A spectacular pressure-induced electronic transition in KTb(MoO₄)₂

A. Jayaraman, S. Y. Wang, S. K. Sharma and S-W. Cheong*

University of Hawai'i at Manoa, Hawai'i Institute of Geophysics and Planetology, Honolulu, HI 96822, USA
*AT&T Bell Laboratories, Murray Hill, NJ 07974, USA

Results of pressure Raman and optical absorption studies are reported for KTb(MoO₄)₂. A phase transformation occurs at 27 kbar when the crystal is pressurized at ambient temperature, in a hydrostatic pressure medium. The sample changes to a deep yellow colour at the transition and visibly contracts in the a-axis direction. The colour shifts red on further pressure increase. The Raman spectral features and the X-ray powder pattern change abruptly at the transition indicating a structural change. The colour change is attributed to 4f-5d transition in Tb initiated by the structural transition, and consequent intervalence charge transfer between Tb and Mo.

THE alkali-rare earth dimolybdates $MLn(MoO_4)_2$ have a rich crystal chemistry[1], and among them the series involving potassium and heavy rare earths crystallize in a layer-type structure, with orthorhombic symmetry D_{2h}^{14} (ref. 2). In $KTb(MoO_4)_2$ the layers consist of $Tb(MoO_4)_2$ groups, while the K ions link the different layers. We thought that application of high pressure might force the system into new structural arrangements, in view of our earlier studies on molybdate systems[3,4]. In fulfillment of this expectation, we find a novel reversible pressure-induced first-order phase transition at 27 kbar hydrostatic pressure, in which, surprisingly, the colour of the sample turns bright yellow. While the pressure-induced structural transition is found to be a common behaviour for the layered-type $KLn(MoO_4)_2$ systems, the colour change is unique to $KTb(MoO_4)_2$. We propose that the colour change is due to 4f-5d charge transfer in Tb, leading to the intervalence charge transfer from $Tb^{3+}Mo^{6+} \rightarrow Tb^{4+}Mo^{5+}$.

High pressure Raman scattering measurements were carried out to 200 kbar on single crystal samples of $KTb(MoO_4)_2$ (KTMO) in the gasketed diamond anvil cell, with 4 : 1 methanol/ethanol mixture as the pressure medium. In some experiments KTMO powder was pressurized directly in the diamond cell up to 350 kbar without any external pressure medium. The pressure was calibrated by the standard ruby fluorescence technique. Optical observations of pressurized samples were made under a microscope.

In Figure 1, the Raman spectra of KTMO taken in the diamond cell at 10 and 32 kbars are shown. The Raman peaks in the 10 kbar spectrum belong to the normal layered D_{2h}^{14} (Pbcn) phase. The spectrum at 32 kbar

is completely different, indicating a pressure-induced phase transition. Actually the transition occurs abruptly near 27 kbars, which becomes directly evident in optical observations of the sample. The sample abruptly changes colour from colourless to a deep yellow colour, and contracts in the a-axis direction. The appearance of the sample before and after this phase transition is shown in Figure 2. The original crystallographic axes of the orthorhombic phase are marked. The dimensional contraction of the a-axis can be seen by comparing the sizes of the samples in Figure 2, which were taken at the same magnification. The bottom picture in Figure 2 is a photomicrograph of a directly pressurized powdered KTMO sample in the diamond cell, at a pressure of 350 kbars. The differences in colour are due to the pressure gradient over the sample area. With increasing pressure the yellow colour shifts towards longer wavelengths in the high pressure phase, because of the shift of the absorption band. The Raman spectral features remain more or less the same up to the highest pressure studied, except that the Raman peaks shift to higher frequency. In Figure 3 we show a plot of the Raman peak frequency as a function of pressure. The phase transition is clearly seen from the discontinuous changes in the Raman spectrum.

The Raman peaks of the ambient pressure phase of KTMO can be assigned from the Raman spectrum of the isostructural $KY(MoO_4)_2$, which has been studied and analysed in great detail using group theoretical techniques[5]. However, the spectrum of the new high
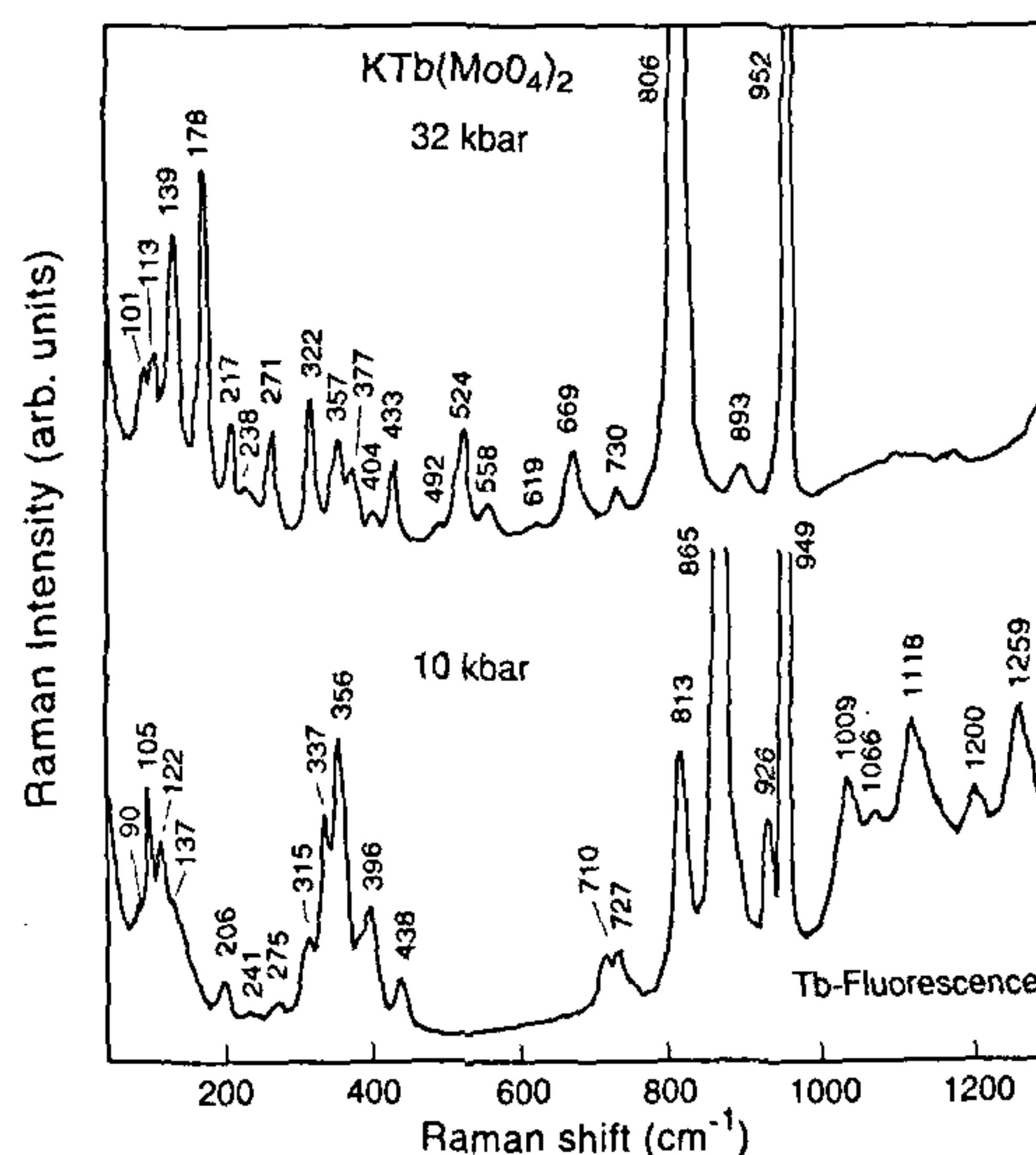

Figure 1. Raman spectra recorded with a single crystal sample at 10 kbar (normal phase) and 32 kbar (high pressure phase) using a diamond anvil cell with methanol/ethanol as pressure medium. The 514.5 nm line of the argon laser was used for Raman excitation at power levels of 30–60 milliwatts.
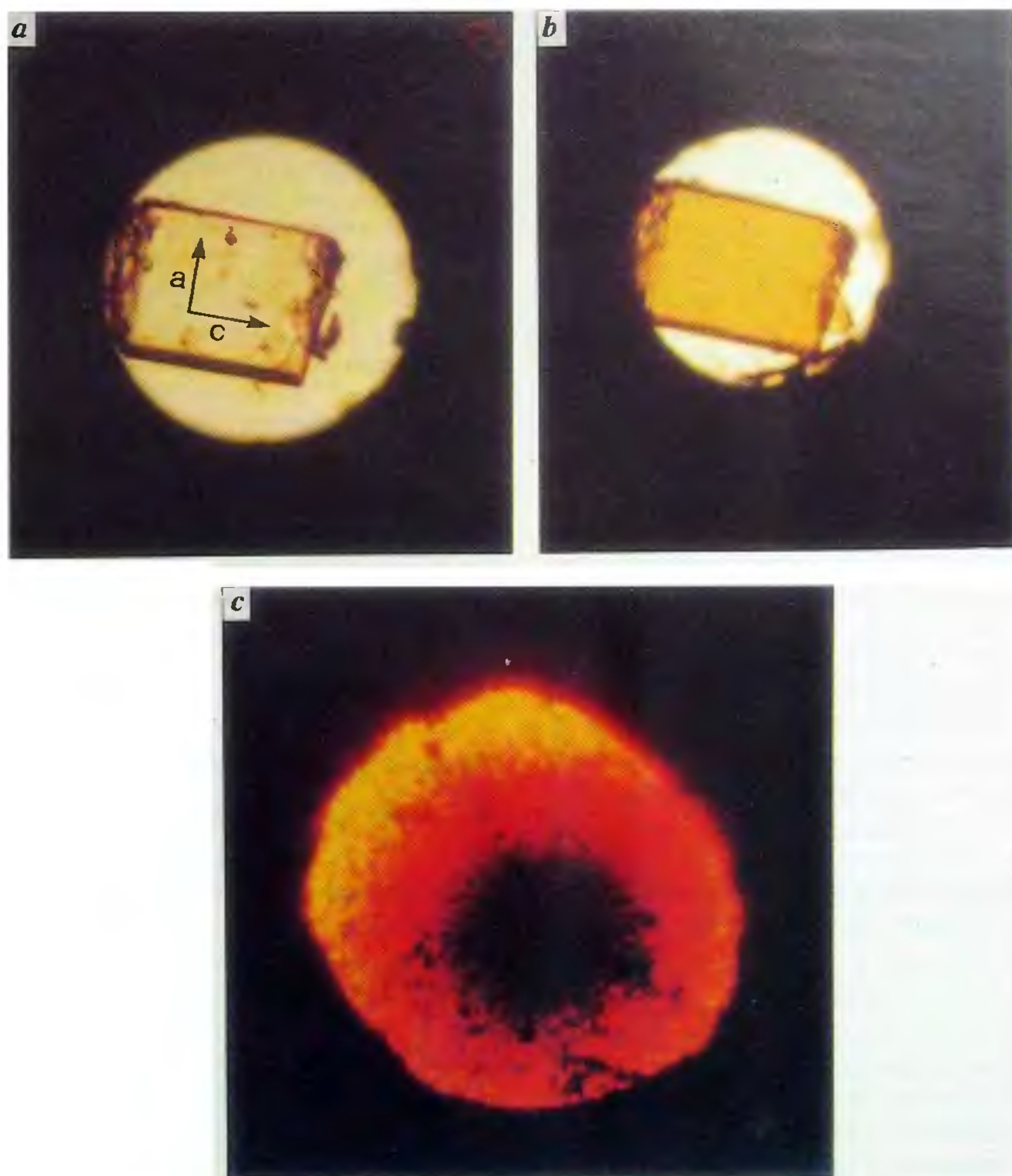
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Figure 2. Photomicrographs of a $KTb(MoO_4)_2$ single crystal sample ($\times 200$) taken in a diamond anvil cell by transmitted light, before (a) and after (b) the 27 kbar phase transition. The pressure-medium was methanol/ethanol. The a- and the c-axes of the original phase are marked. Note the colour change to yellow after the pressure-induced phase transition. The sample contracts in the a-direction at this phase transition and the single crystal nature seems to be preserved. Figure (c) shows powdered KTMO pressurized directly in the diamond cell at a pressure of about 350 kbar. The changes in colour are due to pressure gradient over the sample area. See text for the explanation of the colour change.

pressure phase appears to be more complex, although the gross features are consistent with the fact that the MoO_4 tetrahedral units are still the structural blocks. A structure determination would be necessary before the Raman spectrum can be analysed in detail. A preliminary high pressure X-ray diffraction study shows that the powder diffraction pattern changes near 27 kbars and the data fit an orthorhombic cell with 3.5% smaller volume per formula unit (manuscript in preparation). We have recorded the same type of structure change under pressure in the isostructural $KY(MoO_4)_2$ and $KDy(MoO_4)_2$ near 25 kbar pressure (manuscript in preparation). However, no colour change is observed in these materials.

In the Russian literature[6] a quenchable high pressure–high temperature phase with the β-$KY(WO_4)_2$ structure has been reported for many layer-type alkali rare earth dimolybdates. But our high pressure phase is neither quenchable nor can be indexed on the basis of the β-$KY(WO_4)_2$ type structure.

The colour change at the 27 kbar transition in KTMO is remarkable and is a novel feature of the material.
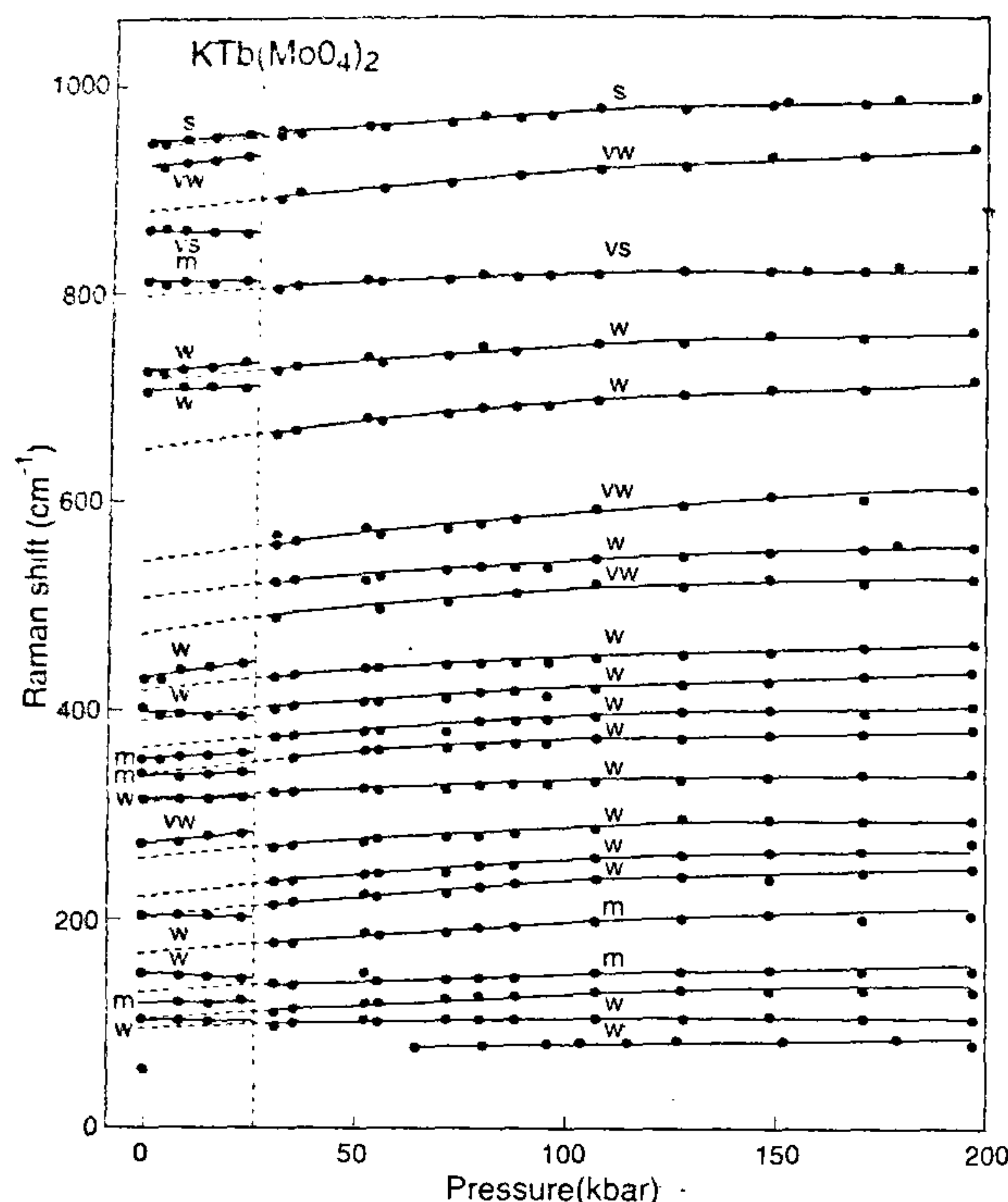
KTb(MoO₄)₂

Figure 3. A plot of the observed Raman peak frequencies as a function of pressure. The vertical dotted line demarcates the phase transition pressure.

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Observation of negative remanence in an organic ferromagnet

S. A. Chavan, J. V. Yakhmi, R. Ganguly and V. K. Jain

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India

DC magnetization measurements on two related ferromagnets, $(NBu_4)_2Mn_2[Cu(opba)]_3 \cdot 6DMSO \cdot H_2O$ ($T_c = 15$ K) and $(NBu_4)_2Mn_2[Cu(opba)]_3$ ($T_c = 22$ K) reveal the unusual phenomenon of negative remanent magnetization.

THE occurrence of spontaneous magnetization in molecular organic materials was first reported in 1986 (ref. 1). Since then different categories of molecular ferromagnets have been synthesized depending on whether the unpaired electrons reside (i) in p orbitals only; (ii) in both p and d orbitals; and (iii) in d orbitals only. Kahn's group has synthesized a number of organic ferromagnets belonging to the last category by arranging ordered Q1D ferrimagnetic bimetallic chains in a bulk lattice in such a way to achieve a net ferromagnetic alignment of spins[2–4]. A typical example of such a bimetallic chain is $Mn^{II}Cu^{II}(obbz) \cdot nH_2O$ [obbz = oxamido bis(benzoato)] with an antiferromagnetic interaction between the adjacent local spins $S_{Mn} = 5/2$ and $S_{Cu} = 1/2$ separated by oxamido and carboxylato bridging groups which transmit the magnetic effects. When assembled appropriately in a 3D lattice, interchain interactions provide ferromagnetic order below 14 K for

We believe that this is due to a charge transfer absorption (4f–5d) arising from a change in the valence state of Tb from 3⁺ to the 4⁺ state. The fact that Tb can exist in both the valence states is well known. The material after the phase transition is still an insulator, which means that the overall charge neutrality should be preserved. The way the charge compensation can happen is that the valence state of Mo becomes Mo^{5+} from Mo^{6+}. This would then be a case of intervalence charge transfer between Tb and Mo from $Tb^{3+}Mo^{6+} \rightarrow Tb^{4+}Mo^{5+}$ similar to the case of TlReO₄ (ref. 7). Our picture for KTMO is that at the structural transition near 27 kbars the oxygens surrounding the Tb ion move closer to the terbium, causing an abrupt increase in the crystal field splitting of the 5d state of terbium. This brings down the 5d energy, facilitating 4f–5d transfer. To preserve charge neutrality the Mo readjusts its valence by the flow of electrons through the ligand. In the case of Y and Dy compounds, a valence change is not possible, and hence no colour change is observed, although an identical pressure-induced structural transition takes place in them. Thus, it is the structural transition that drives the charge transfer transition in KTMO and not the other way.

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