

Nature of paramagnetic centers on the crystal surface of van Vleck paramagnets

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Defect paramagnetic centers Tm^{3+} ($g = 11.6 \pm 1$, initial splitting $\Delta \leq 0.3 \text{ cm}^{-1}$) have been detected on the crystal surface of a finely dispersed powder of a van Vleck dielectric paramagnet $LiTmF_4$ by the methods of magnetic susceptibility and electron spin resonance measurements. It is suggested that these centers be used for dynamic polarization of the nuclei in liquid helium-3 by the solid-effect method.

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1. The magnetic coupling between liquid helium-3 and a solid-state substrate has been studied extensively (see, for example, Refs. 1–7). A large volume of experimental data on the magnetism of adsorbed solid-state layers of He-3 has been accumulated (see, for example, Refs. 8–10). However, the state of the surface of the solid substrate has in no way been taken into account in the study of either the transfer of magnetization through the solid—liquid-helium-3 boundary or the nuclear magnetic relaxation of liquid ^3He near the interface. An exception is Ref. 7, where it was assumed that microcracks, in which the symmetry of the crystal lattice is lowered and as a result different defect paramagnetic centers can appear, are present on the crystal surface. The latter centers, which have a good contact with liquid helium-3, undoubtedly strongly affect the relaxation parameters of liquid helium-3. Examples of such defects are paramagnetic centers which form on the surface of diamagnetic substances as a result of the breaking of electronic bonds. In Ref. 7 we proposed another possible form of these defects: The magnetic properties of van Vleck ions change radically — they become paramagnetic — as a result of the lowering of the symmetry of the crystal electric field at the surface. This hypothesis made it possible to match the results of measurements of the spin kinetics of liquid ^3He in contact with crystals and magnetically ordered powders of the van Vleck dielectric paramagnet $LiTmF_4$. Until now, however, there was no direct proof for the existence of such surface paramagnetic centers.

The objective of our study is to investigate the magnetic surface properties of the van Vleck paramagnet $LiTmF_4$.

2. We studied $LiTmF_4$ powders with two characteristic average particle sizes: 100 μm and 1 μm . Just as in Ref. 3, the “micron” powder was prepared by grinding in a sapphire mortar with the addition of dehydrated alcohol; the coarse-grained powder was obtained without the alcohol. The temperature dependence of the magnetic susceptibility was investigated in the range 4.2–78 K by measuring the inductance of a coil with the

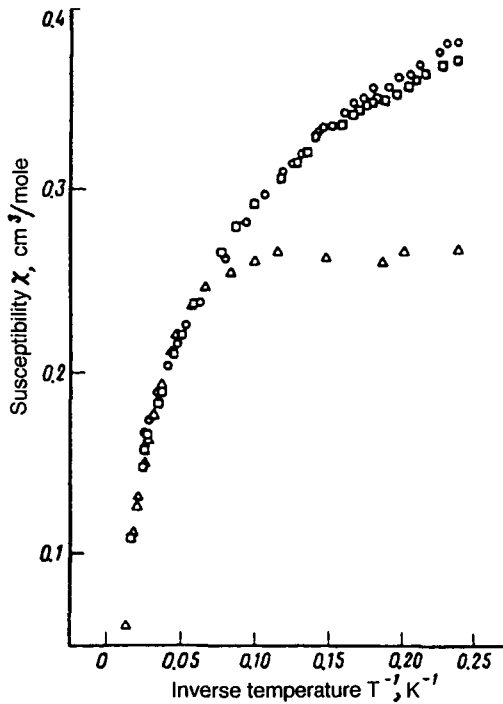


FIG. 1. Temperature dependence of the magnetic susceptibility of $LiTmF_4$ powders (Δ — coarse-grained powder with $100 \mu m$ particles, \square — $1 \mu m$ powder prepared by the method of Ref. 3 with the addition of dehydrated alcohol, \circ — $1 \mu m$ powder prepared in an inert atmosphere of dry 4He).

sample at a frequency of 100 Hz and then subtracting the contribution introduced by the container. The results of the measurements are shown in Fig. 1.

The magnetic susceptibility of the coarse-grained powder (see Δ in Fig. 1) was found to be typical for van Vleck paramagnets: The Curie law is satisfied at high temperatures and the temperature dependence vanishes at low temperatures. The susceptibility scale in Fig. 1 was calibrated taking into account the experimentally determined components of the van Vleck susceptibility tensor.³ In the "micron" powder (see \square in Fig. 1) an additional paramagnetic contribution to the integral susceptibility of the sample is present at temperatures below 10 K. This contribution could be associated with a large increase in the concentration of defect paramagnetic centers as a result of an increase of the surface in the "micron" powder, since according to Ref. 11, the number of defects on the crystal lattice increases exponentially as the particle size decreases. In our case, the concentration of defect centers cannot exceed 5%; this is indicated by the fact that the x-ray diffraction patterns of the two powders are identical.

3. What is the nature of such centers? Such defects can appear either with a lowering of the local symmetry of the crystal lattice as a result of plastic deformations and other mechanical actions during the preparation of the powders or as a result of chemical adsorption — the formation of the chemical compound between ions of the crystal

LiTmF_4 and water molecules adsorbed from air or alcohol (the alcohol, though dehydrated, is an excellent sorbent of water from air).

We now consider the question of the appearance of a paramagnetic contribution to the susceptibility from the standpoint of chemical adsorption. Here the most likely candidates for new chemical compounds on the surface are: thulium hydroxide $\text{Tm}(\text{OH})_3$, thulium trifluoride TmF_3 , and thulium oxyfluoride TmOF . We present below the computed lower energy levels (cm^{-1}) and the corresponding wave functions of the Stark structure of the ground multiplet of the Tm^{3+} ion ($^3\text{H}_6$, $J=6$) in the compounds:

a) thulium hydroxide $\text{Tm}(\text{OH})_3$ (the crystal field parameters are taken from Ref. 12)

$$39.13 \begin{cases} 0.3126|-5\rangle + 0.0142|-1\rangle + 0.9498|1\rangle + 0.0047|5\rangle \\ -0.0047|-5\rangle + 0.9498|-1\rangle - 0.0142|1\rangle + 0.3126|5\rangle \end{cases}$$

$$0 - 0.1014|-6\rangle + 0.9897|0\rangle + 0.1014|6\rangle;$$

b) thulium trifluoride TmF_3 (the crystal field parameters for $\text{Tm}:\text{LaF}_3$ from Ref. 12 were used)

$$75.54 \begin{aligned} & - (0.4224 - 0.0256i)|-6\rangle + (-0.5431 - 0.0565i)|-4\rangle \\ & + (-0.0787 - 0.1248i)|-2\rangle + (0.0458 + 0.0057i)|0\rangle \\ & + (-0.1068 + 0.1018i)|2\rangle + (-0.5404 - 0.0778i)|4\rangle \\ & + (0.4033 + 0.1280i)|6\rangle, \end{aligned}$$

$$71.15 \begin{aligned} & - (0.2659 - 0.0837i)|-5\rangle + (0.4891 - 0.3044i)|-3\rangle \\ & + (0.0587 - 0.2949i)|-1\rangle + (-0.2828 + 0.1021i)|1\rangle \\ & + (-0.2279 + 0.52911i)|3\rangle + (-0.0431 + 0.2755i)|5\rangle, \end{aligned}$$

$$0 \begin{aligned} & - (0.3020 + 0.0000i)|-6\rangle + (-0.4477 - 0.2487i)|-4\rangle \\ & + (-0.2204 - 0.2973i)|-2\rangle + (-0.0516 + 0.1281i)|0\rangle \\ & + (0.3650 - 0.0614i)|2\rangle + (0.4950 + 0.2094i)|4\rangle \\ & + (-0.2177 - 0.2094i)|6\rangle; \end{aligned}$$

c) thulium oxyfluoride TmOF (the crystal field parameters for $\text{Dy}:\text{DyOF}$ from Ref. 13 were used:

$$84.03 \begin{aligned} & - 0.3187|-6\rangle + 0.6236|-3\rangle + 0.1380|0\rangle - 0.6236|3\rangle + 0.3187|6\rangle, \\ 0 & - -0.2769|-6\rangle - 0.6506|-3\rangle - 0.6506|3\rangle + 0.2769|6\rangle. \end{aligned}$$

Our calculations show that all substances listed above are van Vleck paramagnets and not one of them can give at temperatures below 10 K a paramagnetic contribution of any significance to the integral susceptibility of the "micron" powder.

4. Surface paramagnetic centers can thus appear only as a result of local distortions of the crystal lattice on the surface of LiTmF_4 produced as a result of the appearance of microcracks. To prove this assertion, we investigated the temperature dependence of the

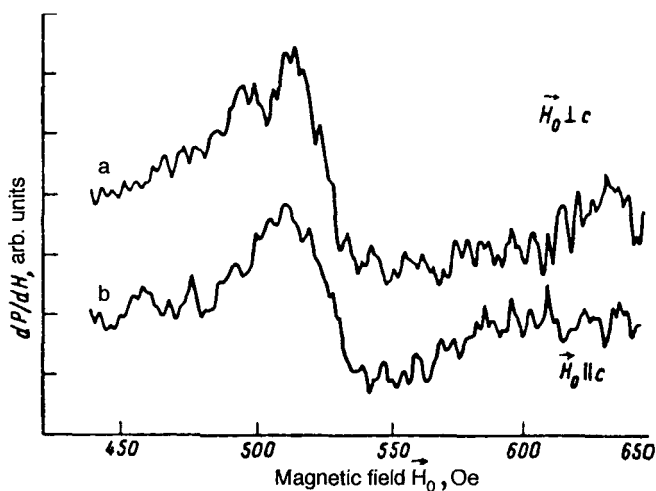


FIG. 2. ESR spectrum ($\lambda = 3$ cm) of paramagnetic Tm^{3+} ions in magnetically ordered micron LiTmF_4 powder at $T = 6.2$ K: a — $\mathbf{H}_1 \parallel \mathbf{H}_0 \perp c'$ (c' — direction of predominant orientation of the crystallographic c axes of the powder particles), linewidth $\delta H = 60$ Oe; b — $\mathbf{H}_1 \parallel \mathbf{H}_0 \parallel c'$, $\delta H = 40$ Oe.

magnetic susceptibility of the “micron” powder prepared in an inert atmosphere of dry ^4He (see Fig. 1). The fact that the temperature dependences of the susceptibilities of the “micron” powders prepared under different conditions are virtually identical supports our idea of the nature of these centers. We note here that according to IR spectroscopy data, the “micron” LiTmF_4 powder prepared with alcohol contains a substantial number of water molecules which appear on the crystal surface as a result of physical adsorption, i.e., without the formation of a new chemical compound.

5. To make a final check of the correctness of our ideas about the nature of such paramagnetic centers, we investigated ESR ($\lambda = 8$ mm and $\lambda = 3$ cm) in all three powders. A very asymmetric wide line (width exceeding 1000 Oe), which is characteristic for mechanically fractured magnetically anisotropic solids,¹⁴ with a g factor of the order of 12 and initial splitting of the energy levels of the paramagnetic centers ≤ 0.3 cm^{-1} , was observed in the “micron” powders. Approximately the same ESR parameters were obtained in Ref. 15 in the investigation of Tm^{3+} ions in the low-symmetry positions in calcium fluorophosphate crystals $\text{Ca}_5(\text{PO}_4)_3\text{F}:\text{Tm}^{3+}$.

It is known that since Tm^{3+} is a non-Kramers ion, the optimal conditions for observing ESR should be satisfied when the rf field \mathbf{H}_1 is oriented parallel to the static magnetic field \mathbf{H}_0 .¹⁶ Experiments performed in a special resonator made it possible to observe Tm^{3+} ESR at liquid-helium temperatures (see Fig. 2). Magnetically oriented micron powder was employed in these experiments. As one can see from Fig. 2, for the principal orientations of the magnetic field \mathbf{H}_0 relative to the direction of predominant orientation of the powder particles c' the position of the line remains unchanged and is determined by the g factor: $g = 11.6 \pm 0.1$. At the same time, the width of the ESR line in these orientations differs by a factor of 1.5. These two facts support our ideas. Orientation of the powder does not generally imply that the local crystallographic axes of the thulium

ions are simultaneously oriented on the surface. At the same time, the anisotropy of the macroscopic magnetization of the oriented powder affects the Tm^{3+} ESR linewidth: The magnetization is maximum and therefore the ESR linewidth is greater in the orientation $\mathbf{H}_0 \perp c'$. The initial splitting of the thulium ions can be determined by comparing ESR data at two frequencies (8.76 GHz and 37.05 GHz): Δ does not exceed 0.3 cm^{-1} . Using the ESR parameters obtained by us, we can estimate the concentration of the defect paramagnetic centers from the additional paramagnetic contribution to the susceptibility. A crude estimate (ignoring the effect of the demagnetizing fields and the distribution of these centers) gives 0.1%, consistent with the x-ray crystallographic data and the Tm^{3+} ESR linewidth.

We note that the ESR of defect thulium ions in the van Vleck paramagnets TmVO_4 and $\text{Tm}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ was observed in Ref. 17 and 18, respectively. In Ref. 17 the question of the nature of these centers remained open, whereas in Ref. 18 it was determined that there exist two weak, slightly different defect positions of the Tm^{3+} ions with twofold symmetry axes perpendicular to the crystallographic axis c of the crystal. The g factor and the initial splitting, however, could not be determined in that study, since the measurements were performed only at a single frequency.

6. In conclusion, we note that the results of our study confirm our assumption concerning the mechanism of the relaxation of liquid He-3 in contact with dielectric crystals.⁷ In addition to the method of dynamic polarization of the nuclei in liquid ^3He , using van Vleck dielectric paramagnets, as proposed in Ref. 19, defect paramagnetic centers which have a good contact with the atoms in liquid helium-3 can also be used to polarize the latter by the solid-effect method. Polarization of the ^3He nuclei can probably be achieved directly and indirectly via the protons in the water molecules adsorbed in microcracks. That magnetization transfer from the protons to the nuclear spins in liquid He-3 can occur has been confirmed in Refs. 5 and 6.

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