of intermediate valence and hybridisation with the surrounding cloud of conduction electrons. In this model, the Pu atoms swing between the $5f^5$ and $5f^6$ configurations and the local magnetic moment fluctuates in time. However, compensating variations in the hybridised bath maintain a constant nonmagnetic ground state. An important question in this respect is whether such a perfect dynamic balance persists in the superconducting phase. The diamagnetic response associated with the Meissner effect prevents addressing this question by macroscopic magnetometry. It was therefore decided to exploit the possibilities afforded by X-ray magnetic circular dichroism (XMCD), a technique that is not, *a priori*, sensitive to diamagnetism, to quantify the Pu properties in the normal phase and in the vortex phase below T_c.

XMCD is a well-established tool to determine spin and angular moments (μ_S and μ_L) of a given atomic shell. This is achieved by using "sum rules" that correlate the integrals of dichroic spectra measured at two spin-orbit split absorption edges. Here, data were collected in the energy range 3.7-4.1 keV, across the plutonium $M_{4,5}$ absorption edges ($3d_{3/2} \rightarrow 5f_{5/2}$ and $3d_{5/2} \rightarrow 5f_{5/2,7/2}$ transitions). The experiment was performed at the **ID12** beamline, using a single crystal containing almost isotopically pure ^{242}Pu, a long-living isotope that strongly reduces self-irradiation damage, allowing the observation of the intrinsic properties of the compound.

Figure 94 shows the spectra obtained at 2.1 K in a field of 17 T applied along the crystallographic c-axis after zero-field cooling from the normal phase. Below T_c, XMCD probes only atoms in the vortex phase, where a magnetic field that
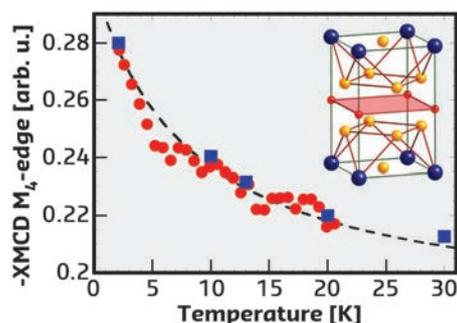

Fig. 95: Temperature dependence of the XMCD signal measured at the M_4 absorption edge. Squares correspond to the integral of the XMCD spectra, whereas circles are the value measured at the peak energy (3968 eV). The inset shows the tetragonal crystal structure of $PuCoGa_5$ (Pu: blue spheres; Co: red spheres; Ga: orange spheres).

can polarise the atomic shells penetrates. Unexpectedly, the results show that μ_L increases significantly between 30 and 2 K, from 0.052(2) to 0.068(2) μ_B. The antiparallel spin component μ_S increases as well, leaving the total induced magnetic moment practically unchanged. The temperature dependence of the XMCD signal at the Pu M_4 edge is shown in **Figure 95**. This quantity, proportional to μ_L-μ_S, increases monotonically from 30 to 2 K, with no anomaly around T_c (lowered to 15.4 K by the applied field). The increase of μ_S with decreasing temperature suggests that the Kondo-like screening responsible for the Pu singlet ground state starts to break down, possibly because of a change in the hybridisation of the 5f electrons with the conduction band.

The results validate electronic structure calculations describing $PuCoGa_5$ as a lattice of Pu Anderson impurities carrying a fluctuating local moment dynamically quenched by the hybridisation with conduction electrons. Understanding how these complex electronic dynamics are related to the formation of Cooper pairs is a significant challenge in the race towards room-temperature superconductivity.

NON-ADIABATIC CRYSTAL-LATTICE DYNAMICS IN SUPERCONDUCTING DIAMOND

The crystal-lattice dynamics of superconducting diamond, investigated through *ab initio* calculations and inelastic X-ray scattering, has revealed the emergence of a non-adiabatic Kohn anomaly. This result constitutes the first observation of the breakdown of the Born-Oppenheimer approximation in the phonon spectra of a three-dimensional solid.

The Kohn anomaly (KA) is one of the most striking manifestations of the influence of electron-phonon coupling on the lattice dynamics of metals **[1]**. KAs result from the screening of lattice vibrations by virtual electronic excitations, and manifest themselves through distinctive

dips in the phonon dispersion relations. The existence of KAs has been confirmed by inelastic neutron scattering experiments in a number of metals, conventional superconductors, as well as superconducting semiconductors. KAs are typically well described in the adiabatic Born-Oppenheimer approximation, whereby electronic and nuclear degrees of freedom are assumed to be decoupled. This picture breaks down whenever the electronic screening takes place on timescales that are comparable to the period of lattice vibrations. Correspondingly non-adiabatic effects may arise, leading to strongly coupled dynamics of electrons and nuclei, which signals a breakdown of the Born-Oppenheimer approximation. However, it has been suggested that non-adiabatic effects might be too small to be observable in three-dimensional solids [2].

The emergence of non-adiabatic effects in the Kohn anomaly of boron-doped diamond was investigated for hole densities that make the system superconducting at low temperature. The dispersion relations of the longitudinal-optical (LO) phonons (marked in red in **Figure 96e**) were analysed using state-of-the-art many-body first-principles calculations and inelastic X-ray scattering (IXS) measurements. IXS spectra were measured at beamline **ID28**. The phonon dispersions have been obtained entirely from first-principles through the evaluation of the phonon self-energy and the phonon spectral function based on the many-body theory of electron-phonon coupling. The measured IXS spectra are shown in **Figure 96a** and **b** as heat maps for pristine (undoped) diamond and for a boron concentration of 10^{21} cm^{-3} for momenta along the Γ-X direction. The computed phonon dispersions are reported in **Figure 96c** and **d**, whereas the full (adiabatic) phonon dispersions are shown in **Figure 96e**.

The IXS spectrum of B-doped diamond reported in **Figure 96b** exhibits a softening of the LO phonon energy by 7 meV as compared to the dispersion measured on the pristine sample and shown in **Figure 96a**. The softening is further accompanied by an increase of the phonon linewidth close to Γ in the doped samples. The softening and linewidth become more pronounced with increasing hole density. Calculations based on the adiabatic Born-Oppenheimer approximation, shown in **Figure 96e**, fail at reproducing these features: the phonon softening is overestimated by 300%, and linewidths may not be inferred at this level of theory. Conversely, the comparison between **Figure 96a** and **b**, and **Figure 96 c** and **d**, indicates that fully non-adiabatic calculations yield phonon energies and linewidths in excellent quantitative agreement with IXS. Besides resolving the long-standing discrepancy between earlier theoretical works and measured phonon dispersions, these results demonstrate a breakdown of the adiabatic Born-Oppenheimer approximation in the phonon dispersion relations of boron-doped diamond, and reveal that these effects may be sizeable also in three-dimensional bulk compounds.

The breakdown of the adiabatic Born-Oppenheimer approximation observed in the lattice dynamics of heavily boron-doped diamond may be explained by considering the timescales involved: while LO phonons oscillate with a period τ_{ph}= 25 fs, the timescale of electronic screening τ_s is set by the plasma frequency ω_{pl} via τ_s= $2\pi/\omega_{pl}$, which, for a doping concentration of $1.4 \cdot 10^{21}$ cm^{-3} corresponds to τ_s= 4 fs. As screening operates on timescales that approach the characteristic phonon period, the assumptions underlying the Born-Oppenheimer approximation cease to hold, and we see the emergence of strong non-adiabatic coupling.

Fig. 96: Measured IXS spectra for the LO phonon (marked in red in panel (e)) of pristine (a) and B-doped (b) diamond along Γ-X. The B-doping concentration n is in units of cm^{-3}. c)-d) Non-adiabatic spectral function obtained from first-principles calculations. e) Adiabatic phonon dispersions.
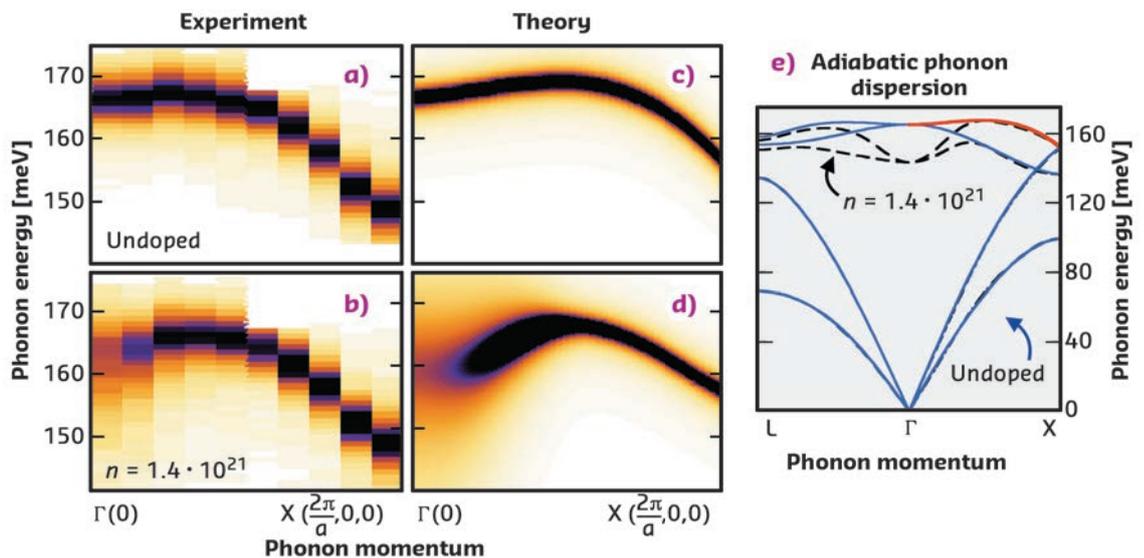
In summary, by combining first-principles calculations of the electron-phonon interaction and high-resolution IXS experiments, the emergence of a non-adiabatic KA in superconducting diamond was demonstrated, and it was shown that a breakdown of the Born-Oppenheimer approximation may lead to sizeable renormalisation effects in the phonon dispersions of three-dimensional crystals. The results call for a systematic investigation of non-adiabatic effects and Kohn anomalies in the phonon dispersions of three-dimensional crystals such as doped semiconductors and transition metal oxides, and their implications on the superconducting properties of these systems. The combination of high-resolution IXS spectroscopy as provided by the **ID28** beamline and state-of-the-art *ab initio* many-body methods offers unique opportunities to explore these and other exciting new directions in the areas of crystal lattice dynamics and electron-phonon interactions.

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WHY APICAL OXYGENS PLAY AGAINST HIGH Tc SUPERCONDUCTIVITY

The complex intertwining of structural, magnetic and electronic properties makes the superconductivity of cuprates a 30-year-old mystery. Using resonant inelastic X-ray scattering (RIXS) to map spin-wave dispersion, out-of-plane oxygen atoms have been found to localise the in-plane electronic wave function, ultimately lowering the maximum reachable superconducting transition temperature (T_c).

Superconductivity of Cu-based layered materials is the deepest mystery of solid state physics: 30 years of intense theoretical and experimental research have not told us what really gives cuprates such a high T_c. The problem is complicated by the fact that magnetic and electronic degrees of freedom are equally important and are strongly influenced by the quasi-2D structure of the system. The superconducting CuO_2 planes are antiferromagnetic in parent compounds while their short-range spin correlation is preserved in superconducting doped materials. However, whether this has significance for the T_c is not known. Moreover, the out-of-plane coordination of Cu ions varies from family to family through the presence of apical ligands (usually oxygen). The influence of the apical ligands on the in-plane transport properties also remains a mystery. This work clarifies these two unknowns.

Resonant inelastic X-ray scattering (RIXS) at the Cu L_3 absorption edge is probably the best technique to measure spin excitations in cuprates at all doping levels across the phase diagram, from antiferromagnetic insulating parent compounds to overdoped Fermi-liquid bad metals **[1, 2]**. The ERIXS spectrometer at beamline **ID32** is currently the leading instrument for high-resolution RIXS and its unique capabilities have been fully exploited in this work. Here, the dispersion of spin-waves was carefully mapped along a symmetry-significant path in the first Brillouin zone, for three parent materials differing by the number of apical oxygen ions (see **Figure 97**, left panel): $CaCuO_2$ (CCO) no apical oxygens, $NdBa_2Cu_3O_{6+x}$ (NBCO) one apical oxygen, $Bi_2Sr_{2-x}La_xCuO_6$ (Bi2201) two apical oxygens. Data from the literature for La_2CuO_4 (LCO) with two apical oxygens was also considered **[3]**.

The comparison in **Figure 98** confirms that the "average" super-exchange Cu-Cu interaction is always very strong, making the most of the spin excitation energy ≈ 300 meV in all materials: the ubiquity of strong antiferromagnetism is confirmed again. More interestingly, it is found that the dispersion along the Brillouin zone boundary (measured by the parameter ΔE_{MBZB}) is strictly related to the number and distance of apical oxygens. The phenomenological analysis by different models confirms that apical oxygen ions tend to localise the exchange interaction to the first and second neighbours. This means that, more generally, hopping integrals follow the same rule, and that wave functions are