly to the lattice phonons than the gap modes. Near similarity of the effective Debye temperatures in all these systems for the gap and resonant modes suggest that they couple to nearly a similar type of distribution of long wavelength acoustic phonons.

Acknowledgments

The experimental work reported here was performed in the Laboratory of Professor J Van der Elsken while one of the authors (ALV) was working in his group at the University of Amsterdam, The Netherlands. The author is indebted to Professor Van der Elsken for providing all the facilities.

References

Alexander R W Jr, Hughes A E and Sievers A J 1970 *Phys. Rev.* B **1** 1563
Barker A S Jr and Sievers A J 1975 *Rev. Mod. Phys.* **47** Suppl. 2, S **1**
Bauerle D 1973 *Springer Tracts in Modern Physics* **68** 76
Bruining J and Van der Elsken J 1975 *Phys. Rev.* B **11** 5123
Eijnthoven R K 1970 *PhD Thesis* University of Amsterdam, Amsterdam (unpublished)
Eijnthoven R K and Van der Elsken J 1969 *Phys. Rev. Lett.* **23** 1455
Elliott R J, Hayes W, Jones G D, Macdonald H F and Sennett C T 1965 *Proc. R. Soc.* A **289** 1
Ivanov M A, Krivoglaz M A, Mirlin D N and Reshina I I 1966 *Sov. Phys.–Solid State* **8** 150
Klein M V 1968 *Physics of Color Centers* ed W B Fowler (New York: Academic Press) ch 7
Landolt–Börnstein New Series 1973 Group III vol 7a ed H-K Hellwegge (Berlin: Springer) p 585
Metselaar R and Van der Elsken J 1968 *Phys. Rev.* **165** 359
Renk K F 1965 *Phys. Lett.* **14** 281