Low-Temperature Physics and Chemistry in Cryomatrice

（Preface）

Studies of materials at low temperatures had a tremendous impact upon the development of physics and science in general, and played a significant role in the emergence and formulation of the quantum theory at the beginning of the 20th century. The earliest attempts at producing low temperatures in the laboratory relied on the cooling effect resulting from dissolution of crystalline solids in water. This method was also employed in the works of Sir Humphry Davy and Michael Faraday started in 1823, who succeeded in liquefying of a variety of gases, and can thus be viewed as pioneers of cryogenic research. Studies of gases at low temperatures, and the observation that their pressure decreases linearly with temperature led in 1848 Kelvin to interpret temperature in terms of kinetic energy. He introduced the concept of an absolute scale, where zero corresponds to the temperature at which constituent atoms and molecules lose all their kinetic energy.

A convenient path to cryogenic research was opened up in 1850's by the observations by Joule and Thompson that gases expanding adiabatically into vacuum have to overcome the weak attractive forces between their atoms or molecules, which results in their cooling. This method was used around 1877 by Cailletet and Pictet to condense a number of hard to liquefy gases, including oxygen, nitrogen, and carbon monooxide, work which in turn kindled the interest of Dewar in cryogenic research. Among his accomplishments, besides invention of the familiar «Dewar flask» was the demonstration that oxygen is paramagnetic; he also succeeded in 1898 in liquefying, and a year later in solidifying hydrogen gas.

An important step in further development of the field was the construction of the first cyclically operating refrigerators based on the Joule-Thompson effect around 1895 by Linde. This made possible large scale liquefaction of air with distilative separation of its components, and greatly facilitated cryogenic research. Finally, helium was liquefied in 1908 by Kamerlingh Onnes who cooled it by liquid hydrogen below its inversion temperature prior to the adiabatic Joule–Thompson expansion.

The history of low temperature physics is intimately intertwined with the history of rare gases. Lord Rayleigh, while making accurate measurements of molecular weights (he wanted to check Prout's hypothesis that the atoms of various elements are built from hydrogen, and have therefore weights that are integral multiples of its atoms) noted that nitrogen obtained from atmospheric air has a different weight than that made chemically. The mystery was solved by Ramsay, who was in 1894 able to show that atmospheric nitrogen contains a new element, the rare gas argon. Ironically, argon was not the first of the rare gases to be discovered. Some 25 years earlier Lockyer observed during solar eclipse a strong yellow spectral line, which he could not attribute to any known element. Janssen then concluded, that this line is due to a new chemical element, presumably present only on the sun, and suggested therefore to name it helium. One year after the discovery of argon, in 1895, Ramsay was able to isolate helium on earth by heating a mineral cleveite, where it forms due to radioactive decay of uranium. These first two members of the «inert» gas family, were soon followed by neon, krypton and xenon, all produced by fractionating liquefied air.

Interestingly, the realization of that rare gas solids and other condensed gases may provide a suitable medium for spectroscopic studies followed very shortly after their discovery. Vegard at the university of Leiden, at that time the Mecca of low temperature research, started already in the early 1920's a series of studies, which would clearly fall into the area which is today called matrix isolation. He investigated luminescence from condensed gases irradiated by x-rays or electrons, in the hope of gaining understanding of the origin of Aurora Borealis and other atmospheric and stratospheric phenomena. Using this method he was for instance the first one to observe the a_u^{3+} X_g^{1+} phosphorescence from the lowest triplet state of molecular nitrogen, which is today known as the Vegard–Kaplan bands.

After a virtual gap of some thirty years, the interest in spectroscopic studies in solid rare gases resurfaced in the early 1950's, when Pimentel coined the phrase «matrix isolation» and when deliberate, systematic studies of species isolated in rare gas solids started. The major goal of matrix isolation studies at that time was the observation and characterization of highly reactive radicals and other reaction intermediates. Such species which otherwise under normal conditions have only a very ephemeral existence, could be stabilized in the

rigid, inert solid, and studied then at leisure by spectroscopic means. Over the next decade virtually hundreds of free radicals, molecular ions, clusters, and similar transient species were generated, detected, and their molecular constants and other properties determined in rare gas matrices.

The condensed rare gases are characterized by weak interatomic interactions, and are therefore usually found to perturb only weakly the isolated «guest» species of interest. Furthermore, the guest spectra in the low temperature solids are invariably greatly simplified, since in most cases the molecular rotation is quenched, so that the entire rotational structure collapses into a sharp zero phonon line. Furthermore, at the low temperatures typically only the vibrationless level of the ground state of the guest is populated, so that «hot bands» and «sequence bands» which often clutter gas phase spectra are absent.

After an initial rapid development of the matrix isolation field, in 1970's alternative techniques were developed for studies of transient species, which completely avoid the medium perturbations inherent in the condensed phase technique. Thus for instance ions, clusters or radicals could be produced in electric discharges, by photolysis, or by laser vaporization, cooled to a few K by an adiabatic expansion, and investigated by laser spectroscopic techniques in the gas phase. In addition to eliminating the medium perturbation problem, such investigations also have the advantage of providing the rotational information which is in general lost in the nonrotating matrix isolated species, and for a while they seemed to spell doom to the matrix isolation technique.

In spite of that, however, if judged by the number of publications and by the frequency of and attendance at conferences on low temperature spectroscopy in solid matrices, one finds that the technique is still very much alive and well, only the emphasis and goals of the matrix studies have in many instances changed. Very often, the perturbations and interactions of the guest with the solid host, which were in the early works viewed as bothersome drawbacks of the technique, now become the main object and emphasis of the study. A wide range of phenomena and elementary excitations specific to condensed samples, such as phonons, librons, excitons and neutral or charged solute solvation become available for study. The low temperatures and weak interatomic interactions in the van der Waals solids often results in slowing down various relaxation processes, and makes them accessible to experimental study. The dynamics of many processes are here not obscured by the much stronger forces present in the more conventional solids, which makes them easier to study experimentally, and model theoretically.

We have mentioned above that the early experimental studies in condensed rare gases originated in Leiden, and matrix isolation was developed by George Pimentel in California. On the other hand, many key contributions towards understanding the spectroscopy and physical properties of impurities and defects in solids originated in the countries of Eastern Europe, including for instance the Ukraine, Russia, Estonia, and others. It is therefore perhaps appropriate, that this collection of papers appears as a special issue of «Fizika Nizkikh Temperatur», a journal which was founded in the «B. Verkin Institute for Low Temperature Physics», and in which many of these early important contributions first appeared. The contributions in this issue were selected to give what we hope to be a fair cross-section of the current activities in this field, and demonstrate the breadth of its applications.

Most of the early matrix isolation studies employed absorption spectroscopy, predominantly in the infrared range, to characterize the samples, but nowadays a much broader repertory of investigation techniques has become available. The samples can be studied at a wide range of wavelengths both in absorption or emission, and they can be excited by tunable or fixed frequency lasers in the infrared, visible or UV, x-rays or electrons. Using picosecond or femtosecond laser techniques, many processes whose dynamics could previously only be indirectly inferred from spectroscopic observations can now be investigated in real time, as for instance exemplified in the contribution by Chergui. Synchrotron radiation is a particularly useful, widely tunable photon source, which is increasingly being applied for matrix studies, as exemplified by the nice EXAFS investigation by Roubin et al., or by the work of Kerins et al. on high lying states of Mg atoms in matrices.

The applications of matrices today extend over an extremely wide range of different fields ranging from single molecules and microscopic properties of solids to bulk properties of solids, or investigation of reactions occurring in the interstellar space. The matrix method is useful in static studies of defects and impurities, and their effect upon the solid state properties, as well as in studies of dynamics on timescales ranging from days to femtoseconds. It yields information about diffusion processes, chemical reactions and charge localization and charge transfer. The information gained from these studies

is useful in varying and fields extending from purely basic science to technologically important fields such as chemical catalysis, semiconductor technology, or laser physics.

Several papers included deal with the traditional goal of matrix isolation, identification of new species, but for their efficient generation are now often employed novel methods, such as vaporization by lasers, which were not available to the early pioneers in the field. Here one could name the papers by Andrews et al. or by Lammers et al. Besides optical spectroscopy, also EPR has traditionally been a very useful technique, used to investigate open shell radicals and their reactions, as nicely demonstrated in the present issue by the manuscript by Misochko et al. Another infrared work exemplifying application to species of astrophysical or atmospheric interest is the infrared investigation of the photolysis of ozone by Chaabouni et al.

While traditional matrix materials were most commonly argon or nitrogen, for a variety of reasons much interest is currently shifting to other solids, for instance solid hydrogen or helium, and several of the manuscripts in this issue deal with these hosts. In the first place, in these very light, so called «quantum hosts» the zero point motion is not negligible compared with the lattice constants and separations of the host atoms, and consequently a variety of «quantum effects» not present in the conventional solids can be observed and studied. In this issue the papers by Ganshin et al., Kiselev et al. and Galtsov et al. deal with such quantum solids. An additional advantage, particularly in the case of parahydrogen, are the very sharp, high resolution spectra which can often be observed. In this collection, for instance the papers by Miki and Momose, or by Tam and Fajardo take advantage of this fact. The possibilities of producing «high energy density materials», and increasing for instance the specific impulse of rocket fuels by stabilizing atoms and reactive intermediates in solid hydrogen were also widely discussed and increase the interest in solid hydrogen or deuterium, and the study by Danilychev and coworkers is relevant in this context.

The specific nature of the trapping site, its symmetry, geometry, and its effects upon the guest properties and spectroscopy are most often quite unknown, and several of the contributions selected, for instance the works by Roubin et al. or Lorenz et al., explore this question. Conversely, the spectra of an atomic or molecular guest whose spectroscopy is well known in the gas phase may be greatly affected by the host when isolated in the condensed matrix.

In this way the guest atom or molecule may be used as a «spy» yielding information for instance about the changes in the trapping site size and local symmetry, and thus about the structural changes and phase transitions occurring in the host solid matrix, as nicely demonstrated here in the paper by Minenko et al.

Inclusion of even very minor concentrations of impurities can often have a profound effect upon the optical, structural, and thermodynamic properties of solids, and this issue and the detailed understanding of such effects is of key importance in many technologically important areas such as for instance semiconductor industry, solid state lasers and many others. Rare gases, with their relatively simple structure provide a very suitable medium for investigating these effects. Such applications are exemplified for instance by the thermal conductivities measurements of matrices doped with a rotating impurity, such as methane in the article by Dudkin et al. or by the sound propagation study by Kiselev et al., and also the study by Freiman et al. on the effect of oxygen impurities upon the cryocrystal thermal and magnetic properties can be mentioned in this context.

The rare gases, besides being a very convenient systems for solid state theoretical modelling, have themselves many potentially very useful characteristics. Thus their optical properties, and in particular their transparence, extending from far infrared into the vacuum ultraviolet range, besides enhancing their usefulness as a medium for spectroscopic matrix isolation studies, potentially also makes them a suitable material for solid state lasers, in particular in the far ultraviolet region. This consideration makes the questions of optical gain, stimulated emission and lasing in rare gas solids, as investigated for instance in the contribution by Chabbi et al., particularly interesting.

One of the drawbacks of the early matrix studies was due to the fact that most methods of generating transient species are not selective, but one typically obtains a complex mixture of products, among which the individual carriers have to be subsequently identified, for instance by a series of laborious isotopic substitution experiments. This problem can be solved if the product of interest is mass selected prior to deposition into the matrix. While such deposition of mass selected species in sufficient yields and concentrations for spectroscopic characterization represents a non-trivial task, in the last few years several groups have made considerable advances in this field, and in this issue

the papers by Fang et al. and by Lorenz et al. describe experiments in this direction.

While rare gases were chosen as suitable matrix isolation «solvents» for their chemical inertness, it is now well known that they are not really inert, but under suitable conditions display a relatively rich chemistry. Since the early days in the Pimentel's laboratory, rare gas matrices also proved to be a convenient reactive medium for the production, stabilization and identification of rare gas compounds. In the last few years there has been a resurgence of activity in this field, and a wealth of novel rare gas compounds has recently been described, with the paper Lundell et al. exemplifying this nice work.

As already noted above, the current range of activities in the matrix isolation is quite broad, in fact so broad that a single special issue can not do it justice. Even the selection of topics and techniques represented here is far from exhaustive. In spite of these limitations and shortcomings, we hope that it will demonstrate that even seventy five years after its earliest beginnings, and some fifty years after its rebirth in the Pimentel's laboratory, matrix isolation remains a very useful, versatile technique, with a wide scope of applications. The chances are good that it will probably easily survive also the next fifty years, as well as most of its current practitioners, and that also future generations of chemists and physicists will, like George Pimentel always used to recommend, try to «keep it cool».

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