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**NEUTRON SPECTROSCOPY OF THE
LIBRATIONAL MODE AMMONIUM IONS
IN THE MONOCLINIC PHASE OF NH₄SCN**

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NEUTRON SPECTROSCOPY OF THE LIBRATIONAL MODES OF THE AMMONIUM ION IN THE MONOCLINIC PHASE OF NH₄SCN: Preprint ITEP 4-02/

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To study ammonium ion dynamics, the temperature dependence of inelastic incoherent neutron scattering (IINS) and quasielastic incoherent neutron scattering (QINS) on NH₄SCN was obtained with the NERA-PR spectrometer. The identification of the translational and librational modes in the generalised phonon density of states (G(E)) was done using the measured IINS spectra of ND₄SCN. For a monoclinic crystal structure of NH₄SCN the librational frequencies of 0→1 and 0→2 transitions were calculated for a tetrahedron in a crystalline field of C₁ symmetry and were compared with the observed results. The appearance of QINS above 200 K is associated with the reorientation of the ammonium ions and is accompanied with the broadening of librational peaks and their merging into one broad maximum on G(E).

НЕЙТРОННАЯ СПЕКТРОСКОПИЯ ЛИБРАЦИОННЫХ МОД ИОНА АММОНИЯ В МОНОКЛИННОЙ ФАЗЕ NH₄SCN

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Проведено исследование влияние температуры на динамику аммония в NH₄SCN с помощью неупругого некогерентного рассеяния нейтронов (ННРН) и квазиупругого некогерентного рассеяния нейтронов (КНРН), измеряемого на спектрометре НЕРА-ПР. Идентификация трансляционных и либрационных мод в обобщенной плотности фоновых состояний (G(T)) проведена, используя спектры ННРН от ND₄SCN. Либрационные частоты для 0→1 и 0→2 переходов вычислены для тетраэдра в кристаллическом поле симметрии C₁ для моноклинной кристаллической структуры NH₄SCN и проведено сравнение с наблюдаемыми результатами. Появление КНРН выше 200 К связано с переориентацией ионов аммония и сопровождается уширением либрационных пиков и их слиянием в один широкий максимум на G(E).

Fig. - 6, Ref. - 19 names.

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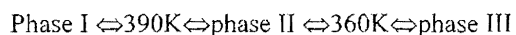
Introduction

The description of the rotational behavior of molecules or molecular ions in condensed matter appears to be a complex problem because it includes two parts: first, librational motion which takes place at a relatively high frequency and second, the reorientational motion which changes from relatively high to relatively low frequency during cooling [1]. These two different types of molecular motion exist in a molecular ionic substance such as ammonium thiocyanate, NH_4SCN , and have been studied using inelastic neutron scattering (INS). To the INS spectra there contributes inelastic incoherent neutron scattering (IINS) and quasielastic incoherent neutron scattering (QINS). The IINS is used to study the librational motion of molecular ions and QINS is used to study the reorientational motion of molecular ions.

This paper presents the results of the study of the librational motion and reorientational motion of the ammonium ions in NH_4SCN using respectively IINS and backscattering on NERA-PR neutron spectrometer (FLNP JINR, Dubna, Russia) for the temperature range of the monoclinic phase. The identification of librational modes in ammonium thiocyanate is carried out with the IINS of ND_4SCN . The librational frequencies of NH_4SCN and ND_4SCN have been computed and compared with the observed values. Above 200 K the reorientational motion of the ammonium ions leads to the broadening of the widths of the librational peaks in the IINS spectra and their merging into one broad maximum.

Experimental results

Ammonium thiocyanate is selected for neutron scattering investigation for it is a molecular ionic crystal formed of a molecular ammonium ion and a molecular thiocyanate ion. This compound undergoes a series of phase transitions [2]:



The crystal structures of these phases were studied by x-ray single crystal diffraction and neutron single crystal and powder diffraction [3-8]. It is shown that in the tetragonal phase I (space group $I4/mcm$, $Z=4$) the ammonium ions and

thiocyanate ions are disordered, in the orthorhombic phase II (space group $Pbcm$, $Z=4$) thiocyanate ions are ordered but the ammonium ions are disordered, and in the monoclinic phase III (space group $P2_1/c$, $Z=4$) the ammonium ions are ordered. The crystal structure of the monoclinic phase III of NH_4SCN were studied in detail using combined x-ray and neutron single crystal diffraction methods. As a result, the atomic positions of N, S, C and H were established [6]. Therefore the monoclinic phase of NH_4SCN is suitable for model calculations of the librational frequencies.

The neutron scattering experiments were carried out with protonated ammonium thiocyanate, NH_4SCN , and deuterated ammonium thiocyanate, ND_4SCN , in order to decompose the vibrational spectrum of ammonium thiocyanate into translational and librational modes. A sample of protonated ammonium thiocyanate was prepared from a high purity substance with the impurity content less than 0.1%. Due to ammonium thiocyanate being highly hygroscopic, the sample was dried at 75°C. A sample of deuterated ammonium thiocyanate was prepared by a standard method of evaporation from a heavy water solution. The degree of deuteration determined by NMR was 98%.

The IINS spectra of the protonated and deuterated samples of ammonium thiocyanate were measured on the NERA-PR time-of-flight neutron spectrometer at the IBR-2 high flux pulsed neutron source [9] over the temperature range of the monoclinic phase from 10 to 357 K. The IINS spectra were transformed into the generalised phonon density of states $G(E)$ with a computer program [10].

On NERA-PR neutron spectrometer the QINS spectra are measured by nearly backscattering from the (111) planes of copper single crystals set at the scattering angles 30, 40, 50, 80, 90 and 100 degrees. Thus QINS spectra are measured in the inverted geometry of scattering tuning the machine to an energy of 4.76 meV with a resolution of ca. 0.050 meV [9].

The $G(E)$ spectra from protonated and deuterated ammonium thiocyanate at 10 K are presented in Fig. 1. A comparison of these spectra shows that they have similar profiles except for the difference in the positions of peaks on the energy scale. This difference permits us to determine the librational modes of the ammonium ion because the librational frequencies of protonated ammonium ions are greater than those of deuterated ammonium ion by a factor of $(2)^{1/2}$. Such relations hold at NH_4SCN energies which are between 300 and 400 cm^{-1} . The maximums in the energy region from zero to 150 cm^{-1} correspond to acoustic translational phonons and those between 150 and 250 cm^{-1} correspond to optical translational phonons. A comparison of the translational and librational phonons observed in NH_4SCN and ND_4SCN is carried out in Table 1.

The temperature dependence of IINS spectra of protonated ammonium thiocyanate is studied in the temperature region from 130 to 357 K. The measured IINS spectra and the calculated $G(E)$ spectra as a function of the temperature are

presented in Fig. 2 and Fig.3, respectively. There is observed a marked temperature effect on the spectra. At 130 K there are splits between acoustic and optical translational phonons and between optic translational and librational phonons. An increase in the temperature is accompanied with the disappearance of these splits. The QINS contribution appears on the wings of an elastic peak from pyrolytic graphite monochromators at $\lambda_0=4.15 \text{ \AA}$ above 193 K. Up to this temperature the broadening of the librational peaks takes place due to anharmonicity [11]. Above this temperature the widths of the maximums increase as a result of increased reorientation of the ammonium ions. In order to separate the contributions of anharmonicity and reorientation of the ammonium ions to the broadening of the maximums, QINS spectra are measured by backscattering on the NERA-PR neutron spectrometer. Some QINS spectra obtained by backscattering on NH_4SCN are presented in Fig. 4. Each QINS spectrum is the result of a sum of QINS spectra obtained at six different scattering angles, which is done for the sake of statistics. The backscattering resolution or full width at half maximum of elastic peaks (FWHM_i or shorter W_i) of copper monochromators (0.05 meV) is better than that of pyrolytic graphite monochromators of the neutron spectrometer (0.6 meV).

The temperature dependence of the librational energies E_i ($i=1,\dots,4$) of four librational subbands and their W_i ($i=1,\dots,4$) are presented in Fig. 5a and Fig. 5b, respectively.

The monotonic temperature dependence of E_i and W_i begins to change sharply near 200 K. Above this temperature the broadening of the librational mode widths leads to the formation of a wide librational band near 255 K and the translational and the librational bands are not distinct near 357 K.

The QINS spectra are presented as sums of elastic scattering spectra described by a Gaussian function and quasielastic scattering spectra described by a Lorentzian function. The temperature dependence curves of the widths of the Gaussians (W_g) and Lorentzians (W_l) are determined and illustrated in Fig. 6a. It is shown in Fig. 6b that the temperature dependence of the Lorentzian widths W_l is described by as an Arrhenius behavior.

Model calculations

A1. Introduction.

In the low temperature monoclinic phase of NH_4SCN , the site symmetry of the ammonium ion is C_1 . Due to this low symmetry, there are many parameters in the rotational potential function of the ammonium ion [12]. The only way to determine all these parameters is to derive them from atom-atom potentials. The

potential functions of a number of groups of ammonium compounds have been derived from atom-atom potentials [13]. The ammonium solids are classified by the atom which is the nearest neighbor to the ammonium ion. The interaction between the hydrogen atoms of the ammonium ion and the nearest neighbor is the interaction which makes the largest contribution to the rotational potential function. Rotational potential functions have been derived from atom-atom potentials for ammonium-chlorine [14], ammonium-fluorine [15], and ammonium-oxygen compounds [16]. In the low temperature monoclinic phase of NH_4SCN , the nearest neighbor to the ammonium ion is the nitrogen atom. Since no other ammonium-nitrogen compounds have been studied, it is not possible to analyze the rotational properties of the ammonium ion as has been accomplished for other ammonium solids.

A2. Derivation of the rotational potential function.

The derivation of the rotational potential function from atom-atom potentials has been given by Yasuda for the study of solid methane [17]. The interaction between a hydrogen atom of an ammonium ion with any other atom X in the crystal is given by

$$\phi(R_{ik}) = A_{HX} \exp(-\alpha_{HX} R_{ik}) - C_{HX}/R_{ik}^6 - D_{HX}/R_{ik}^8 - q_H q_X / R_{ik} \quad (1)$$

The effective charge on the hydrogen atom of the reference ammonium ion is represented by q_H and the effective charge on the atom X is q_X . The first term on the right-hand side of Eq. (1) is the repulsive term and r^{-6} and r^{-8} terms are the leading terms in the van der Waals attraction term. The charge on the hydrogen atom of the ammonium ion is set at 0.19 electron units [14].

A3. Librational frequencies of NH_4SCN .

The crystal structure of NH_4SCN has been determined at 81 K by neutron diffraction [6]. Using the co-ordinates of the hydrogen atoms, it is necessary to rotate all the atoms in the crystal to get the ammonium ion in its standard orientation, which has the two-fold axis of the ammonium ion aligned along the c-axis and one of the hydrogen atoms lies at a 45 degree angle off the a-axis [16].

The procedure followed to derive the rotational potential function from atom-atom potentials is similar to the procedure followed for previous studies [14-16], except for the determination of the hydrogen-nitrogen atom-atom potentials. The charge on NH_4^+ is set at one electron unit. The partial charges for the other atoms are set using the work of Coppens, et al. as a guide [18]. The largest contribution to the rotational potential function comes from the hydrogen-nitrogen interaction. The parameters for this interaction are taken from the hydrogen-oxygen interaction that has been determined previously [16]. The parameter C in

Eq. (1) is allowed to change from its value for the hydrogen-oxygen interaction, while the parameters in the repulsive term in Eq. (1) are assumed to be the same for the hydrogen-nitrogen interaction as they are for the hydrogen-oxygen interaction. The value of C is determined for the hydrogen-nitrogen interaction by comparing the computed and observed librational frequencies. By increasing the value of C by about 67%, the computed librational frequencies are in agreement with the observed frequencies. The computed librational frequencies are given in Table 2 under the model I. Varying the value of C does not have a significant effect on the splitting of the librational frequencies, it simply adjusts the frequencies either up or down. The librational frequencies are computed from the rotational potential function by diagonalizing the Hamiltonian matrices. The procedure for the computing the hindered rotational energy levels for a tetrahedron in a crystalline field of C symmetry has been previously outlined [12].

A procedure similar to that described above for deriving the rotational potential function was also employed. Rather than using the hydrogen-oxygen interaction, the hydrogen-chlorine interaction was used as a basis for the hydrogen-nitrogen interaction. The value of D in Eq. (1) was set at zero. Lowering the value of C by 40% gives a rotational potential function that will give librational frequencies that agree with the observed librational frequencies. These computed librational frequencies are given in Table 2 under the model II.

The values of C determined by the two different approaches described above are nearly the same, $2.0 \cdot 10^5 \text{cm}^{-1} \text{\AA}^6$ when using H-Cl parameters and $2.05 \cdot 10^5 \text{cm}^{-1} \text{\AA}^6$ when using the H-O parameters. This shows that the parameters used in the repulsive potential do not have a significant effect on the value of C determined for the H-N interaction.

The model used in this paper predicts three different librational frequencies, while four different frequencies are observed. The observed frequencies at 380cm^{-1} are missing among the computed librational frequencies. Each of the computed librational frequencies is composed of five states, one with A nuclear spin state, one E state, and three T states. In Table 2, the librational frequencies corresponding to the $0 \rightarrow 2$ transitions are also given.

Conclusions

The results of the study of the molecular ionic compound NH_4SCN are presented. The investigation of the effect of anharmonicity and ammonium molecular ion reorientation on the $G(E)$ spectra is studied using inelastic and quasielastic incoherent neutron scattering in a temperature range from 10 to 357 K. It is shown with the help of computer modeling that some librational energies can be predicted within good coincidence but there are also difficulties which must be

understood. Temperature has a significant effect on the shape of the $G(E)$ spectrum of NH_4SCN . An increase in the temperature from 10 K to 200 K causes the broadening of the librational peaks on $G(E)$ due to anharmonicity. Above this temperature the main contribution to the broadening occurs due to ammonium ion reorientation. This temperature depends on the potential barrier of the reorientation.

Acknowledgments

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Table 1. A comparison of the translational and librational phonons observed in NH_4SCN and ND_4SCN (energy in cm^{-1})

NH_4SCN	ND_4SCN	$\sqrt{H/V^D}$
318	234	1.359
351	255	1.376
380	278	1.367
409	298	1.372

Table 2. The experimental energies of the librational modes for NH_4SCN and ND_4SCN and the calculated energies of these modes for the models I and II.

Transition	NH_4SCN	NH_4SCN	ND_4SCN	NH_4SCN		ND_4SCN	
	Optic [19]	IINS	IINS	Model I	Model II	Model I	Model II
0-1	315	318	234	312	322	230	236
	354	351	255	353	347	260	256
	375	380	278				
		409	298	417	405	305	297
0-2		598		598	615	447	
				644	646	479	
		671		682	670	507	
				716	712	529	
		753		756	736	556	
				807	780	596	

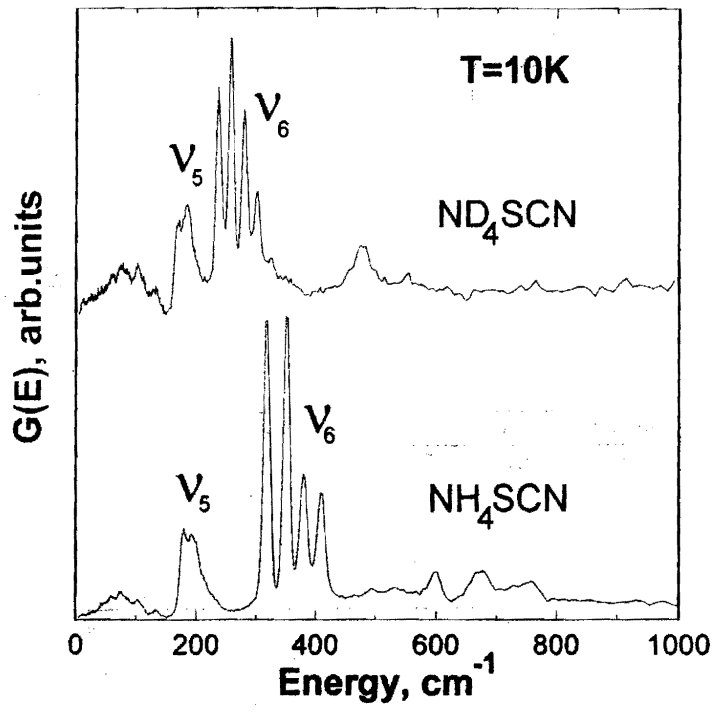


Fig. 1. The generalized phonon density of states $G(E)$ for NH_4SCN and ND_4SCN at 10 K.

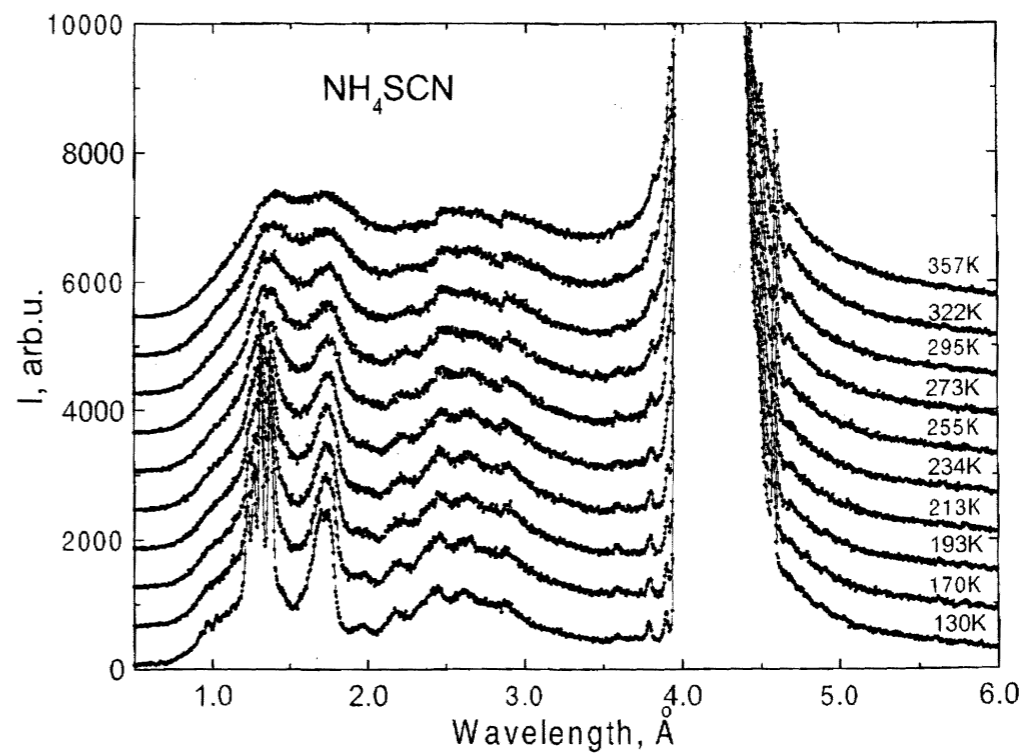


Fig. 2. The temperature dependence of the IINS spectra of NH₄SCN.

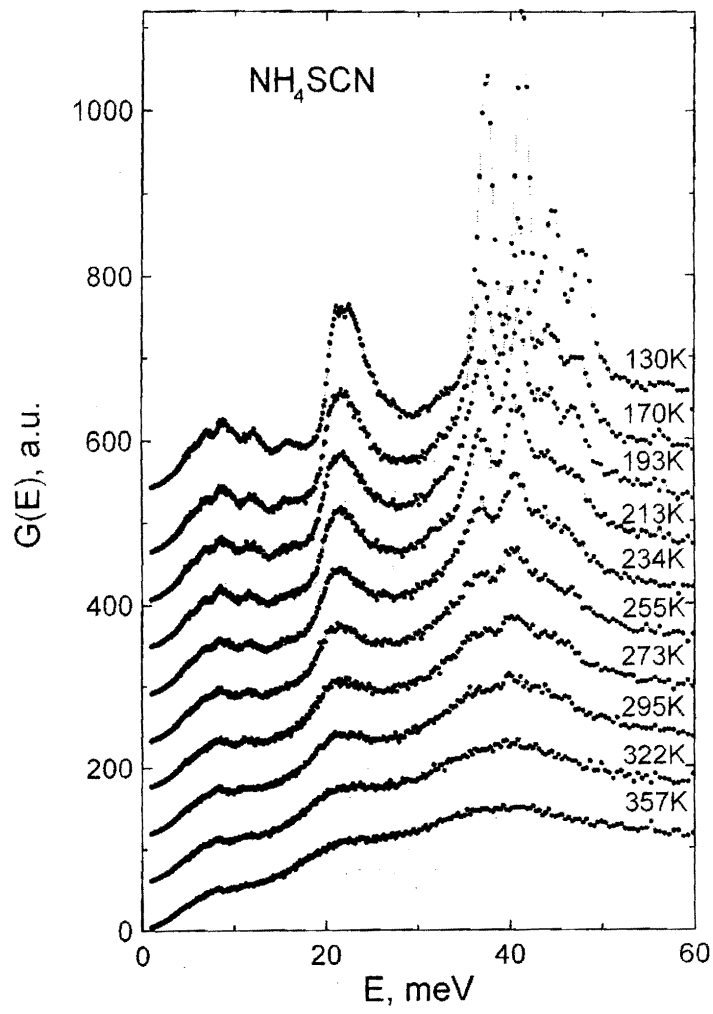


Fig. 3. The temperature dependence of the $G(E)$ spectra of NH_4SCN .

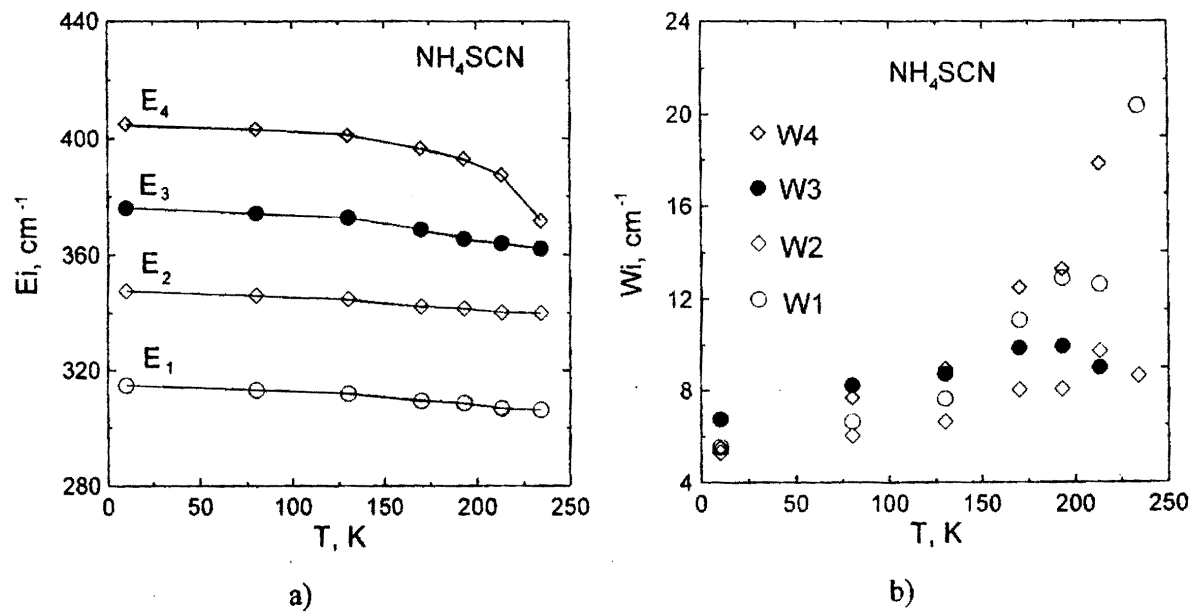


Fig. 4. The temperature dependence of (a) -the energies of the librational modes E_i ($i=1,\dots,4$), (b) - full widths at half maximum of the librational peaks W_i ($i=1,\dots,4$) for NH_4SCN .

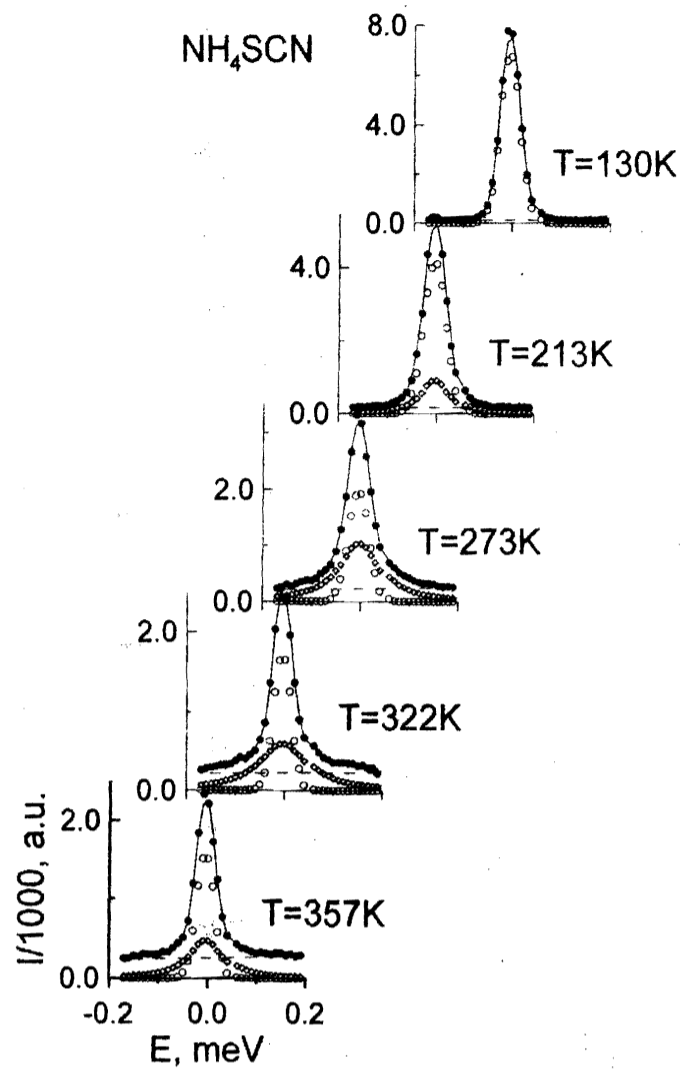


Fig. 5. The temperature evolution of the QINS spectra for NH_4SCN .

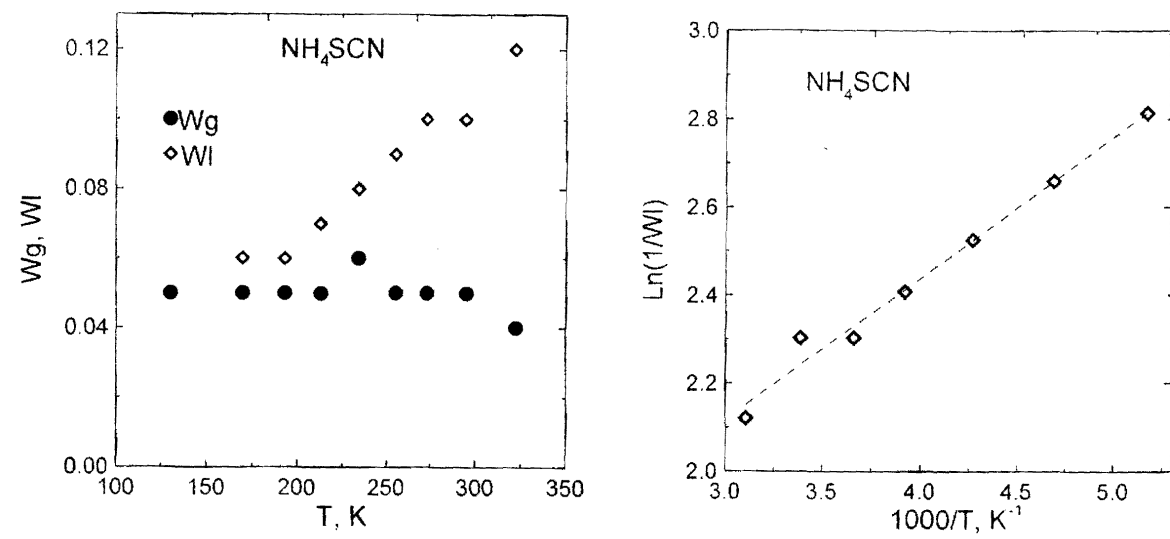


Fig. 6. The temperature dependence of (a) - the W_g (Gaussian) and W_l (Lorentzian) widths (in meV) corresponding to decomposition of the QINS spectra, (b) - the Arrhenius law for W_l .

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