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A modification of the commercial ESR900 cryostat to enable three-dimensional electron-paramagnetic-resonance studies of crystals

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Complete orientation studies of *X*-band electron-paramagnetic-resonance spectra of crystals largely benefit from the possibility to measure the spectrum for any orientation of the magnetic field with respect to the crystal without the need to remount the crystal. We report on a modification of a commercial cryostat to allow such experiments down to liquid helium temperatures and demonstrate its performance. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2908163]

Electron-paramagnetic-resonance (EPR) spectroscopy concerns the measurement of microwave transitions between different electron spin states of a paramagnetic system in an external magnetic field. In general, the wave function of a paramagnet is anisotropic, which renders the EPR spectrum dependent on the direction of the magnetic field. Within the concept of the spin Hamiltonian, the orientation dependence of the primary EPR observables, the fields of resonance, translates into the tensorial nature of the Zeeman, zero-field-splitting, hyperfine, and/or quadrupole interactions. The study of the electronic structure of a paramagnetic species benefits largely from the complete knowledge of the corresponding tensors (typically g, D, A, and Q). This in turn requires nonrandom samples, preferably single crystals, and a three-dimensional orientation study of the EPR spectrum. Such a measurement may not always be easy, in particular, so when it has to be performed at cryogenic temperatures. Most groups involved in this type of research therefore make use of homebuilt equipment.

Here, we report on a modification of the commercial Oxford ESR900 cryostat to allow such studies. This cryostat is commonly used for EPR measurements at various temperatures and *X*-band frequencies using TE_{102} type of resonators. The modification enables us to vary the orientation of a crystal in the resonator in two mutually perpendicular planes and to perform a complete three-dimensional orientation study of the EPR spectrum at temperatures down to liquid helium. We describe the modification in detail and illustrate its performance.

The commercial cryostat with the goniometer in place enables the rotation of the crystal around the vertical axis. We refer to this rotation angle as the "gonio angle." To make a device that allows rotation of the crystal in two mutually orthogonal planes presents a challenge because of the limited space available inside the cryostat, its specific geometry, and the requirement that materials inside the resonator have to be microwave transparent. The whole cooled volume has to fit into the quartz Dewar with an inner diameter of 6 mm.

The overall structure is shown in Fig. 1, and exploded view of the mechanical construction is shown in Fig. 2. The crystal is placed inside the quartz tube (1), which has an inner diameter of 2.3 mm, an outer diameter of 2.8 mm, and a length of 3.7 mm. The quartz tube in turn is placed inside the rexolite support (2) in such a way as to allow free rotation around its axis. The aluminum knob (3) on top, provided with an angular scale, controls this rotation. A Bevel gear of ratio of 1:1 (4) transmits the rotation around the vertical axis into a rotation around a horizontal axis, which is transmitted to the rotation of the sample tube through the flax wire (5). We refer to this rotation angle as the "dial angle." The spring (6) connected to the wire provides optimal friction for the rotation of the quartz tube. A rexolite cover tube (7) with an outer diameter of 5.9 mm serves to secure the quartz tube in its position in the support and to guide the helium flow along the sample. The original sample support made out of quartz

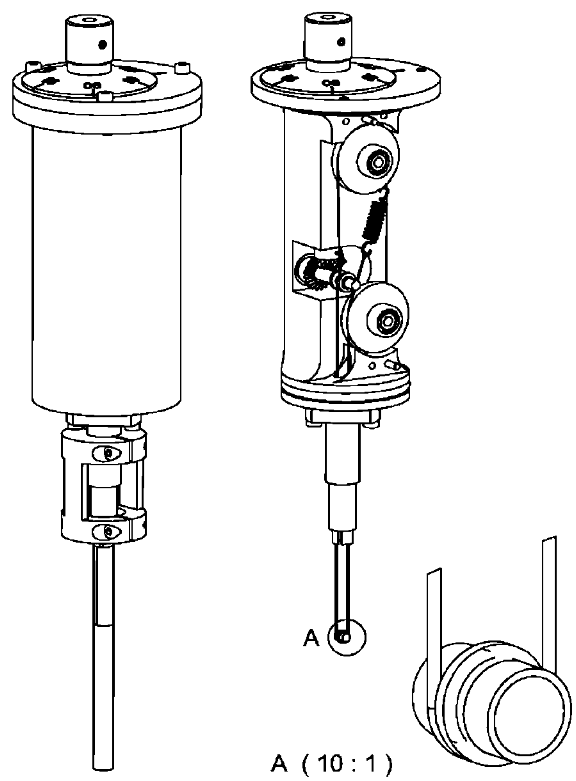

FIG. 1. Overall view of the modified ESR900 cryostat. The detail A represents the flax wire wound around the sample tube.

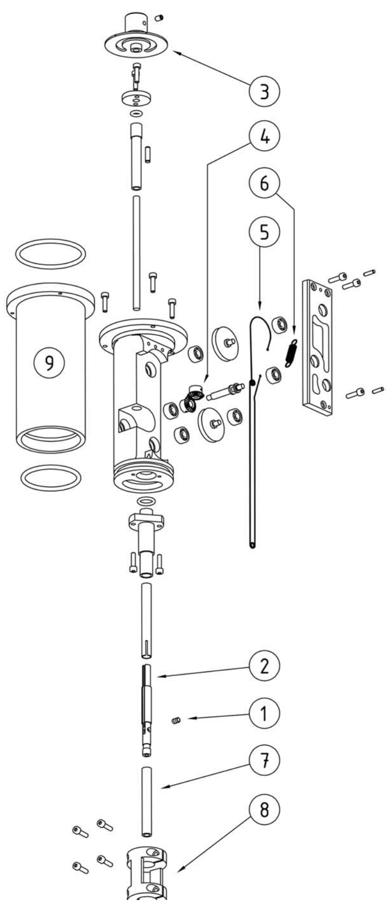

FIG. 2. Exploded view of the construction. Further explanation is given in the text.

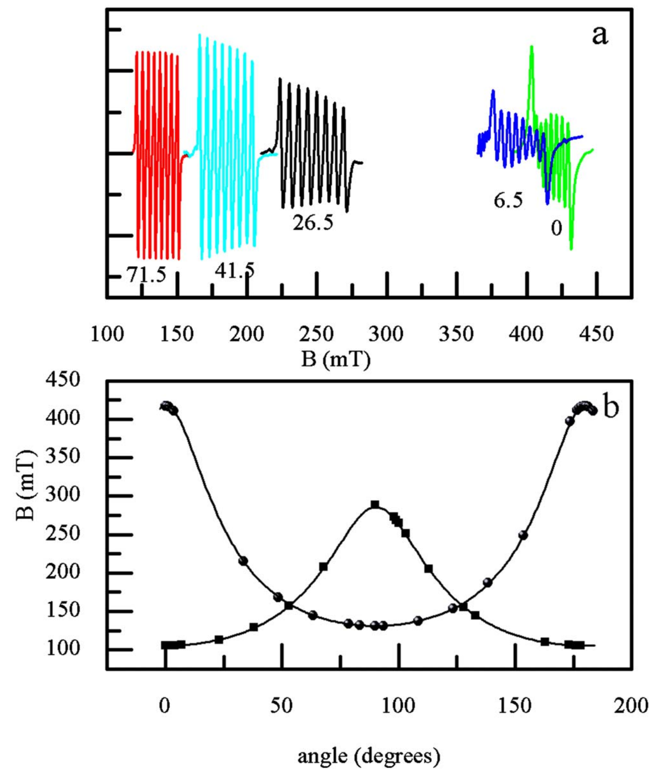

FIG. 3. (Color online) Data from the *X*-band EPR study at 5 K of a single crystal of 1% Co in Zn[(phenyl)$_2$P(S)NP(S)(iso-propyl)$_2$]$_2$. (a) Representative cw EPR spectra for some orientations of the magnetic field in a plane containing the g_x-axis (the direction of g_x corresponds to 0°).(b) The center of the resonance fields as a function of the orientation of the magnetic field in two planes. The circles refer to the same plane as the spectra in (a). The squares refer to a plane that contains the g_z-axis (the direction of g_z corresponds to 0°). The curves correspond to fits based on the spin Hamiltonian including the Zeeman interaction and the zero-field splitting (cf. Ref. 3).

was removed from the cryostat. In addition, the original brass collar was replaced by one with a larger outer diameter. This diameter closely matches the inner diameter of the rexolite cover. When in operation, the device is positioned in the cryostat in such a way that the rexolite cover tube is precisely on top of the brass collar. The clamp (8) fixes the device with respect to the goniometer. The aluminum cover (9) provides isolation of the inner volume of the cryostat from the air outside.

In order to test the new device, we made use of a single crystal of ZnO doped with Mn(II). The insert allows the independent rotation of the sample around two mutually perpendicular axes: around the vertical axis by the gonio angle and around the axis of the sample tube, which is in the horizontal plane, by the dial angle. In order to calibrate the scale of the dial, we first determine the orientation of the axis of the sample tube (i.e., the rotation axis corresponding to the dial angle) with respect to the (fixed) direction of the magnetic field in the horizontal plane. When the axis of the sample tube is aligned with the field, no change of the EPR spectrum of the crystal should be observed upon rotation of the dial. When this axis is perpendicular to the magnetic field, dial rotation corresponds to a rotation in a plane that contains the magnetic field. Consequently, the EPR spectrum of the crystal should be identical for two angles that differ by 180°. This criterion provides for an accurate calibration. The procedure also allows the definition of the orientations in a laboratory reference axes system, which is, for example, relevant when coupling EPR data with X-ray diffraction data for the same crystal. The orientation of the axis of the sample tube perpendicular to the magnetic field may serve as reference point for the gonio angle and the vertical axis as reference point for the dial angle.

The reproducibilities of the positioning of the sample with respect to the direction of the magnetic field are found to be ±0.5° for the gonio angle and ±1° for the dial angle. In the case of the dial, this reproducibility is achieved only when the wire is always pulled at from the side of the spring (6). For the proper use of the insert, the wire has to be kept under tension to avoid slipping of the wire with respect to the quartz tube. Subsequently we performed tests upon cooling, again by using the ZnO/Mn(II) crystal. We found no difference compared to room temperature as regards the reproducibility of the sample orientation, but it turned out that the position of the dial angle shifts during the cooling down of the insert. This effect is connected with the thermal shrinking of the materials. The EPR spectrum ($S=5/2$, $I=5/2$) for this system corresponds to an axial g-tensor.[1] It consists of five sextuplets of lines and presents maximum width when the magnetic field is parallel to the axial g axis. So, starting at room temperature from an orientation where the width of the spectrum is maximal and keeping the gonio angle fixed, we observed a shift in the position of the dial angle between room temperature and 5 K of about 10°. In evaluating data this shift has to be corrected for.

An illustration of the performance of the new insert is represented in Fig. 3. The data concern a single crystal of Zn[(phenyl)$_2$P(S)NP(S)(iso-propyl)$_2$]$_2$ (Ref. 2) doped with 1% cobalt ($S=3/2$). Besides this crystal, a small ZnO crystal was mounted on the sample holder for calibration of the shift in the dial angle upon cooling ($12\pm2°$ in this case). The spectra of the two crystals overlapped only for a few orientations. For the cobalt complex effective g-values at X-band are $g_x{}'=1.65$, $g_y{}'=2.38$, and $g_z{}'=6.44$. The spectra in Fig. 3(a) concern orientations in a plane containing the principal g_x axis (corresponding to 0°), each electron spin transition being split by the cobalt nuclear-hyperfine interaction ($I=7/2$). In Fig. 3(b), we summarize the centers of the fields of resonance as a function of the orientation of the magnetic field with respect to the crystal for two planes, one containing the g_x axis and corresponding to the data in Fig. 3(a), the other containing the g_z axis. The complete study of this cobalt complex provided the zero-field-splitting tensor and the g-tensor, and the curves represent the corresponding fits to the data. A full description of the EPR investigation of this four-sulfur coordinated cobalt complex will be published elsewhere.[3] In the present context, we emphasize that all spectra for orientations of the magnetic field in different planes were obtained in the ESR900 cryostat without remounting the crystal.

We have described a modification of the ESR900 cryostat, which can easily be realized in any laboratory. It enables the study of the X-band EPR spectrum of a single crystal down to liquid helium temperatures for all orientations of the magnetic field mounting the crystal only once.

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