Research Projects Agency through the Center for Materials Research at Stanford University and the National Science Foundation.

[1] C. N. Berglund and W. E. Spicer, Phys. Rev. 136, A1030, A1044 (1964).

[2] N. V. Smith and W. E. Spicer, Opt. Commun. 1, 157 (1969). A similar result has been obtained in Al and In by R. Y. Koyama, thesis, Stanford University, 1969 (unpublished); R. Y. Koyama and W. E. Spicer, to be published; and more recently in Pd by J. F. Janak, D. E. Eastman, and A. R. Williams, to be published.

[3] D. E. Eastman, J. Appl. Phys. 40, 1387 (1969).

[4] See W. E. Spicer, Phys. Rev. 154, 385 (1967), and references therein. More recent successes of a predominantly nondirect interpretation include reports by A. Y.-C. Yu and W. E. Spicer, Phys. Rev. 167, 674 (1968); W. F. Krolikowski, thesis, Stanford University, 1967 (unpublished); and Eastman, Ref. 3.

[5] D. Brust, Phys. Rev. 139, A489 (1965).

[6] L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. 152, 505 (1966).

[7] G. A. Burdick, Phys. Rev. 129, 138 (1963).

[8] W. F. Krolikowski and W. E. Spicer, Phys. Rev. (to be published).

INTENSITY DISTRIBUTION IN THE SIDEBAND SPECTRUM OF NO_3^- IN KI

R. K. Eijnthoven and J. van der Elsken
Laboratory for Physical Chemistry, University of Amsterdam, Amsterdam, The Netherlands

(Received 3 November 1969)

The 1400-cm^{-1} absorption band of the nitrate impurity in potassium iodide shows at 4.2°K a considerable amount of fine structure. The intensity distribution of this fine structure is governed by the anharmonic coupling of the internal vibration of the nitrate ion with nearly unperturbed phonons. This distribution can be calculated satisfactorily by first-order perturbation theory.

It is known that the intensity distribution in sideband spectra must contain information about interactions in crystals. Therefore it is important to look for the weight factor that determines the contributions of the combinations to the total absorption. Thus far, consideration to this weight factor has only been given for the sideband spectra of an electronic transition[1] and of the absorption due to *U* centers.[2] The lack of details in the reported[3,4] sideband spectra of internal vibrations of complex ions in solid solutions made consideration of a weight factor inopportune.

We present here high-resolution spectra of the sideband absorption of the ν_3 internal vibration of the nitrate ion as an impurity in potassium iodide recorded at 4.2°K. The spectra show enough details to allow a comparison with a simple theory describing the coupling between internal vibration and lattice phonons.

Single crystals of KI doped with nitrate were grown from the molten salt. The length of the crystals used in our experiments was about 15 mm, with nitrate concentrations in the range of 10^{17} to 10^{18} cm^{-3}. Figure 1 shows the infrared absorption spectrum of such a crystal in the 1400-cm^{-1} region obtained with a Perkin-Elmer E14 spectrometer, resolution = 0.2 cm^{-1}. For the consideration of the interaction between internal vibration and undisturbed phonon spectrum some features of the experimental spectrum have to be disregarded. In the first place there is a relatively strong absorption peak with some very sharp sidebands at about 1423 cm^{-1} that arises from an overtone of the ν_4 vibration

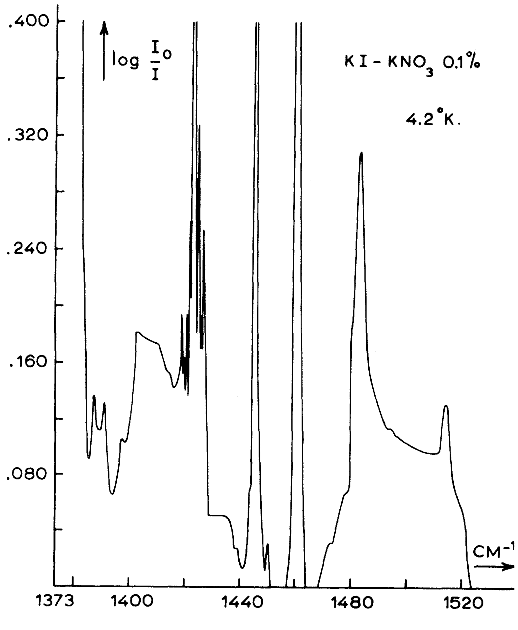

FIG. 1. The sideband spectrum of the ν_3 internal vibration of NO_3^- in a KI single crystal.

of the nitrate ion. A comparison with the absorption spectrum obtained with $N^{15}O_3^-$ makes it easy to sort out these contributions. In the second place there are the absorptions at 1446 and 1461 cm^{-1} that arise from gap modes and the absorption around 1518 cm^{-1} that arises from local modes caused by the nitrate impurity in the host lattice. The remainder of the sideband spectrum arises from the normal lattice vibrations and is shown in Fig. 2 together with the theoretical frequency distribution according to shell-model calculations.[5] There is some resemblance between the experimental spectrum and the frequency distribution spectrum; in particular the position of the gap, the approximate position of the maximum of the optical branch, and some sharp cutoffs in the acoustic branch agree quite well. However, it is clear that a strongly frequency-dependent weight factor governs the intensity distribution in the combination band.

To approach this weight factor theoretically we wish to develop here a simple model for anharmonic interaction. We introduce in the potential energy function the anharmonicity which is held responsible for the coupling between the normal coordinates as a modulation on the harmonic term:

$$V_{lm} = V_{lm}^0[1 + c_{lm}(a_l - a_m)],$$

where V_{lm}^0 is the harmonic term in the Taylor expansion, $\partial^2 V/\partial x_l \partial x_m$; a_l and a_m are the real displacements of the atoms l and m from their equilibrium positions. The coefficient $c_{lm} \neq 0$ when l and m are nearest neighbors.[6] a_l is temperature and time dependent and is given by

$$a_l = \sum\nolimits_\beta u_l^\beta \exp(i\omega_\beta t) P_\beta(T).$$

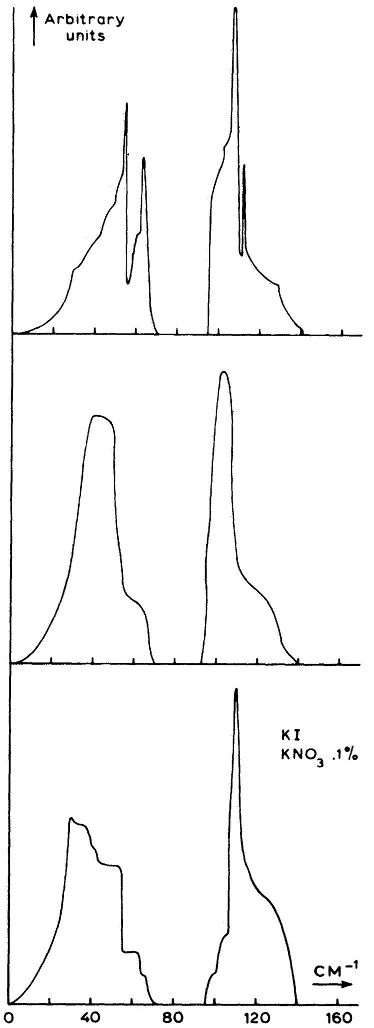

FIG. 2. From top to bottom: Theoretical frequency distribution from shell-model calculations; theoretical sideband spectrum calculated from shell-model data according to the theory presented here; experimental sideband spectrum.

$P_\beta(T)$ converts the normalized eigenvectors U_K^α corresponding to the lattice vibration with frequency ω_α in the harmonic approximation to the actual amplitudes at temperature T. The equation becomes

$$V = V(0) + \sum_{lm} V_{lm} x_l x_m + \sum_{lm} W_{lm} x_l x_m \sum_\beta P_\beta(T)(u_l^\beta - u_m^\beta)\exp(i\omega_\beta t).$$

This equation can be solved by the methods of standard time-dependent perturbation theory. The solutions are

$$Z_K^\alpha = u_K^\alpha \exp(i\omega_\alpha t) + \sum\nolimits_\beta S_\beta^K \exp[i(\omega_\alpha + \omega_\beta)t] P_\beta(T),$$

where

$$S_\beta^K = \sum_\gamma \frac{u_K^\gamma}{(\omega_\alpha + \omega_\beta)^2 - \omega_\gamma^2} \sum_{lm} W_{lm} u_m^\alpha u_l^\gamma (u_l^\beta - u_m^\beta).$$

The ω_α is here the frequency of the internal vibration of the nitrate ion, about 1400 cm^{-1}. The summations over β and γ extend over all lattice vibrations and over the internal vibrations. The maximum frequency of the lattice vibrations is about 150 cm^{-1}. This means that the one term in S_β for which $\omega_\gamma = \omega_\alpha$ is much larger than the others. Just this term gives[7]

$$Z_K{}^\alpha = u_K{}^\alpha \exp(i\omega_\alpha t) + \sum_\beta \frac{u_K{}^\beta \exp[i(\omega_\alpha + \omega_\beta)t]}{\omega_\beta(\omega_\beta + 2\omega_\alpha)} \sum_{lm} W_{lm} u_l{}^\alpha u_m{}^\alpha (u_l{}^\beta - u_m{}^\beta).$$

U^α describes the response of the lattice to the internal vibration. The contribution to the dipole moment changing with frequency $\omega_\alpha + \omega_\beta$ is given by $\sum_K S_\beta{}^K P_\beta(T) e_K$. The square of this sum corresponds to the infrared absorption intensity. We calculated the contributions to the sideband spectrum using the eigenvectors and eigenfrequencies originating from undisturbed model calculations that were made available to us by R. A. Cowley. This implies that the localized translational and librational modes of the impurity will not emerge from our calculations. These were already discarded from our experimental data. With the aid of a suitable interpolation method we could perform this calculation for 400 000 frequencies lying in the full first Brillouin zone. Sorting these frequencies in bins of one wave number we obtained a histogram of which the smoothed version is shown in Fig. 2. Comparison of the experimental spectrum with the curve so obtained shows a much better agreement than a comparison with the frequency distribution. Noteworthy is the absence of the sharp peaks at 55 and 64 cm^{-1} that arise from saddle points of the LA and TA branches at the zone boundary in the $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$ direction. In these regions of q space the positive ions move with a very small amplitude only. Since according to the theory given here these amplitudes govern the magnitude of the contribution to the sideband absorption, this absence was to be expected. Still a detailed comparison shows some differences as for instance a shift of about 8 cm^{-1} of the peak in the optical branch. These differences might arise from the high sensitivity of the calculated results to the details of the interaction mechanism.

This work is part of the research program of the Foundation for Fundamental Research of Matter (F.O.M.) and was made possible by financial support from the Netherlands Organization for Pure Research (Z.W.O.).

---

[1] T. Timusk and M. Buchanan, Phys. Rev. 164, 345 (1967).

[2] B. Fritz, U. Gross, and D. Bäurle, Phys. Status Solidi 11, 231 (1965); T. Gethins, T. Timusk, and E. J. Woll, Phys. Rev. 157, 744 (1967), N. X. Xinh, Phys. Rev. 163, 896 (1967); J. B. Page and B. G. Dick, Phys. Rev. 163, 910 (1967); T. Timusk and M. V. Klein, Phys. Rev. 141, 664 (1966).

[3] M. A. Cundill and W. F. Sherman, Phys. Rev. 168, 1007 (1968).

[4] R. Metselaar and J. van der Elsken, Phys. Rev. 165, 359 (1968).

[5] C. Dolling, R. A. Cowley, C. Schittenhelm, and I. M. Thorson, Phys. Rev. 147, 577 (1966).

[6] R. A. Cowley, Advan. Phys. 12, 421 (1963).

[7] This term corresponds approximately to Eq. (13) in the paper by Klein; the theory given here is slightly modified.

INTRINSIC MAGNETIC-FIELD QUENCHING OF KONDO SCATTERING: OBSERVATION BY ELECTRON TUNNELING

D. L. Losee* and E. L. Wolf*
Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

(Received 23 September 1969)

An inherent magnetic-field quenching of Kondo scattering occurs via lifetime broadening of the spin-flipped intermediate states. This effect and other intrinsic features of the *s-d* exchange problem are revealed by high-field tunneling studies of magnetic scattering.

Kondo[1] has shown that localized magnetic moments, exchange coupled to the conduction electrons in a metal, lead to anomalous scattering which varies as $-\ln T$. The anomaly occurs in the third-order transition probability

$$W_{ij} \propto \delta(E_i - E_j) \sum_{k \neq i} \frac{H_{ik}{}' H_{kj}{}' H_{ji}{}'}{E_i - E_k} \to J\rho_{\mathrm{F}} \int_{-E_0}^{E_0} \frac{\tanh(\frac{1}{2} - \beta\epsilon)\, d\epsilon}{E_i - \epsilon} \delta(E_i - \mathrm{F}_j), \tag{1}$$