

does not seem possible to identify the nature of the initial excitation with certainty. However, it is known that in such (n, γ) processes, a variety of short-lived and long-lived excited localized electronic states are produced. An atom in an excited electronic state can be expected to have a changed force constant K . If it changes to a significantly larger value, a localized mode can result, and narrowing can occur. Perhaps a more likely effect is a temporary reduction in K , which can cause effects similar to a hot localized mode, since χ^2 varies inversely with K .

Additional features of the relaxation of a hot localized mode include the thermal shift and the emission and absorption of phonons such that there is zero net energy loss to the gamma ray during its emission.⁸ A more detailed account of the relaxation of localized modes and other mechanisms which cause narrowing will be published elsewhere.

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EXTERNAL MODES OF VIBRATION OF SMALL POLYATOMIC IONS ISOLATED IN ALKALI HALIDES

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When a small polyatomic impurity ion is substitutionally isolated in an alkali-halide lattice, the frequencies of the normal modes of the free ion are perturbed by no more than a few percent. The vibration of the ion as a whole with respect to the supporting lattice, termed an external mode of vibration [Decius et al.¹] and clearly representing the part played by the impurity in the perturbed lattice vibrations of the crystal, would, however, be expected to be strongly dependent on the supporting lattice. Although direct observation of these modes in the far infrared is hampered by the very strong host-lattice absorption, Sievers and Lytle² have observed some bands in KI doped with KNO₂, by working at low temperatures.

Even at liquid-helium temperatures some of this region is masked by the host-lattice absorption, which broadens to obscure most of the region as the temperature rises. Combination of the external modes with strongly active internal modes can, however, be observed in the near infrared where the host lattice is transparent at all temperatures. This type of spectrum, which can be described as $\nu(\text{internal}) \pm \nu(\text{external})$, has been observed for several different ions, each isolated in a variety of alkali halides; and the pressure dependence of some of these spectra has been obtained.

As is indicated for this type of spectrum in the case of the NCO⁻ ion isolated in KBr in

the paper by Decius *et al.*,¹ the sharper structure is only found in positions corresponding to frequencies at which the pure host lattice is unwilling to vibrate (i.e., in the gap between the acoustic and optic modes or above the optic modes). The broader structure would appear to be best considered as a measure of the distorted density of states in the vicinity of the impurity ion. Comparison of the numbers in Table I with the equivalent host-lattice dispersion curves shows that for this to be true, the presence of the impurity must cause a large local distortion of the transverse acoustic mode, with much smaller modifications of the other modes. Table I also shows that, as expected, no sharp structure has been found in any case where the impurity ion was heavier than the host ion which it replaced.

Since the sharper structure seems to be located either within the narrow gap between acoustic and optic modes or just above the optic modes for the pure crystal, it seems probable that these features can be used to investigate the corresponding points in the dispersion

curve for the pure lattice. With this in mind, the pressure dependence of the spectra summarized in the table has been investigated—using a modified Drickamer type of high-pressure optical cell working at 90°K and giving a maximum available pressure of 50 kbar.

Taking for example the $\nu_3 \pm \nu_{(\text{ext.})}$ region of the spectrum of NCO^- isolated in KBr, it was found that initially a steady increase in separation from ν_3 was recorded with increasing pressure accompanied by only a slight broadening of the features, possibly due to pressure inhomogeneity. Figure 1 shows this separation change with pressure expressed as a percentage of the zero-pressure separation. It can be seen that the frequencies of the sharp doublet, originally at 97.4 and 99.7 cm^{-1} , and the gap between acoustic and optic modes, increased by 14% before the phase change of the KBr at 18 kbar. Since the nature of the spectrum did not seem to change appreciably during the application of pressure, it seems reasonable to conclude that the energy equivalent to the gap between the acoustic and op-

Table I. External mode frequencies (cm^{-1}) for polyatomic ions isolated in alkali halides at 100°K obtained from $\nu_{(\text{int.})} \pm \nu_{(\text{ext.})}$ spectra. The two columns per ion indicate frequencies below and above the lowest optical mode.

	NCO^-		Sharp (or relatively sharp) structure						Approximate maxima of broad structure				
			N_3^-		BO_2^-		NO_3^-		CN^-	NCO^-	NO_3^-	CN^-	
NaCl	... ^a		... ^a		... ^a		... ^a			86		45	147
												132?	189
NaBr	117								109				
	123		124						114	90	136	35	154
	127								122	106	165		197?
NaI	91		105						93			26	165?
	105								126	35	172		
KCl	... ^a		... ^a		... ^a		... ^a		... ^b	52	147		... ^b
									... ^b	115	194		
KBr									... ^b	41	105		... ^b
	97.4	167.5	97	178	102	169	93	175		79	122	143	
	99.7	183.6					103			84	157		
KI									... ^b		103		... ^b
	77.8	152.1	80	145	88	139?	74	182		31	119	111	
	82.2	172.5					89			59	133		
RbCl	... ^a		... ^a		... ^a		... ^a		... ^b	36	109		... ^b
									... ^b	87	101		
RbBr		141		155					... ^b	31			... ^b
		153.6							... ^b				
RbI									... ^b	24	87		... ^b
		114.5		126						57			
										62	101		

^aImpurity heavier than replaced ion.

^b $\nu_{(\text{int.})}(\text{CN}^-)$ is so broad in these lattices at 100°K that $\nu_{(\text{int.})} \pm \nu_{(\text{ext.})}$ are not observable.

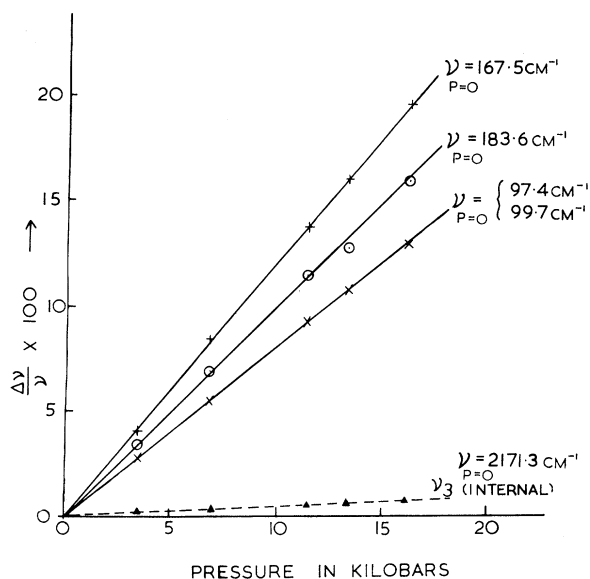


FIG. 1. The effect of pressure on the external modes of vibration of NCO^- isolated in KBr at 90°K , obtained from $\nu_3 \pm \nu(\text{ext.})$.

tic modes also increased by this amount. The increases shown by the frequencies above the optic modes are even more marked. In fact the component originally at 167 cm^{-1} apparently remained close to the maximum longitudinal optic frequency and increased by about 20% before the phase change, and the band originally at 184 cm^{-1} showed an increase of 17%.

At pressures above the phase change of the KBr, the spectrum in the vicinity of ν_3 showed

no equivalent sharp features although some broader structure could be seen roughly symmetrically spaced about the new ν_3 position. This high-pressure spectrum must be related to the phonon distribution in the high-pressure form of the KBr. On releasing the pressure the original low-pressure phase spectrum was again recorded.

An indication of the probable region containing the more localized external vibrational frequencies of a given ion has been obtained from calculations of longitudinal, transverse, and torsional vibrations of the ion using calculated force constants and assuming an infinitely massive containing well. Values of ν within about 30% of observed sharp structure and showing the observed large pressure dependence have been obtained. This gives confidence in the use of these force constants when comparing the observed frequencies with perturbed lattice vibration calculations such as those due to Bjork.³

Thus as well as investigating the vibrations of the different impurity ions within the various supporting lattices, this work yields information about the pressure dependence of the basic lattice modes of the alkali halides, both in their normal structure and in their high-pressure modifications.

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HEAT MAGNETIZATION*

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By heat magnetization we mean the phenomenon (which is yet to be observed) in which a material which has no spontaneous long-range magnetic order at zero temperature becomes magnetized as it is heated beyond a critical temperature $T_1 > 0$ [Fig. 1, curve (a)]. In this Letter we obtain the criteria for the occurrence of this phenomenon for a simple model of a ferromagnet which has a direct relevance to

the magnetic behavior of some rare-earth materials.¹⁻⁸

In rare-earth materials the $2J+1$ directional degeneracy of the $4f$ -shell electrons of the ion is lifted by the crystal field. This usually prevents full alignment of the ionic moments by their exchange interactions and plays a major role in the determination of their magnetic ordering properties. In the effective-field ap-