Van Vleck Magnetism and High Magnetic Fields: new effects and new perspectives

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Van Vleck or polarization paramagnets represent a rather wide class of solid-state magnets that has been studied for a long time. Van Vleck paramagnetism is as universal a magnetic property of solids as diamagnetism. It is caused by the elastic deformation of the electron shell of an atom or ion by an external magnetic field, giving rise to an induced magnetic moment. Thus, unlike orientational paramagnetism, where already-formed magnetic moments of atoms or ions are ordered in a magnetic field, Van Vleck paramagnetism is of a polarizational nature. The static magnetic susceptibility of these magnets obeys a Curie law at high temperatures and becomes constant at low temperatures. The quantum mechanical theory developed by Van Vleck explains this behavior of the magnetic susceptibility by the absence of a magnetic moment in the ground state of the ion (the electronic ground state is either a singlet or a nonmagnetic doublet) and the appearance of a contribution to the susceptibility due to virtual transitions induced by the Zeeman interaction with the external magnetic field between the ground and excited states of the ion. Van Vleck paramagnetism most often occurs in crystals containing non-Kramers rare-earth (RE) ions, i.e., RE ions with an even number of electrons in the unfilled 4*f*- shells (e.g., Pr^{3+}, Eu^{3+}, Tb^{3+}, Ho^{3+}, Tm^{3+}), where the crystalline electric field lifts the degeneracy of the ground multiplet $^{2S+1}L_J$, leading to typical splittings of the Stark structure of the order of 10–100 cm^{-1}. These splittings greatly exceed the energy of the RE ion in the usual moderate magnetic fields, so that the Zeeman effect can be calculated using perturbation theory.

The isotopes ^{141}Pr, ^{159}Tb, ^{165}Ho, and ^{169}Tm have a 100% abundance (the abundances of the europium isotopes ^{151}Eu and ^{153}Eu are 47.8% and 52.2%, respectively) and a nonzero nuclear spin, and therefore compounds of these elements posses nuclear as well as electronic magnetism. The rather strong hyperfine interaction makes these substances extremely interesting from the standpoint of studying electronic–nuclear magnetism. The magnetic field induced at the nucleus of the Van Vleck RE ion is many times greater values (up to several hundred) of the paramagnetic shifts of the NMR lines. This causes many interesting features in the NMR of rare-earth ions, which accordingly can be classified as a phenomenon intermediate between ordinary NMR and electron paramagnetic resonance (EPR). This so-called ‘‘enhanced’’ NMR is one of the most important methods for studying the magnetic properties of Van Vleck paramagnets. The results of these studies have been reviewed in Refs. 1–4.

The majority of crystals of intermetallic compounds with non-Kramers RE ions have cubic symmetry, while the symmetry of crystals of insulating compounds is ordinarily lower; this leads to extremely high anisotropy of the effective gyromagnetic ratio of the nuclear spins of Van Vleck ions. Such anisotropy, which is not observed in ordinary NMR, emphasizes further the intermediate character of ‘‘enhanced’’ NMR.

Because of these features, Van Vleck paramagnets can be used for cooling nuclear spin systems and for studying the effects of nuclear magnetic ordering at higher temperatures than in the case of ordinary nuclear paramagnets.

The magnetic properties of insulating Van Vleck paramagnets have been quite well studied in the region of low temperatures and moderate magnetic fields, where the energy of the Zeeman interaction is many times smaller than the characteristic energies of the Stark splitting. As we have said, the main method of experimental study of these substances under such conditions is ‘‘enhanced’’ NMR. Optical spectroscopy is not very informative because of the rather large inhomogeneous broadening, and ordinary EPR has been observed only on impurity paramagnetic ions, which can sometimes introduce substantial local distortions to the crystal lattice of the Van Vleck paramagnets. Further increase of the magnetic field leads to violation of the conditions of applicability of perturbation theory, which has been used in obtaining all of the theoretical results concerning Van Vleck paramagnets. It is very important that applied high magnetic field allows to change the distance between Stark levels of the ground multiplet so it is possible to use the resonant methods for investigations. Besides such magnetic fields lead to the further distortions of 4*f*-shells and consequently to essential changes in the electron-nuclear magnetism.

In the present report we review the results of our theoretical and experimental investigations of new effects in insulating Van Vleck paramagnets at high magnetic fields [5-7] and discuss the possible perspectives of such investigations. We will discuss the following effects:

1. *High–frequency EPR*. It allows to observe transition between Stark levels of the ground multiplet and to verify or estimate CEF constants. It is important for example in the case of skutterudites containing Van Vleck ions because the complete information about CEF parameter is still absent.
2. *The coupled 4f-electron-phonon excitations*. They appear due to the distortions of 4*f*-shell by applied magnetic field and provide a rather wide possibilities for the investigations of cooperative phenomena.
3. *Electron-nuclear states and hyperfine interactions*. High magnetic fields cause the great mixing of electronic and nuclear states in Van Vleck paramagnets and number of new effects appear.
4. *Magnetic coupling with liquid He-3*. A high magnetic polarization of Van Vleck paramagnets can be transferred to the liquid He-3. The possibility of such dynamic polarization is discussed.

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