with the data obtained from the single-crystal X-ray and powder neutron diffraction refinements, while the coordinate of Al(*e*), $z_{Al(e)}$, was poorly determined by the 00*l* electron data. This is mainly due to the fact that the heavy Zr(*e*) atom masked the Al(*e*) atom, which smeared out along the *z* axis because of its anisotropically large temperature factor found by single-crystal X-ray diffraction. Although this indicates the limitation of the CBED technique, it should be pointed out that a kinematic interpretation on high-order systematic reflections recorded in a CBED disc with large Bragg and convergent angles is feasible and as a simple technique it can be applied to μm-sized crystals in TEM experiments. It will also be promising to apply the technique to thermal or mechanical *in situ* observations in an electron microscope, at least for a quick semi-quantitative estimation on atomic structure variations of a μm-sized crystal. A detailed discussion of the technique based upon the data obtained from Al_3Zr will be presented elsewhere.

The differences between the temperature factors refined by single-crystal X-ray diffraction and powder neutron diffraction can be explained by several facts. Firstly, the anisotropic thermal effects were not taken into account in the powder neutron diffraction refinement, while the data from single-crystal X-ray diffraction results show that the Al(*e*) atom has significant anisotropic thermal behaviour. However, the neutron data confirm that Al(*e*) thermally vibrates more than Al(*c*) and Al(*d*). Secondly, various errors usually manifest themselves in the temperature factors and, lastly, the thermal histories of the samples for the two techniques are different and the powder sample for the neutron diffraction may have been more disordered.

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Absolute Optical Chirality of Ammonium Dihydrogen Phosphate

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Abstract

A theoretical prediction of optical rotation is made for the non-enantiomorphous material ammonium dihydrogen phosphate (ADP), based entirely on the known crystal structure. It is predicted that the (100) section, with axes chosen according to Khan & Baur [*Acta Cryst.* (1973), **B29**, 2721–2726], should be optically laevorotatory. Measurement of this material's optical rotation is reported for the first time using a specially constructed polarimeter. Together with X-ray Bijvoet-pair measurements, it has been possible to determine the *absolute optical chirality*, with the result that in the (100) section $\rho = -6.8\,(5)^\circ\ \mathrm{mm}^{-1}$ (laevo) and in the (010) section $\rho = +6.8\,(5)^\circ\ \mathrm{mm}^{-1}$ (dextro) for a wavelength $\lambda = 589.3$ nm.

Introduction

Ammonium dihydrogen phosphate (ADP) crystallizes in the non-enantiomorphic non-polar space

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group $I\bar{4}2d$ (D_{2d}^{12}) and is isomorphous with the tetragonal phase of potassium dihydrogen phosphate (KDP). The structure was determined to high precision by Khan & Baur (1973). Although much has been reported concerning the physical properties of ADP, nothing has been published regarding the possibility of optical rotation (circular birefringence) in this material. The main reason for this is that in the point group $\bar{4}2m$ (D_{2d}) no optical rotation is theoretically possible down the optic axis direction along [001]. It should be realized, however, that it is allowed within the (001) plane according to the symmetry of the gyration tensor (Nye, 1979). There are only two gyration components, $g_{11} = -g_{22}$, showing that along [100] and [010] one can expect to observe maximum optical rotations of equal magnitudes but opposite signs within the same crystal. These directions correspond to the chiral symmetry axes (Glazer & Stadnicka, 1989). The problem with observing the effect in these directions is that linear optical birefringence is present too, and this dominates, making the much smaller effect of rotation impossible to see directly. In special cases, such as in $AgGaS_2$ (Hobden, 1968), which crystallizes in the same point group, the birefringence may change sign, passing through zero at a particular wavelength of light, thus allowing the rotation to become directly observable; however, this is not true in ADP (Vishnevskii, Romanyuk & Stefanskii, 1965; Vishnevskii & Stefanskii, 1966). As a result, until recently, no study had been made of the absolute optical chirality (Glazer & Stadnicka, 1989), *i.e.* the link between absolute structure and a chiroptical property, for any non-enantiomorphic crystal.

The present paper reports one of the first such measurements [another case that has been studied recently is that of $KTiOPO_4$, which crystallizes in point group *mm*2, a non-enantiomorphic but polar group (Thomas, Tebbutt & Glazer, 1991)]. This has only become possible through the use of a specially constructed polarimeter (Moxon & Renshaw, 1990) based on the HAUP apparatus of Kobayashi & Uesu (1983). As will be shown below, we have been able to predict both the sign and order of magnitude of the optical rotation along [100] and [010] using the program of Devarajan & Glazer (1986). This prediction has been confirmed using our polarimeter, and measurements of the X-ray intensities of Bijvoet pairs (anomalous dispersion) have been made on a fragment of the *same* crystal in order to determine the absolute optical chirality for the first time.

Prediction of optical rotation

Fig. 1 shows a (100) projection of the ADP structure refined by Khan & Baur (1973). According to Glazer & Stadnicka (1986), the sign of the optical rotation should be related to the sense of the helical arrangements of the closest and most polarizable species in the structure, here oxygen and the nitrogen representing the ammonium cation. In this projection we find a non-symmetric right-handed structural helix consisting of the atoms $N—O_a—O_b$, described by the notation *RS*2/3 of Glazer & Stadnicka (1986). There are four such helices per ⟨100⟩ projection per unit cell. In order to determine whether light rotates in the same or the opposite sense as these helices, it is necessary to consider the anisotropy of the O and N polarizabilities. On the basis that the atoms will be more polarizable in directions of close contacts, we find that the largest polarizabilities tend to lie tangential to the helices, especially in the case of the oxygens. This is further supported by the fact that we usually find that the maximum polarizabilities lie roughly perpendicular to the maximum thermal displacements (see later in Fig. 6). Thus the (100) projection, as defined by the coordinates of Khan & Baur (1973), should rotate light in the *same* sense as the helices, *i.e.* laevorotatory.

A more precise prediction was made using the program of Devarajan & Glazer (1986). Given isotropic polarizability volumes this program calculates refractive indices and the magnitude and sign of optical rotation *via* a point-dipole approximation. This approach has proved very successful in the past, and we were interested to see if it could be used here in a purely predictive sense.

The refractive indices at $\lambda = 589.3$ nm (Na *D* line) are, according to Winchell & Winchell (1964), $n_o =$

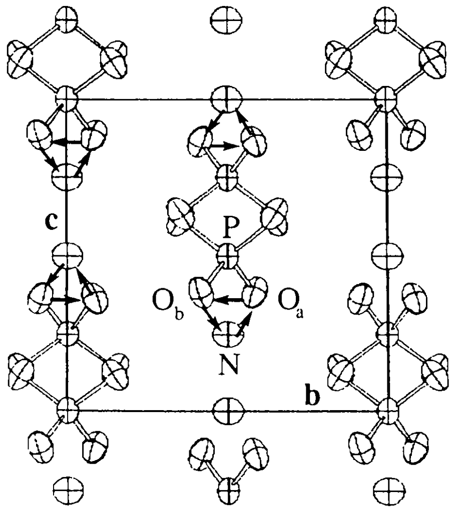

Fig. 1. (100) projection of the ammonium dihydrogen phosphate structure according to Khan & Baur (1973). Atoms are represented by thermal ellipsoids at the 75% probability level. Contacts of the *RS*2/3 helices are marked. The distances are: $N—O_a = 2.909\,(1)$, $O_a—O_b = 2.536\,(1)$, $O_b—N = 2.909\,(1)$ Å, and the fractional heights are $N = 0.0000$, $O_a = 0.3534\,(1)$ and $O_b = 0.6466\,(1)$.

1.5246 and $n_e = 1.4792$, uniaxial negative. The fractional coordinates of all atoms, except for the hydrogens, were input to the program, together with *estimated* isotropic polarizability volumes, α, for O, N and P, based on previous experience. These values were then adjusted, within acceptable limits (see, for example, Tessman, Khan & Shockley, 1954), in order to obtain the best fit to the refractive indices: for $\alpha(\mathrm{O}) = 1.587$, $\alpha(\mathrm{N}) = 1.014$ and $\alpha(\mathrm{P}) = 0.010$ Å^3, the calculated refractive indices were $n_o = 1.5247$ and $n_e = 1.4790$. With these values a rotatory power $\rho = -16^\circ\,\mathrm{mm}^{-1}$ was calculated for [100], the negative sign corresponding to laevorotation (for [010] we calculated $\rho = +16^\circ\,\mathrm{mm}^{-1}$).

Measurement of optical rotation

A large optically clear crystal of ADP was obtained by seeded growth and slow evaporation at room temperature from an aqueous solution of pure recrystallized ammonium dihydrogen phosphate. The habit consisted of a combination of {100} and {101} faces, in agreement with that described by Groth (1908).

In order to carry out the optical experiments, slices were cut and polished on (100) and (010), initially with an approximate thickness of 0.5 mm (the first sample was subsequently polished to 0.2 mm). Optical-rotation measurements were made using the HAUP apparatus constructed at the Clarendon Laboratory (Moxon & Renshaw, 1990). In this system, the magnitude and sign of the ellipticity, k, of the normal modes of optical polarization which pass through the crystal are measured. This is determined by the relative magnitude of the linear and circular birefringences, and hence does not require knowledge of the sample thickness. Since the circular birefringence is very small compared with the linear birefringence, the value of k is also very small, typically 3×10^{-4} for ADP. By comparing the measured values of $2k\sin\Delta$ with $\sin\Delta$ (Δ being the phase difference between the normal optical modes on passing through the crystal) one can obtain the sign of k and hence the sign of rotation. The results for $2k\sin\Delta$ and $\sin\Delta$ for the two samples are shown in Figs. 2 and 3. From the relative phases of these curves we can say with certainty that the rotation is negative for the (100) section and positive for the (010) section.

The value of $2k$ is very small (*cf.* in quartz $2k \simeq 6 \times 10^{-3}$) and random errors in k are typically of the order of 5×10^{-5}. From the k values measured at each wavelength, the rotation ρ can be calculated as a function of λ. The results can be fitted to a Drude-type formula (Fig. 4)

$$\rho = \frac{-0.5603}{\lambda^2 - \lambda_o^2} + 2.647,$$

where $\lambda_o = 0.2704$ µm and ρ is given in ° mm^{-1}. The measured rotation at 589.3 nm turned out to be $-6.8\,(5)^\circ\,\mathrm{mm}^{-1}$ for the (100) section.

Measurement of intensities of Bijvoet pairs

Normally, the most precise way of measuring Bijovet-pair intensities, in order to determine absolute structure, is through the so-called 'extended-face method'. In this technique a crystal slice larger than the diameter of the X-ray beam is used. By arranging the surface so that Bijvoet pairs are produced by equivalent reflections on either side of the plate normal, differences in absorption are eliminated, thus allowing a direct comparison between each Friedel-related reflection to be made.

However, in the present case, the surface of the plate with optical laevorotation $\rho = -6.8^\circ\,\mathrm{mm}^{-1}$ for $\lambda = 589.3$ nm was of the {100} type and so all suitable reflections from such a face had to have at least one index h, k or $l = 0$: calculations using the known structural coordinates showed that there are no Bijvoet pairs possible with this condition.

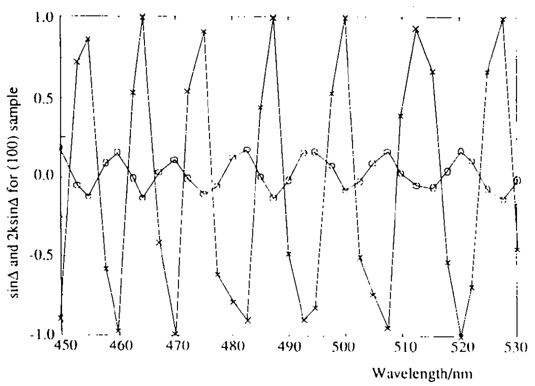

Fig. 2. Measurement of $2k\sin\Delta$ (o) and $\sin\Delta$ (×) as a function of wavelength for the ADP (100) slice.

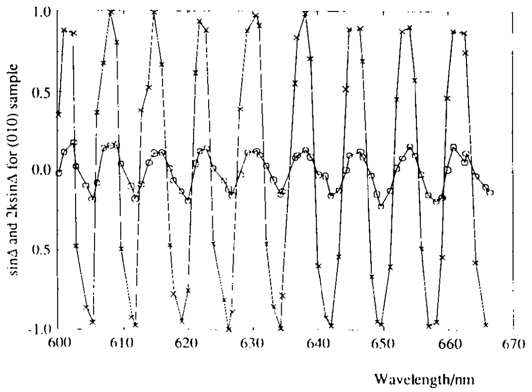

Fig. 3. Measurement of $2k\sin\Delta$ (o) and $\sin\Delta$ (×) as a function of wavelength for the ADP (010) slice.

It was therefore necessary to cut a small piece from the large slice, at the same time taking great care to maintain a knowledge of its orientation with respect to that of the large slice. This was done by painting the surface of the slice with ink before cutting out the small crystal. The smallest intact crystal that we could produce in this way measured approximately 0.6 × 0.6 × 0.5 mm. This was oriented automatically on a Stoe STADI-4 diffractometer using the standard random-search procedure. Graphite-monochromated Cu $K\alpha$ radiation was used with a collimator diameter of 0.8 mm. The lattice parameters, which were obtained using a double step-scan for positive and negative 2θ, were $a = 7.4932\,(4)$, $c = 7.549\,(1)$ Å, in close agreement with those of Khan & Baur [$a = 7.4997\,(4)$ and $c = 7.549\,(1)$ Å]. The marked reference face of the crystal was then oriented into the viewing position of the diffractometer and its indices were found to be (010). Transformation was made to the orientation matrix so that, for convenience, the indices of this reference face became (100).

Using the published structural parameters, we calculated $F^2(hkl)$ for all reflections up to $\theta = 50°$. Atomic scattering factors and $\Delta f'$ and $\Delta f''$ were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). As a result, we selected several sets of Bijvoet pairs. These were measured in the conventional way. A series of ψ scans was carried out in order to allow absorption corrections to be made. With $\mu R = 1.53$ the Stoe *EMPIR* program was used coupled with data reduction to produce a list of observed structure factors. After averaging appropriate groups of reflections, the observed Bijvoet pairs [$F^2(hkl)$ and $F^2(\bar{h}kl)$] were compared with those calculated (Table 1).

In Table 1, it can be seen that in all but one Bijvoet pair (332/$\bar{3}$32), the signs of the differences F^2 of the observed reflections agree with those calculated. The actual percentage differences tend to be larger for the observed Bijvoet pairs. This is probably due to a combination of factors, such as inaccuracies in the absorption correction, the small values of $\Delta f''$ for phosphorus using Cu $K\alpha$ radiation, and possibly the fact that the crystal used was rather large compared with the X-ray beam diameter. Nevertheless, the consistency of the signs leaves us in no doubt that the reference face, and hence the laevorotatory section of the crystal used for the optical measurement, was correctly assigned to (100) with respect to the choice of axes of Khan & Baur (1973). It can be seen therefore that, despite the difficulty of this type of experiment, our prediction of the sign of ρ, and even, to some extent, its order of magnitude, based on structural grounds has been confirmed by the combination of optical and X-ray measurements made on the same sample.

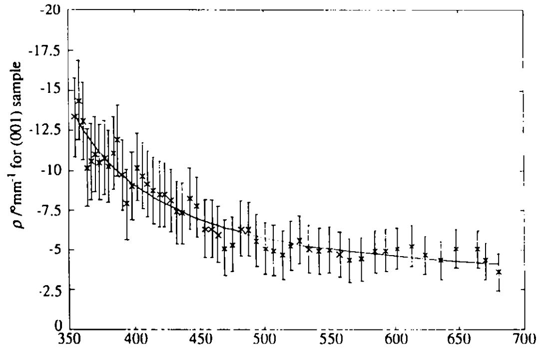

Fig. 4. Measured optical rotatory dispersion (with error bars) for (100) ADP. The smooth curve is a Drude-type fit.

Table 1. *Comparison of observed and calculated differences of structure factors squared* (*on an arbitrary scale*) *for the ADP crystal with the main face observed to be optically laevorotatory*

The indices *hkl* below are based on the assumption that this face is referred to as (100). Intensities of equivalent reflections were averaged.

h	k	l	$F_o^2(hkl)$	$F_o^2(\bar{h}kl)$	ΔF_o^2 (%)	ΔF_c^2 (%)
1	1	2	42457	46587	−10	−2
1	2	1	17641	18548	−5	−4
1	2	3	12498	14386	−15	−4
1	3	2	38131	39259	−3	−4
2	3	1	20607	21453	−4	−3
2	3	3	24663	25643	−4	−3
3	3	2	36776	33494	+9	−5
2	2	4	33481	36470	−9	−4
3	4	1	20449	18496	+10	+3
2	5	1	8464	9511	−12	−7
2	3	5	14203	13298	+6	+4
3	5	2	25689	22317	+13	+6
1	3	6	21509	20903	+3	+4
3	6	1	16691	15956	+4	+2

Further calculations of the optical rotation

We have seen that it has been possible to successfully use the program of Devarajan & Glazer (1986) to predict the sign and approximate order of magnitude of the optical rotation in ADP. It is instructive to investigate whether the point-dipole model used in the program can be fine-tuned to obtain a much closer fit to the observed refractive indices and rotation simultaneously. In order to do this, we carried out a series of calculations in which the polarizability volumes of the N and O atoms were varied (the value of α_P was small and kept constant for convenience). The resulting calculated ordinary and extraordinary refractive indices plus the rotatory power are plotted in Fig. 5 as a function of the polarizability ratio defined as:

$$\text{ratio} = \frac{16\alpha_O}{(4\alpha_N + 16\alpha_O + 4\alpha_P)},$$

where α_P was set equal to 0.01 Å^3. By adjusting α_O and α_N appropriately, the denominator was kept throughout to a total α value of 30 Å^3 per unit cell in order to maintain the average refractive index in agreement with the Clausius–Mosotti formula

$$\tfrac{4}{3}\pi\alpha = V_{\text{cell}}\,\frac{\bar{n}^2-1}{\bar{n}^2+2}.$$

Thus, a ratio equal to zero effectively means the absence of any oxygen contribution and a ratio equal to one effectively means no nitrogen (ammonium ion actually) contribution.

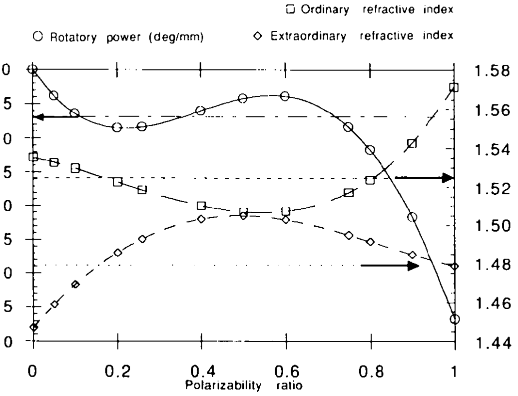

Fig. 5. Calculated values of n_o (□), n_e (◇) and ρ in $^\circ$ mm^{-1} (○) from the program of Devarajan & Glazer (1986), plotted as a function of the polarizability ratio $16\alpha_O/(4\alpha_N + 16\alpha_O + 4\alpha_P)$. The horizontal lines indicate the observed values of ρ, n_o and n_e from top to bottom, respectively.

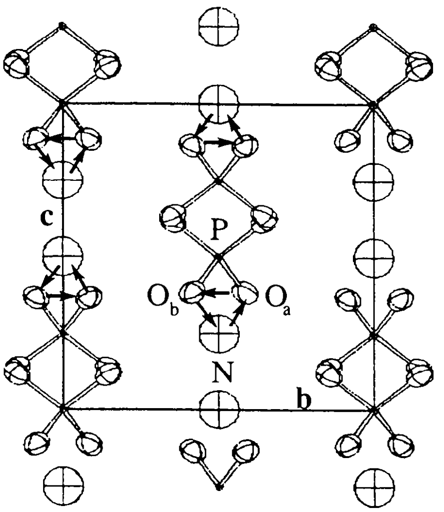

Fig. 6. (100) projection of the ADP structure with ellipsoids representing the calculated anisotropic polarizability volumes, according to the program of Devarajan & Glazer (1986).

It can be seen in Fig. 5 that the calculated optical rotatory power remains negative, showing that at least the calculation of the sign is correct. Note that for a ratio equal to zero the optical rotatory power is also zero, thus indicating that it is the presence of oxygen that determines the occurrence of optical rotation in ADP. On the graph horizontal lines indicate the observed values of the refractive indices and rotatory power, and it can be seen that there are three regions of the ratio for which some agreement is obtained, close to ratios of 0.1, 0.4 and 0.7. These ratios correspond to the following values for the polarizability volumes: ratio = 0.1, $\alpha_N = 6.72$, $\alpha_O = 0.19$ Å^3; ratio = 0.4, $\alpha_N = 4.48$, $\alpha_O = 0.75$ Å^3; ratio = 0.7, $\alpha_N = 2.25$, $\alpha_O = 1.31$ Å^3. The first two are unphysical since they correspond to polarizability volumes for O that are much smaller than normally encountered in crystalline solids, whereas the results for a ratio of 0.7 make more physical sense. However, while this ratio gives quite a good fit to the rotatory power and the correct sign for the birefringence, the calculated ordinary refractive index n_o is too small and the calculated extraordinary refractive index n_e is too large. However, by making the input polarizabilities slightly anisotropic to start with, setting $\alpha_{11} = \alpha_{22}$ and $\alpha_{33} = 0.95\alpha_{11}$ for all atoms and a ratio of 0.71 [corresponding to $\alpha_{11}(\mathrm{N}) = 2.18$ and $\alpha_{11}(\mathrm{O}) = 1.33$ Å^3], we get the result $n_o = 1.5247$, $n_e = 1.4792$, $\rho = -6.8^\circ$ mm^{-1}, which is in precise agreement with the observed values [$n_o = 1.5246$, $n_e = 1.4792$, $\rho = -6.8\,(5)^\circ$ mm^{-1}].

Fig. 6 shows a plot of the (100) projection of the structure of ADP with ellipsoids representing the calculated anisotropic polarizability volumes, showing that indeed the longest ellipsoid axes tend to be tangential to the N—O_a—O_b helix described earlier, as well as perpendicular to the observed thermal ellipsoids shown in Fig. 1.

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A Position-Space Model for Superconductivity in $YBa_2Cu_3O_{7-x}$

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Abstract

$M_r = 666.2$, orthorhombic, $Pmmm$, $Z = 1$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $F(000) = 294$, $T = 298$ K. Data set (1): $a = 3.847\,(4)$, $b = 3.875\,(4)$, $c = 11.70\,(1)$ Å, $V = 174.44\,(5)$ Å^3, $D_x = 6.341$ Mg m^{-3}, $\mu = 29.24$ mm^{-1}, $R = 0.055$, $wR = 0.041$ (O5 excluded), $R = 0.053$, $wR = 0.037$ (O5 included) for 1132 unique reflections. Data set (2): $a = 3.842\,(1)$, $b = 3.886\,(1)$, $c = 11.690\,(4)$ Å, $V = 174.55\,(2)$ Å^3, $D_x = 6.338$ Mg m^{-3}, $\mu = 29.32$ mm^{-1}, $R = 0.046$, $wR = 0.041$ (O5 excluded), $R = 0.046$, $wR = 0.040$ (O5 included) for 1134 unique reflections. The structure is disordered with an O4 site occupancy of 0.54 (2) for data set (1) and 0.64 (2) for data set (2). The $\Delta\rho$ maps for the structure have characteristics consistent with those of cubic perovskites, but modified as expected for the distorted structure. For both experiments, the nature of the depletion of electron density near Cu1 is as expected for a cooperative Jahn–Teller-distorted Cu system. Its radial dependence is consistent with depletion of paired spins along the Cu1—O1 bond, and of unpaired spins along the Cu1—O5—Cu1 vector. $\Delta\rho$ associated with Cu2 is strikingly dissimilar to that near Cu1. The density near the O5 site is not accounted for adequately by a disordered model since the mean-square amplitudes of vibration with refined occupation determined by least squares are non-physical. The main characteristics of $\Delta\rho$ in the (001) plane containing the O5 site could be inferred from the $\Delta\rho$ topology of the archetypal $KCuF_3$ structure which has been accurately determined. The mechanism proposed for coupling the redistributed electron density with the vibrational motion of Cu1 in the [100] direction involves modulation by that motion of the antiferromagnetic exchange between adjacent Cu1 atoms.

Introduction

In the standard BCS theory of superconductivity, electron pairs with momentum/spin $\hbar\mathbf{k}^{\uparrow}$, $-\hbar\mathbf{k}^{\downarrow}$ are coupled to hole pairs with momentum $\hbar\mathbf{k}'^{\uparrow}$, $-\hbar\mathbf{k}'^{\downarrow}$ by phonon interactions which lower the total energy (Rickayzen, 1965). This is usually represented in **k** space. Most high-T_c superconducting compounds reported to date contain Cu and have distorted perovskite structures. As BCS theory gives a satisfactory description of type I and type II superconductors, **k**-space representations are preferred in most theoretical studies of the high-T_c oxide superconductors. However, as the coherence length in the oxide system is closer to the cell size, position-space treatments may have some advantages in explaining the phenomenon.

It is probable that the electron density has characteristics common to the perovskite series which are relevant to the superconducting properties of particular members. The simplest distorted member of that structural class, $KCuF_3$, is not superconducting, but its electron density can be determined with high precision because it contains no atoms with high atomic number. Accurate analyses of $KCuF_3$ by Spadaccini (1988), Tanaka, Konishi & Marumo (1979), Tanaka & Marumo (1982) and Buttner, Maslen & Spadaccini (1990), provide the information necessary for a detailed comparison with superconducting perovskites.

Johnson, McHenry, Counterman, Collins, Donovan, O'Handley & Kalonji (1988) have proposed a

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